Structurally Diverse Rh(I) and Mn(I) Complexes Derived from the New Ambidentate Indene Ligand, (1-{^{i}Pr$_2$P(S)}-2-{NMe$_2$})C$_9$H$_6$

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ELECTRONIC SUPPLEMENTARY INFORMATION

Experimental Section

Experimental Section

General Considerations. All manipulations were conducted in the absence of oxygen and water under an atmosphere of dinitrogen, either by using standard Schlenk methods or within an mBraun Inc. glovebox apparatus, utilizing glassware that was oven-dried (130 ºC) and evacuated while hot prior to use. Celite (Aldrich) was oven dried (130 ºC) for 5 days and then evacuated for 24 h prior to use. Alumina (Aldrich, neutral, 150 mesh, activity Brockmann II) was degassed and dehydrated *in vacuo* for 48 h at temperatures between 200 and 300 ºC and subsequently deactivated with 2% deionized water under argon prior to use. All non-deuterated solvents were deoxygenated and dried by sparging with N_2 gas, followed by passage through a double-column solvent purification system provided by mBraun Inc. Dichloromethane and tetrahydrofuran were purified over two alumina-packed columns, while toluene and pentane were purified over one alumina-packed column and one column packed with copper-Q5 reactant. The solvents used within the glovebox were stored over activated 3Å molecular sieves. C_6D_6 (Aldrich) was degassed by using three repeated freeze-pump-thaw cycles and then dried over 3Å molecular sieves for 24 h prior to use. $CDCl_3$ (Aldrich) was degassed by using three repeated freeze-pump-thaw cycles, dried over CaH_2 for 7 d, and distilled *in vacuo*. Sulfur powder, *n*-BuLi (1.6 M in hexanes), $NaN(SiMe_3)_2$, and $BrMn(CO)_5$ were obtained from Aldrich and were used as received, while $[CODRhCl]_2$ (COD = η^4-(1,5-cyclooctadiene)) was obtained from Strem and was dried *in vacuo* for 24 h prior to use. 1-(Diisopropylphosphino)-2-(dimethylamino)indene (**1**) was prepared using literature methods.[1] Unless otherwise stated, ^1H and ^{13}C NMR data were collected at 300K on a Bruker AV-500 spectrometer operating at 500.1 and 125.8 MHz, respectively, with chemical shifts reported in parts per million downfield of tetramethylsilane. In some cases, slightly fewer than expected independent ^1H or ^{13}C NMR resonances were observed, despite prolonged data acquisition times. ^1H and ^{13}C NMR chemical shift assignments are based on data obtained from ^1H-^{13}C HSQC and ^1H-^{13}C HMBC NMR experiments.[2] Unless otherwise stated, ^{31}P NMR data were collected at 298K on a Bruker AC-250 spectrometer operating at 101.3 MHz, with signals referenced externally to 85% H_3PO_4 in water. Variable-temperature ^1H and ^{31}P NMR studies involving **3** were also conducted on a Bruker AC-250 spectrometer, with temperature calibrations carried out using an external MeOH/MeOD standard.[2] The $\Delta G^{\ddagger}$ value quoted for the dynamic process involving **3** was determined at 279K by use of the Gutowsky-Holm approximation.[2,3] IR spectra were collected on a Bruker VECTOR 22 FT-IR instrument, using Nujol mulls. Elemental analyses were performed by Canadian Microanalytical Service Ltd., Delta, British Columbia, Canada.

Preparation of 1-(diisopropylphosphine sulfide)-2-(dimethylamino)indene (2). A Schlenk flask containing a magnetic stir bar was charged with 1-(diisopropylphosphino)-2-(dimethylamino)indene (**1**) (0.73 g, 2.7 mmol) and then was sealed with a septum. Magnetic stirring was initiated and then a suspension of sulfur (0.12 g, 3.8 mmol) in dichloromethane (20 mL) was transferred *via* cannula to the Schlenk flask containing **1**. Upon completion of the slurry transfer, the resulting mixture was stirred for 1 h; at this stage, ^{31}P NMR data obtained from the reaction mixture indicated clean conversion to **2**. The dichloromethane and other volatile materials were then removed *in vacuo*. Within the glovebox, the residual solid was dissolved in toluene (15 mL) and passed down an alumina column (0.5 cm x 5 cm). Removal of the toluene and other volatile materials *in vacuo* yielded **2** as an analytically pure yellow solid (0.71 g, 2.3 mmol, 87%). Anal. Calcd for $C_{17}H_{26}PSN$: C 66.44; H 8.52; N 4.56. Found: C 66.46; H 8.59; N 4.72. ^1H NMR (C_6D_6): δ 7.61 (d, $^3J_{HH}$ = 7.4 Hz, 1H, C4-H), 7.19 (t, $^3J_{HH}$ = 7.5 Hz, 1H, C5-H),

7.06 (d, $^3J_{HH}$ = 7.4 Hz, 1H, C7-H), 6.92 (t, $^3J_{HH}$ = 7.7 Hz, 1H, C6-H), 5.44 (s, 1H, C3-H), 4.19 (d, $^2J_{PH}$ = 17.6 Hz, 1H, C1-H), 2.49 (s, 6H, NMe$_2$), 2.28-2.16 (m, 2H, P(C*H*Me$_2$)), 1.19 (d of d, $^3J_{PH}$ = 16.9 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me*$_a$Me$_b$)), 0.99 (d of d, $^3J_{PH}$ = 17.0 Hz, $^3J_{HH}$ = 7.1 Hz, 3H, P(CH*Me*$_c$Me$_d$)), 0.93 (d of d, $^3J_{PH}$ = 16.7 Hz, $^3J_{HH}$ = 6.9 Hz, 3H, P(CHMe$_a$*Me*$_b$)), 0.79 (d of d, $^3J_{PH}$ = 16.6 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_c$*Me*$_d$)); ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 158.6 (d, $^2J_{PC}$ = 5.0 Hz, C2), 146.5 (d, $^3J_{PC}$ = 3.8 Hz, C3a), 135.4 (d, $^2J_{PC}$ = 4.6 Hz, C7a), 127.5 (C5), 125.2 (d, $^4J_{PC}$ = 2.7 Hz, C4), 121.3 (d, $^4J_{PC}$ = 1.9 Hz, C6), 118.5 (C7), 105.7 (d, $^3J_{PC}$ = 3.8 Hz, C3), 50.6 (d, $^1J_{PC}$ = 30.2 Hz, C1), 43.5 (s, NMe$_2$), 26.4 (d, $^1J_{PC}$ = 45.5 Hz, P(*C*HMe$_2$)), 26.3 (d, $^1J_{PC}$ = 47.4 Hz, P(*C*HMe$_2$)), 18.4 (d, $^2J_{PC}$ = 1.9 Hz, P(CH*Me*$_c$Me$_d$)), 17.2 (d, $^2J_{PC}$ = 2.3 Hz, P(CH*Me*$_a$Me$_b$)), 16.8 (d, $^2J_{PC}$ = 2.7 Hz, P(CHMe$_c$*Me*$_d$)), 16.5 (d, $^2J_{PC}$ = 1.9 Hz, P(CHMe$_a$*Me*$_b$)); ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 72.8. Crystals of **2** suitable for single-crystal X-ray diffraction analysis were grown from toluene at -35 °C.

Preparation of [κ^2-*N*,*S*-(1-^{i}Pr$_2$PS-2-Me$_2$N-indene)RhCOD]$^+$BF$_4^-$ (3). To a glass vial containing a magnetically stirred suspension of [RhCODCl]$_2$ (0.094 g, 0.19 mmol) in THF (2 mL) was added a suspension of AgBF$_4$ (0.075 g, 0.38 mmol) in THF (3 mL); a yellow solution was generated immediately along with a white precipitate. The supernatant solution was separated from the precipitate by filtration through Celite, and the solution was transferred to a glass vial containing a magnetically stirred solution of compound **2** (0.12 g, 0.38 mmol) in THF (3 mL); after 30 s, a dark orange-red precipitate started to form. After 3 additional hours, the reaction supernatant solution was decanted and the remaining solid (**3**) was washed with pentane (3 mL). Any remaining solvent or other volatile materials were then removed *in vacuo*, yielding **3** as an analytically pure orange-red solid (0.18 g, 0.29 mmol, 76%). Anal. Calcd for C$_{25}$H$_{38}$PSNRhBF$_4$: C 49.61; H 6.33; N 2.31. Found: C 49.78; H 6.54; N 2.34. ^{1}H NMR (CDCl$_3$): δ 7.20-7.15 (m, 2H, aryl-Hs), 7.10 (d, $^3J_{HH}$ = 7.0 Hz, 1H, C4-H or C7-H), 6.96 (t, 1H, C5-H or C6-H), 5.21 (d, $^2J_{PH}$ = 8.6 Hz, 1H, C1-H), 4.37 (m, 2H, COD), 4.08 (m, 2H, COD), 3.31 (broad s, 6H, NMe$_2$), 2.82 (m, 1H, P(C*H*Me$_2$)), 2.53 (m, 1H, P(C*H*Me$_2$) or COD), 2.41 (m, 2H, P(C*H*Me$_2$) and/or COD), 2.18 (broad m, 2H, COD), 1.98 (broad m, 2H, COD), 1.70 (broad m, 2H, COD), 1.44 (d of d, $^3J_{PH}$ = 18.4 Hz, $^3J_{HH}$ = 6.9 Hz, 3H, P(CH*Me*$_2$)), 1.39-1.32 (m, 6H, P(CH*Me*$_2$)), 0.96 (d of d, $^3J_{PH}$ = 17.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me*$_2$)); ^{13}C{^{1}H} NMR (CDCl$_3$): δ 145.8 (C3a or C7a), 131.0 (C7a or C3a), 129.4 (aryl-*C*H), 124.6 (aryl-*C*H), 123.7 (aryl-*C*H), 119.8 (aryl-*C*H), 84.6 (m, COD), 82.2 (m, COD), 47.8 (d, *J* = 26.8 Hz, C1), 44.6 (broad m, NMe$_2$), 32.6 (broad m), 30.8, (d, *J* = 40.0 Hz), 30.0 (d, *J* = 36.1 Hz), 29.9-29.5 (broad m), 17.8 (P(CH*Me*$_2$)), 17.5 (P(CH*Me*$_2$)), 17.4 (P(CH*Me*$_2$)), 16.5 (P(CH*Me*$_2$)); ^{31}P{^{1}H} NMR (CDCl$_3$): δ 103.5.

Preparation of κ^2-*C*,*S*-(1-^{i}Pr$_2$PS-2-Me$_2$N-indenyl)RhCOD (4). To a magnetically stirred suspension of **3** (0.069 g, 0.11 mmol) in THF (3 mL) was added a suspension of NaN(SiMe$_3$)$_2$ (0.021 g, 0.11 mmol) in THF (3 mL) *via* Pasteur pipette. Some precipitate formed upon addition and the reaction mixture was left stirring for 3 h. A ^{31}P NMR spectrum taken of the reaction solution revealed the presence of a single phosphorus-containing product at 82.9 ppm. After the solvent and other volatile materials were removed *in vacuo*, the residue was extracted with pentane (3 mL) and the pentane solution containing **4** was filtered through Celite and then dried *in vacuo*. The residue was then taken up in toluene (3 mL) and crystallized at -35 °C, giving **4** as an analytically pure yellow solid (0.040 g, 0.077 mmol, 70%). Anal. Calcd for C$_{25}$H$_{37}$PSNRh: C 58.02; H 7.21; N 2.71. Found: C 57.88; H 6.94; N 2.63. ^{1}H NMR (C$_6$D$_6$): δ 8.26 (d, $^3J_{HH}$ = 7.2 Hz, 1H, C4-H or C7-H), 7.44 (d, $^3J_{HH}$ = 7.0 Hz, 1H, C7-H or C4-H), 7.23-7.15 (m, 2H, C5-H and C6-H), 6.16 (s, 1H, C3-H), 4.50 (broad m, 2H, COD), 4.30 (broad s, 2H, COD), 3.35 (m, 1H,

P(CHMe$_2$)), 3.13 (s, 6H, NMe$_2$), 2.73 (m, 1H, P(CHMe$_2$)), 2.50-1.15 (m, 11H, COD and P(CHMe_2)), 1.07 (d of d, $^3J_{PH}$ = 16.9 Hz, $^3J_{HH}$ = 7.1 Hz, 3H, P(CHMe_2)), 0.82 (d of d, $^3J_{PH}$ = 17.1 Hz, $^3J_{HH}$ = 7.2 Hz, 3H, P(CHMe_2)), 0.67 (d of d, $^3J_{PH}$ = 16.9 Hz, $^3J_{HH}$ = 7.2 Hz, 3H, P(CHMe_2)); ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 161.9 (d, J = 1.8 Hz, C2), 138.2 (d, J = 9.5 Hz, C3a or C7a), 137.1 (d, J = 4.1 Hz, C7a or C3a), 120.8 (C4 or C7), 120.1 (C5 or C6), 117.4 (C7 or C4), 117.3 (C6 or C5), 103.6 (d, $^3J_{PC}$ = 8.2 Hz, C3), 80.4-77.3 (m, COD), 76.5 (d, $^1J_{RhC}$ = 13.9 Hz, COD), 45.9 (NMe$_2$), 31.4 (d, $^1J_{PC}$ = 31.9 Hz, P(CHMe$_2$)), 29.2-28.2 (m, COD and P(CHMe$_2$)), 26.5 (d of d, $^1J_{PC}$ = 47.4 Hz, $^1J_{RhC}$ = 11.2 Hz, C1), 15.1 (2 P(CHMe_2)), 14.9 (P(CHMe_2)), 14.4 (P(CHMe_2)); ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 82.9. Crystals of **4** suitable for single-crystal X-ray diffraction analysis were grown from diethyl ether at -35 °C.

Preparation of η^5-(3-^{i}Pr$_2$PS-2-Me$_2$N-indenyl)Mn(CO)$_3$ (5). A 1.6M hexanes solution (pre-cooled to -35 °C) of *n*-BuLi (0.20 mL, 0.32 mmol) was added dropwise *via* syringe to a glass vial containing a magnetically stirred solution (pre-cooled to -35 °C) of **2** (0.099 g, 0.32 mmol) in toluene (5 mL) over 2 min, producing a faint yellow solution. The vial containing the reaction mixture was then sealed with a PTFE-lined cap and left to stir for 1.5 h at ambient temperature; the clean lithiation of **2** was monitored *in situ* by the disappearance of a ^{31}P NMR signal corresponding to **2**, and the appearance of a single new resonance at 54 ppm. A mixture of BrMn(CO)$_5$ (0.089 g, 0.32 mmol) in toluene (5 mL) was then transferred to the reaction mixture *via* Pasteur pipette, and the reaction vial was re-sealed. A dark solution formed immediately and after stirring for 3 d the solution changed to a yellow-orange color and a white precipitate formed. The reaction mixture was then filtered through Celite and the supernatant was dried *in vacuo*, yielding **5** as an analytically pure orange solid (0.14 g, 0.31 mmol, 96%). Anal. Calcd for C$_{20}$H$_{25}$PSNO$_3$Mn: C 53.93; H 5.66; N 3.14. Found: C 53.61; H 5.72; N 3.26. ^{1}H NMR (C$_6$D$_6$): δ 9.42 (d, $^3J_{HH}$ = 8.0 Hz, 1H, C4-H or C7-H), 7.06 (d, $^3J_{HH}$ = 8.1 Hz, 1H, C7-H or C4-H), 6.80-6.72 (m, 2H, C5-H and C6-H), 4.46 (s, 1H, C1-H), 3.16 (m, 1H, P(CHMe$_2$)), 2.18 (m, 1H, P(CHMe$_2$)), 2.09 (s, 6H, NMe$_2$), 1.77 (d of d, $^3J_{PH}$ = 18.6 Hz, $^3J_{HH}$ = 6.0 Hz, 3H, P(CHMe_2)), 1.31 (d of d, $^3J_{PH}$ = 17.3 Hz, $^3J_{HH}$ = 5.7 Hz, 3H, P(CHMe_2)), 1.08 (d of d, $^3J_{PH}$ = 17.9 Hz, $^3J_{HH}$ = 6.8 Hz, 3H, P(CHMe_2)), 1.77 (d of d, $^3J_{PH}$ = 17.1 Hz, $^3J_{HH}$ = 6.7 Hz, 3H, P(CHMe_2)); ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 223.7 (CO), 138.7 (C2), 129.0 (C4 or C7), 127.1 (C5 or C6), 126.1 (C6 or C5), 124.7 (C7 or C4), 105.5 (d, J = 7.3 Hz, C7a or C3a), 100.0 (d, J = 7.6 Hz, C3a or C7a), 61.5 (C1), 46.2 (NMe$_2$), 30.7 (m, P(CHMe$_2$)), 28.0 (m, P(CHMe$_2$)), 19.6 (P(CHMe_2)), 19.2 (P(CHMe_2)), 18.5 (P(CHMe_2)), 17.2 (P(CHMe_2)); ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 64.4. FTIR (cm^{-1}) ν(CO): 2014, 1945, 1931. Crystals of **5** suitable for single-crystal X-ray diffraction analysis were grown from diethyl ether at -35 °C.

References:

1. M. Stradiotto, J. Cipot and R. McDonald *J. Am. Chem. Soc.* 2003, **125**, 5618.

2. S. Braun, H.-O. Kalinowski and S. Berger *150 and More Basic NMR Experiments*; Wiley-VCH: Toronto, 1998.

3. H. S. Gutowsky and C. H. Holm *J. Chem. Phys.* 1956, **25**, 1228.

Table 1a. Crystallographic Experimental Details for **2**.

A. Crystal Data

formula	$C_{17}H_{26}NPS$
formula weight	307.42
crystal dimensions (mm)	$0.51 \times 0.14 \times 0.12$
crystal system	orthorhombic
space group	*Pbca* (No. 61)
unit cell parameters[a]	
a (Å)	17.3157 (19)
b (Å)	10.8344 (12)
c (Å)	17.787 (2)
V (Å^3)	3337.0 (6)
Z	8
ρ_{calcd} (g cm^{-3})	1.224
μ (mm^{-1})	0.281

B. Data Collection and Refinement Conditions

diffractometer	Bruker PLATFORM/SMART 1000 CCD[b]
radiation (λ [Å])	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	–80
scan type	ω scans (0.3°) (20 s exposures)
data collection 2θ limit (deg)	52.84
total data collected	22338 ($-21 \leq h \leq 21$, $-13 \leq k \leq 13$, $-21 \leq l \leq 22$)
independent reflections	3424 ($R_{int} = 0.0440$)
number of observed reflections (*NO*)	2883 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	direct methods (*SHELXS–86[c]*)
refinement method	full-matrix least-squares on F^2 (*SHELXL–93[d]*)
absorption correction method	multi-scan (*SADABS*)
range of transmission factors	0.9670--0.8698
data/restraints/parameters	3424 [$F_o^2 \geq -3\sigma(F_o^2)$] / 0 / 187
goodness-of-fit (*S*)[e]	1.064 [$F_o^2 \geq -3\sigma(F_o^2)$]
final *R* indices[f]	
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0338
wR_2 [$F_o^2 \geq -3\sigma(F_o^2)$]	0.0887
largest difference peak and hole	0.433 and –0.178 e Å^{-3}

[a]Obtained from least-squares refinement of 4392 reflections with $4.58° < 2\theta < 52.70°$.

[b]Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

Table 1a. Crystallographic Experimental Details for **2**. (continued)

[c]Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467–473.

[d]Sheldrick, G. M. *SHELXL-93*. Program for crystal structure determination. University of Göttingen, Germany, 1993. Refinement on F_o^2 for all reflections (all of these having $F_o^2 \geq -3\sigma(F_o^2)$). Weighted *R*-factors wR_2 and all goodnesses of fit S are based on F_o^2; conventional *R*-factors R_1 are based on F_o, with F_o set to zero for negative F_o^2. The observed criterion of $F_o^2 > 2\sigma(F_o^2)$ is used only for calculating R_1, and is not relevant to the choice of reflections for refinement. *R*-factors based on F_o^2 are statistically about twice as large as those based on F_o, and *R*-factors based on ALL data will be even larger.

[e]$S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0415P)^2 + 1.3507P]^{-1}$ where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$).

[f]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Table 2a. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for **2**.

Atom	x	y	z	U_{eq}, Å^2
P	0.01997(2)	0.28897(3)	0.10468(2)	0.02134(11)*
S	-0.05663(2)	0.41442(4)	0.13340(3)	0.03408(13)*
N	0.17391(7)	0.18671(12)	-0.00144(7)	0.0264(3)*
C1	0.11556(8)	0.35876(13)	0.07984(8)	0.0219(3)*
C2	0.17926(8)	0.26611(14)	0.05988(8)	0.0239(3)*
C3	0.23575(9)	0.26916(15)	0.11225(9)	0.0274(3)*
C3A	0.21944(9)	0.36460(15)	0.16718(9)	0.0263(3)*
C4	0.26157(10)	0.40317(16)	0.22964(9)	0.0334(4)*
C5	0.23484(10)	0.50327(18)	0.27041(9)	0.0375(4)*
C6	0.16770(10)	0.56414(16)	0.25023(10)	0.0355(4)*
C7	0.12402(9)	0.52452(15)	0.18862(9)	0.0293(4)*
C7A	0.15012(9)	0.42388(14)	0.14776(8)	0.0246(3)*
C8	0.23396(9)	0.09221(16)	-0.00513(10)	0.0337(4)*
C9	0.16266(11)	0.24473(19)	-0.07476(9)	0.0388(4)*
C10	-0.01352(9)	0.20292(14)	0.02204(8)	0.0255(3)*
C11	-0.08265(10)	0.12073(17)	0.04288(10)	0.0356(4)*
C12	-0.03730(10)	0.29090(17)	-0.04104(9)	0.0338(4)*
C13	0.03153(9)	0.17378(15)	0.17944(9)	0.0291(3)*
C14	0.07885(11)	0.05986(17)	0.15831(11)	0.0425(5)*
C15	0.05807(12)	0.22850(19)	0.25434(10)	0.0448(5)*

Anisotropically-refined atoms are marked with an asterisk (*). The form of the anisotropic displacement parameter is: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$.

Table 3a. Selected Interatomic Distances (Å) for **2**.

Atom1	Atom2	Distance	Atom1	Atom2	Distance
P	S	1.9665(6)	C3A	C4	1.393(2)
P	C1	1.8728(15)	C3A	C7A	1.405(2)
P	C10	1.8347(15)	C4	C5	1.384(3)
P	C13	1.8346(16)	C5	C6	1.384(3)
N	C2	1.392(2)	C6	C7	1.399(2)
N	C8	1.461(2)	C7	C7A	1.386(2)
N	C9	1.461(2)	C10	C11	1.537(2)
C1	C2	1.533(2)	C10	C12	1.529(2)
C1	C7A	1.522(2)	C13	C14	1.528(2)
C2	C3	1.351(2)	C13	C15	1.529(2)
C3	C3A	1.450(2)			

Table 4a. Selected Interatomic Angles (deg) for **2**.

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
S	P	C1	112.23(5)	C3	C3A	C4	130.47(15)
S	P	C10	110.25(5)	C3	C3A	C7A	109.07(13)
S	P	C13	110.82(6)	C4	C3A	C7A	120.42(15)
C1	P	C10	107.19(7)	C3A	C4	C5	118.54(16)
C1	P	C13	110.44(7)	C4	C5	C6	121.22(16)
C10	P	C13	105.64(7)	C5	C6	C7	120.74(16)
C2	N	C8	114.89(13)	C6	C7	C7A	118.41(16)
C2	N	C9	116.26(13)	C1	C7A	C3A	108.62(13)
C8	N	C9	110.88(13)	C1	C7A	C7	130.75(15)
P	C1	C2	115.23(10)	C3A	C7A	C7	120.63(15)
P	C1	C7A	110.33(10)	P	C10	C11	110.32(11)
C2	C1	C7A	101.80(12)	P	C10	C12	110.88(11)
N	C2	C1	122.55(13)	C11	C10	C12	109.18(13)
N	C2	C3	127.11(14)	P	C13	C14	115.44(12)
C1	C2	C3	110.20(13)	P	C13	C15	113.62(12)
C2	C3	C3A	109.93(14)	C14	C13	C15	111.49(15)

Table 5a. Torsional Angles (deg) for **2**.

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
S	P	C1	C2	177.64(9)	P	C1	C2	C3	-113.61(13)
S	P	C1	C7A	63.08(11)	C7A	C1	C2	N	-178.17(13)
C10	P	C1	C2	-61.17(12)	C7A	C1	C2	C3	5.79(16)
C10	P	C1	C7A	-175.73(10)	P	C1	C7A	C3A	116.89(12)
C13	P	C1	C2	53.44(13)	P	C1	C7A	C7	-63.12(19)
C13	P	C1	C7A	-61.12(12)	C2	C1	C7A	C3A	-5.91(15)
S	P	C10	C11	-69.54(12)	C2	C1	C7A	C7	174.08(15)
S	P	C10	C12	51.54(12)	N	C2	C3	C3A	-179.41(14)
C1	P	C10	C11	168.04(11)	C1	C2	C3	C3A	-3.58(17)
C1	P	C10	C12	-70.89(12)	C2	C3	C3A	C4	-178.41(16)
C13	P	C10	C11	50.25(13)	C2	C3	C3A	C7A	-0.42(18)
C13	P	C10	C12	171.32(11)	C3	C3A	C4	C5	175.77(16)
S	P	C13	C14	169.86(11)	C7A	C3A	C4	C5	-2.0(2)
S	P	C13	C15	-59.55(14)	C3	C3A	C7A	C1	4.23(16)
C1	P	C13	C14	-65.13(14)	C3	C3A	C7A	C7	-175.76(13)
C1	P	C13	C15	65.46(14)	C4	C3A	C7A	C1	-177.54(14)
C10	P	C13	C14	50.45(14)	C4	C3A	C7A	C7	2.5(2)
C10	P	C13	C15	-178.96(13)	C3A	C4	C5	C6	0.2(2)
C8	N	C2	C1	-170.92(13)	C4	C5	C6	C7	1.2(3)
C8	N	C2	C3	4.4(2)	C5	C6	C7	C7A	-0.8(2)
C9	N	C2	C1	57.24(19)	C6	C7	C7A	C1	178.99(15)
C9	N	C2	C3	-127.42(17)	C6	C7	C7A	C3A	-1.0(2)
P	C1	C2	N	62.44(17)					

Table 6a. Least-Squares Planes for **2**.

Plane	Coefficients[a]			Defining Atoms with Deviations (Å)[b]			
1	9.000(10)	6.686(6)	-10.509(10) 2.642(4)				
				C3A 0.0136(11)	C4 -0.0058(11)		
				C5 -0.0056(12)	C6 0.0093(12)		
				C7 -0.0014(11)	C7A -0.0100(10)		
2	8.305(12)	7.054(8)	-10.464(15) 2.668(5)				
				C3A -0.0231(9)	C3 0.0139(5)		
				C1 -0.0132(5)	C7A 0.0224(9)		
3	8.224(14)	7.661(14)	-9.32(3) 2.955(7)				
				C1	C2	C3	
				N̲ -0.081(5)			

Dihedral angle between planes 1 and 2:   3.02(13)°

Dihedral angle between planes 2 and 3:   4.9(2)°

[a]Coefficients are for the form $ax+by+cz = d$ where x, y and z are crystallographic coordinates.
[b]Underlined atoms were not included in the definition of the plane.

Table 7a. Anisotropic Displacement Parameters (U_{ij}, Å^2) for **2**.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
P	0.0196(2)	0.0242(2)	0.0202(2)	-0.00121(15)	0.00134(14)	-0.00063(14)
S	0.0256(2)	0.0340(2)	0.0427(3)	-0.01074(18)	0.00590(17)	0.00334(17)
N	0.0223(6)	0.0325(7)	0.0243(7)	-0.0026(5)	0.0017(5)	0.0029(5)
C1	0.0212(7)	0.0245(7)	0.0201(7)	0.0024(6)	0.0009(6)	-0.0011(6)
C2	0.0211(7)	0.0269(8)	0.0237(8)	0.0037(6)	0.0038(6)	-0.0008(6)
C3	0.0221(8)	0.0313(8)	0.0288(8)	0.0026(7)	0.0002(6)	-0.0001(6)
C3A	0.0233(7)	0.0306(8)	0.0250(8)	0.0038(6)	0.0008(6)	-0.0062(6)
C4	0.0291(9)	0.0416(10)	0.0296(9)	0.0037(7)	-0.0048(7)	-0.0085(7)
C5	0.0385(10)	0.0479(10)	0.0261(9)	-0.0040(8)	-0.0019(7)	-0.0176(8)
C6	0.0397(10)	0.0356(9)	0.0312(9)	-0.0083(7)	0.0079(7)	-0.0134(8)
C7	0.0287(8)	0.0289(8)	0.0303(9)	-0.0011(7)	0.0043(7)	-0.0060(7)
C7A	0.0249(7)	0.0268(8)	0.0220(8)	0.0026(6)	0.0019(6)	-0.0079(6)
C8	0.0261(8)	0.0344(9)	0.0405(10)	-0.0062(7)	0.0026(7)	0.0034(7)
C9	0.0424(10)	0.0507(11)	0.0234(9)	-0.0010(8)	0.0020(7)	0.0090(9)
C10	0.0243(8)	0.0294(8)	0.0229(8)	-0.0037(6)	0.0003(6)	-0.0005(6)
C11	0.0330(9)	0.0397(9)	0.0339(9)	-0.0061(8)	-0.0005(7)	-0.0117(8)
C12	0.0294(9)	0.0454(10)	0.0267(9)	0.0021(8)	-0.0051(7)	-0.0002(7)
C13	0.0291(8)	0.0359(9)	0.0224(8)	0.0062(7)	0.0015(6)	-0.0063(7)
C14	0.0466(11)	0.0395(10)	0.0414(10)	0.0178(9)	0.0025(9)	0.0061(8)
C15	0.0555(12)	0.0558(12)	0.0230(9)	0.0101(8)	-0.0030(8)	-0.0214(10)

The form of the anisotropic displacement parameter is:

$$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$$

Table 8a. Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms for **2**.

Atom	x	y	z	U_{eq}, Å^2
H1	0.1089	0.4190	0.0377	0.026
H3	0.2797	0.2166	0.1130	0.033
H4	0.3076	0.3617	0.2439	0.040
H5	0.2631	0.5307	0.3130	0.045
H6	0.1511	0.6336	0.2785	0.043
H7	0.0776	0.5656	0.1751	0.035
H8A	0.2352	0.0462	0.0423	0.040
H8B	0.2842	0.1316	-0.0136	0.040
H8C	0.2228	0.0354	-0.0466	0.040
H9A	0.1251	0.3120	-0.0701	0.047
H9B	0.1434	0.1833	-0.1106	0.047
H9C	0.2120	0.2779	-0.0928	0.047
H10	0.0295	0.1493	0.0036	0.031
H11A	-0.1042	0.0838	-0.0028	0.043
H11B	-0.1223	0.1708	0.0677	0.043
H11C	-0.0655	0.0552	0.0770	0.043
H12A	-0.0486	0.2434	-0.0866	0.041
H12B	0.0049	0.3488	-0.0512	0.041
H12C	-0.0834	0.3369	-0.0258	0.041
H13	-0.0218	0.1420	0.1892	0.035
H14A	0.0725	-0.0036	0.1971	0.051
H14B	0.1335	0.0825	0.1544	0.051
H14C	0.0609	0.0277	0.1099	0.051
H15A	0.0512	0.1672	0.2943	0.054
H15B	0.0273	0.3020	0.2658	0.054
H15C	0.1127	0.2514	0.2509	0.054

Table 1b. Crystallographic Experimental Details for **4**.

A. Crystal Data

formula	$C_{25}H_{37}NPRhS$
formula weight	517.50
crystal dimensions (mm)	0.64 x 0.20 x 0.08
crystal system	monoclinic
space group	$P2_1/c$ (No. 14)
unit cell parameters[a]	
a (Å)	10.1379 (7)
b (Å)	12.4282 (8)
c (Å)	18.8478 (13)
β (deg)	93.7628 (11)
V (Å^3)	2369.6 (3)
Z	4
ρ_{calcd} (g cm^{-3})	1.451
μ (mm^{-1})	0.888

B. Data Collection and Refinement Conditions

diffractometer	Bruker PLATFORM/SMART 1000 CCD[b]
radiation (λ [Å])	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	−80
scan type	ω scans (0.3°) (20 s exposures)
data collection 2θ limit (deg)	52.74
total data collected	15830 ($-12 \leq h \leq 11$, $-15 \leq k \leq 15$, $-23 \leq l \leq 23$)
independent reflections	4830 (R_{int} = 0.0314)
number of observed reflections (*NO*)	4087 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	Patterson search/structure expansion (*DIRDIF–99*[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–93*[d])
absorption correction method	multi-scan (*SADABS*)
range of transmission factors	0.9323–0.6002
data/restraints/parameters	4830 [$F_o^2 \geq -3\sigma(F_o^2)$] / 0 / 262
goodness-of-fit (*S*)[e]	1.020 [$F_o^2 \geq -3\sigma(F_o^2)$]
final *R* indices[f]	
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0281
wR_2 [$F_o^2 \geq -3\sigma(F_o^2)$]	0.0770
largest difference peak and hole	0.734 and −0.274 e Å^{-3}

[a]Obtained from least-squares refinement of 5212 reflections with 5.20° $< 2\theta <$ 52.74°.

[b]Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

Table 1b. Crystallographic Experimental Details for **4**. (continued)

[c]Beurskens, P. T.; Beurskens, G.; de Gelder, R.; Garcia-Granda, S.; Israel, R.; Gould, R. O.; Smits, J. M. M. (1999). The *DIRDIF-99* program system. Crystallography Laboratory, University of Nijmegen, The Netherlands.

[d]Sheldrick, G. M. *SHELXL-93*. Program for crystal structure determination. University of Göttingen, Germany, 1993. Refinement on F_o^2 for all reflections (all of these having $F_o^2 \geq -3\sigma(F_o^2)$). Weighted *R*-factors wR_2 and all goodnesses of fit *S* are based on F_o^2; conventional *R*-factors R_1 are based on F_o, with F_o set to zero for negative F_o^2. The observed criterion of $F_o^2 > 2\sigma(F_o^2)$ is used only for calculating R_1, and is not relevant to the choice of reflections for refinement. *R*-factors based on F_o^2 are statistically about twice as large as those based on F_o, and *R*-factors based on ALL data will be even larger.

[e]$S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (*n* = number of data; *p* = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0406P)^2 + 1.2457P]^{-1}$ where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$).

[f]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Table 2b. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for **4**.

Atom	x	y	z	U_{eq}, Å^2
Rh	0.226552(17)	-0.003238(13)	0.215617(9)	0.02248(7)*
S	0.09809(6)	-0.11269(6)	0.28852(3)	0.03435(16)*
P	0.25200(6)	-0.08424(5)	0.35896(3)	0.02176(13)*
N	0.2118(2)	0.17774(17)	0.37100(11)	0.0349(5)*
C1	0.3412(2)	0.02132(18)	0.31956(12)	0.0234(5)*
C2	0.3289(2)	0.13444(19)	0.34671(12)	0.0274(5)*
C3	0.4491(3)	0.1841(2)	0.35001(13)	0.0338(6)*
C3A	0.5471(2)	0.1114(2)	0.32673(13)	0.0313(5)*
C4	0.6827(3)	0.1259(3)	0.31788(15)	0.0428(7)*
C5	0.7554(3)	0.0427(3)	0.29348(16)	0.0485(8)*
C6	0.6962(3)	-0.0542(3)	0.27513(16)	0.0427(7)*
C7	0.5614(3)	-0.0697(2)	0.28122(14)	0.0344(6)*
C7A	0.4866(2)	0.01174(18)	0.30924(13)	0.0262(5)*
C11	0.2953(3)	0.1388(2)	0.16838(13)	0.0319(5)*
C12	0.3723(3)	0.0529(2)	0.14751(13)	0.0341(6)*
C13	0.3606(3)	0.0016(2)	0.07429(16)	0.0466(7)*
C14	0.2611(4)	-0.0904(3)	0.06878(15)	0.0534(8)*
C15	0.1539(3)	-0.0822(2)	0.12031(13)	0.0372(6)*
C16	0.0772(3)	0.0087(2)	0.12930(15)	0.0374(6)*
C17	0.0910(3)	0.1101(2)	0.08596(16)	0.0460(7)*
C18	0.1848(3)	0.1911(2)	0.12292(14)	0.0409(6)*
C21	0.1903(3)	-0.0435(2)	0.44514(13)	0.0314(5)*
C22	0.2964(3)	0.0013(2)	0.49817(14)	0.0432(7)*
C23	0.1056(3)	-0.1288(2)	0.47806(16)	0.0466(7)*
C24	0.3506(3)	-0.20822(19)	0.36877(13)	0.0306(5)*
C25	0.4607(3)	-0.2031(2)	0.42805(15)	0.0418(7)*
C26	0.2675(3)	-0.3094(2)	0.37451(15)	0.0412(6)*
C27	0.0953(3)	0.1839(2)	0.32269(15)	0.0391(6)*
C28	0.2277(3)	0.2760(3)	0.41268(17)	0.0543(9)*

Anisotropically-refined atoms are marked with an asterisk (*). The form of the anisotropic displacement parameter is: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$.

Table 3b. Selected Interatomic Distances (Å) for **4**.

Atom1	Atom2	Distance	Atom1	Atom2	Distance
Rh	S	2.3811(7)	C3A	C7A	1.411(3)
Rh	C1	2.233(2)	C4	C5	1.366(5)
Rh	C11	2.116(2)	C5	C6	1.379(5)
Rh	C12	2.137(3)	C6	C7	1.392(4)
Rh	C15	2.135(2)	C7	C7A	1.390(4)
Rh	C16	2.153(3)	C11	C12	1.394(4)
S	P	2.0127(8)	C11	C18	1.512(4)
P	C1	1.783(2)	C12	C13	1.518(4)
P	C21	1.849(2)	C13	C14	1.524(5)
P	C24	1.840(2)	C14	C15	1.508(4)
N	C2	1.407(3)	C15	C16	1.388(4)
N	C27	1.445(3)	C16	C17	1.513(4)
N	C28	1.455(3)	C17	C18	1.522(4)
C1	C2	1.504(3)	C21	C22	1.525(4)
C1	C7A	1.504(3)	C21	C23	1.522(4)
C2	C3	1.364(4)	C24	C25	1.528(4)
C3	C3A	1.434(4)	C24	C26	1.522(4)
C3A	C4	1.407(4)			

Table 4b. Selected Interatomic Angles (deg) for **4**.

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
S	Rh	C1	81.07(6)	C2	C3	C3A	109.7(2)
S	Rh	C11	158.03(8)	C3	C3A	C4	131.1(2)
S	Rh	C12	163.56(8)	C3	C3A	C7A	109.0(2)
S	Rh	C15	92.96(8)	C4	C3A	C7A	119.9(3)
S	Rh	C16	95.23(8)	C3A	C4	C5	119.7(3)
C1	Rh	C11	95.06(9)	C4	C5	C6	120.7(3)
C1	Rh	C12	98.14(9)	C5	C6	C7	120.9(3)
C1	Rh	C15	158.78(10)	C6	C7	C7A	119.6(3)
C1	Rh	C16	162.44(10)	C1	C7A	C3A	108.4(2)
C11	Rh	C12	38.26(10)	C1	C7A	C7	132.1(2)
C11	Rh	C15	97.72(10)	C3A	C7A	C7	119.2(2)
C11	Rh	C16	81.92(10)	Rh	C11	C12	71.71(15)
C12	Rh	C15	81.87(11)	Rh	C11	C18	110.17(17)
C12	Rh	C16	90.19(10)	C12	C11	C18	125.2(2)
C15	Rh	C16	37.76(11)	Rh	C12	C11	70.03(14)
Rh	S	P	81.41(3)	Rh	C12	C13	113.13(19)
S	P	C1	104.30(8)	C11	C12	C13	124.5(2)
S	P	C21	109.58(9)	C12	C13	C14	112.9(2)
S	P	C24	108.17(9)	C13	C14	C15	114.0(2)
C1	P	C21	111.99(11)	Rh	C15	C14	110.49(19)
C1	P	C24	111.77(11)	Rh	C15	C16	71.85(15)
C21	P	C24	110.75(11)	C14	C15	C16	124.6(3)
C2	N	C27	119.2(2)	Rh	C16	C15	70.39(14)
C2	N	C28	115.5(2)	Rh	C16	C17	112.32(18)
C27	N	C28	110.7(2)	C15	C16	C17	122.6(3)
Rh	C1	P	90.90(10)	C16	C17	C18	112.4(2)
Rh	C1	C2	112.09(15)	C11	C18	C17	113.1(2)
Rh	C1	C7A	109.51(15)	P	C21	C22	114.26(19)
P	C1	C2	119.35(17)	P	C21	C23	113.56(19)
P	C1	C7A	121.59(16)	C22	C21	C23	112.3(2)
C2	C1	C7A	102.85(19)	P	C24	C25	113.88(18)
N	C2	C1	124.0(2)	P	C24	C26	113.54(18)
N	C2	C3	125.6(2)	C25	C24	C26	111.3(2)
C1	C2	C3	110.1(2)				

Table 5b. Torsional Angles (deg) for **4**.

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
C1	Rh	S	P	-9.75(6)	C1	Rh	C15	C14	-71.5(3)
C11	Rh	S	P	-91.07(18)	C1	Rh	C15	C16	167.5(2)
C12	Rh	S	P	78.7(3)	C11	Rh	C15	C14	55.0(2)
C15	Rh	S	P	149.77(8)	C11	Rh	C15	C16	-66.02(18)
C16	Rh	S	P	-172.44(8)	C12	Rh	C15	C14	20.0(2)
S	Rh	C1	P	10.89(7)	C12	Rh	C15	C16	-100.96(17)
S	Rh	C1	C2	-111.47(17)	C16	Rh	C15	C14	121.0(3)
S	Rh	C1	C7A	135.05(15)	S	Rh	C16	C15	-88.07(16)
C11	Rh	C1	P	169.10(10)	S	Rh	C16	C17	153.7(2)
C11	Rh	C1	C2	46.73(18)	C1	Rh	C16	C15	-164.9(3)
C11	Rh	C1	C7A	-66.75(16)	C1	Rh	C16	C17	76.8(4)
C12	Rh	C1	P	-152.50(10)	C11	Rh	C16	C15	113.87(18)
C12	Rh	C1	C2	85.14(18)	C11	Rh	C16	C17	-4.3(2)
C12	Rh	C1	C7A	-28.34(17)	C12	Rh	C16	C15	76.39(17)
C15	Rh	C1	P	-64.0(3)	C12	Rh	C16	C17	-41.8(2)
C15	Rh	C1	C2	173.6(2)	C15	Rh	C16	C17	-118.2(3)
C15	Rh	C1	C7A	60.1(3)	Rh	S	P	C1	12.48(8)
C16	Rh	C1	P	89.9(3)	Rh	S	P	C21	132.54(9)
C16	Rh	C1	C2	-32.4(4)	Rh	S	P	C24	-106.63(9)
C16	Rh	C1	C7A	-145.9(3)	S	P	C1	Rh	-13.18(8)
S	Rh	C11	C12	175.37(14)	S	P	C1	C2	102.94(18)
S	Rh	C11	C18	-62.9(3)	S	P	C1	C7A	-126.87(18)
C1	Rh	C11	C12	96.73(15)	C21	P	C1	Rh	-131.60(10)
C1	Rh	C11	C18	-141.53(18)	C21	P	C1	C2	-15.5(2)
C12	Rh	C11	C18	121.7(2)	C21	P	C1	C7A	114.7(2)
C15	Rh	C11	C12	-66.28(17)	C24	P	C1	Rh	103.46(10)
C15	Rh	C11	C18	55.5(2)	C24	P	C1	C2	-140.42(18)
C16	Rh	C11	C12	-100.69(16)	C24	P	C1	C7A	-10.2(2)
C16	Rh	C11	C18	21.05(19)	S	P	C21	C22	-168.59(17)
S	Rh	C12	C11	-173.87(19)	S	P	C21	C23	60.8(2)
S	Rh	C12	C13	66.1(3)	C1	P	C21	C22	-53.3(2)
C1	Rh	C12	C11	-87.85(15)	C1	P	C21	C23	176.1(2)
C1	Rh	C12	C13	152.2(2)	C24	P	C21	C22	72.2(2)
C11	Rh	C12	C13	-120.0(3)	C24	P	C21	C23	-58.4(2)
C15	Rh	C12	C11	113.59(16)	S	P	C24	C25	-172.29(17)
C15	Rh	C12	C13	-6.4(2)	S	P	C24	C26	-43.5(2)
C16	Rh	C12	C11	76.63(16)	C1	P	C24	C25	73.4(2)
C16	Rh	C12	C13	-43.4(2)	C1	P	C24	C26	-157.76(18)
S	Rh	C15	C14	-144.3(2)	C21	P	C24	C25	-52.2(2)
S	Rh	C15	C16	94.73(16)	C21	P	C24	C26	76.6(2)

Table 5b. Torsional Angles for **4**. (continued)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
C27	N	C2	C1	-60.7(3)	C4	C3A	C7A	C1	-176.5(2)
C27	N	C2	C3	125.5(3)	C4	C3A	C7A	C7	-2.1(4)
C28	N	C2	C1	163.8(2)	C3A	C4	C5	C6	2.2(4)
C28	N	C2	C3	-10.1(4)	C4	C5	C6	C7	-0.2(5)
Rh	C1	C2	N	69.1(3)	C5	C6	C7	C7A	-3.0(4)
Rh	C1	C2	C3	-116.25(19)	C6	C7	C7A	C1	177.0(3)
P	C1	C2	N	-35.3(3)	C6	C7	C7A	C3A	4.1(4)
P	C1	C2	C3	139.41(19)	Rh	C11	C12	C13	104.9(3)
C7A	C1	C2	N	-173.4(2)	C18	C11	C12	Rh	-102.2(2)
C7A	C1	C2	C3	1.3(3)	C18	C11	C12	C13	2.7(4)
Rh	C1	C7A	C3A	117.50(18)	Rh	C11	C18	C17	-34.9(3)
Rh	C1	C7A	C7	-56.0(3)	C12	C11	C18	C17	46.5(4)
P	C1	C7A	C3A	-138.76(18)	Rh	C12	C13	C14	-8.5(3)
P	C1	C7A	C7	47.8(4)	C11	C12	C13	C14	-89.5(3)
C2	C1	C7A	C3A	-1.8(2)	C12	C13	C14	C15	26.1(4)
C2	C1	C7A	C7	-175.3(3)	C13	C14	C15	Rh	-30.8(3)
N	C2	C3	C3A	174.3(2)	C13	C14	C15	C16	50.7(4)
C1	C2	C3	C3A	-0.3(3)	Rh	C15	C16	C17	104.5(2)
C2	C3	C3A	C4	177.1(3)	C14	C15	C16	Rh	-102.8(3)
C2	C3	C3A	C7A	-1.0(3)	C14	C15	C16	C17	1.7(4)
C3	C3A	C4	C5	-179.0(3)	Rh	C16	C17	C18	-13.3(3)
C7A	C3A	C4	C5	-1.1(4)	C15	C16	C17	C18	-93.7(3)
C3	C3A	C7A	C1	1.8(3)	C16	C17	C18	C11	31.8(4)
C3	C3A	C7A	C7	176.2(2)					

Table 6b. Least-Squares Planes for **4**.

Plane	Coefficients[a]				Defining Atoms with Deviations (Å)[b]
1	1.330(6)	-4.080(10)	17.431(5)	5.948(4)	

C1	-0.0108(18)	C2	-0.0157(18)
C3	-0.0008(19)	C3A	0.021(2)
C4	-0.013(2)	C5	-0.002(2)
C6	-0.005(2)	C7	-0.015(2)
C7A	0.042(2)		
Rh	-1.875(2)	P	0.988(3)
N	0.075(3)		

[a]Coefficients are for the form $ax+by+cz = d$ where x, y and z are crystallographic coordinates.
[b]Underlined atoms were not included in the definition of the plane.

Table 7b. Anisotropic Displacement Parameters (U_{ij}, Å^2) for **4**.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Rh	0.02220(11)	0.02516(11)	0.02009(11)	-0.00030(7)	0.00159(7)	-0.00246(7)
S	0.0280(3)	0.0438(4)	0.0306(3)	0.0072(3)	-0.0031(3)	-0.0139(3)
P	0.0190(3)	0.0247(3)	0.0218(3)	-0.0012(2)	0.0027(2)	-0.0014(2)
N	0.0428(13)	0.0321(11)	0.0299(11)	-0.0058(9)	0.0022(10)	0.0101(10)
C1	0.0207(11)	0.0250(11)	0.0245(11)	-0.0026(9)	0.0013(9)	0.0010(9)
C2	0.0323(13)	0.0285(12)	0.0212(11)	0.0001(9)	0.0008(10)	0.0015(10)
C3	0.0438(16)	0.0294(12)	0.0276(12)	-0.0047(10)	-0.0019(11)	-0.0089(11)
C3A	0.0280(13)	0.0382(13)	0.0270(12)	0.0028(10)	-0.0033(10)	-0.0073(10)
C4	0.0310(15)	0.0548(17)	0.0420(16)	0.0008(13)	-0.0020(12)	-0.0178(13)
C5	0.0234(14)	0.072(2)	0.0503(18)	0.0104(16)	0.0041(13)	-0.0053(14)
C6	0.0286(14)	0.0518(17)	0.0490(16)	0.0138(13)	0.0129(12)	0.0101(12)
C7	0.0272(13)	0.0347(13)	0.0421(14)	0.0070(11)	0.0090(11)	0.0029(10)
C7A	0.0216(12)	0.0326(12)	0.0244(11)	0.0046(9)	0.0003(9)	-0.0027(9)
C11	0.0398(15)	0.0313(12)	0.0248(12)	0.0032(10)	0.0040(11)	-0.0102(11)
C12	0.0285(14)	0.0475(15)	0.0269(12)	0.0049(11)	0.0064(10)	-0.0043(11)
C13	0.0527(19)	0.0581(19)	0.0306(14)	-0.0002(12)	0.0161(13)	0.0083(14)
C14	0.079(2)	0.0504(18)	0.0312(15)	-0.0108(13)	0.0081(15)	0.0040(17)
C15	0.0478(17)	0.0361(14)	0.0267(12)	-0.0042(11)	-0.0052(11)	-0.0103(12)
C16	0.0305(14)	0.0484(16)	0.0319(13)	0.0069(11)	-0.0080(11)	-0.0092(12)
C17	0.0427(17)	0.0483(16)	0.0459(16)	0.0152(13)	-0.0064(13)	0.0032(13)
C18	0.0528(18)	0.0353(14)	0.0348(14)	0.0066(11)	0.0050(13)	0.0025(13)
C21	0.0348(14)	0.0342(12)	0.0261(12)	0.0000(10)	0.0098(11)	0.0028(11)
C22	0.0549(19)	0.0510(17)	0.0238(13)	-0.0067(11)	0.0039(12)	-0.0009(14)
C23	0.0571(19)	0.0427(16)	0.0432(16)	0.0010(13)	0.0278(14)	-0.0028(14)
C24	0.0350(14)	0.0303(12)	0.0276(12)	0.0018(10)	0.0092(10)	0.0032(10)
C25	0.0372(16)	0.0457(16)	0.0421(15)	0.0062(13)	-0.0008(12)	0.0107(12)
C26	0.0511(18)	0.0310(13)	0.0431(15)	0.0046(11)	0.0149(13)	0.0010(12)
C27	0.0312(14)	0.0411(15)	0.0457(16)	-0.0078(12)	0.0068(12)	0.0067(11)
C28	0.062(2)	0.0528(18)	0.0475(17)	-0.0230(15)	-0.0029(15)	0.0177(16)

The form of the anisotropic displacement parameter is:

$$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$$

Table 8b. Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms for **4**.

Atom	x	y	z	U_{eq}, Å^2
H3	0.4653	0.2560	0.3654	0.041
H4	0.7236	0.1932	0.3288	0.051
H5	0.8475	0.0518	0.2891	0.058
H6	0.7482	-0.1111	0.2581	0.051
H7	0.5209	-0.1356	0.2663	0.041
H11	0.3428	0.1890	0.2027	0.038
H12	0.4643	0.0528	0.1702	0.041
H13A	0.4483	-0.0259	0.0628	0.056
H13B	0.3336	0.0572	0.0386	0.056
H14A	0.2195	-0.0924	0.0198	0.064
H14B	0.3090	-0.1591	0.0772	0.064
H15	0.1073	-0.1515	0.1284	0.045
H16	-0.0147	-0.0066	0.1428	0.045
H17A	0.0029	0.1437	0.0772	0.055
H17B	0.1240	0.0909	0.0393	0.055
H18A	0.2236	0.2365	0.0865	0.049
H18B	0.1339	0.2387	0.1532	0.049
H21	0.1291	0.0181	0.4338	0.038
H22A	0.3485	0.0555	0.4747	0.052
H22B	0.3545	-0.0573	0.5157	0.052
H22C	0.2543	0.0343	0.5382	0.052
H23A	0.0369	-0.1532	0.4427	0.056
H23B	0.0641	-0.0982	0.5190	0.056
H23C	0.1612	-0.1900	0.4936	0.056
H24	0.3962	-0.2158	0.3235	0.037
H25A	0.5120	-0.1370	0.4232	0.050
H25B	0.5189	-0.2656	0.4247	0.050
H25C	0.4218	-0.2035	0.4743	0.050
H26A	0.1980	-0.3106	0.3358	0.049
H26B	0.2270	-0.3099	0.4203	0.049
H26C	0.3239	-0.3730	0.3711	0.049
H27A	0.0227	0.2162	0.3472	0.047
H27B	0.0700	0.1114	0.3066	0.047
H27C	0.1142	0.2283	0.2816	0.047
H28A	0.1412	0.2998	0.4271	0.065
H28B	0.2661	0.3322	0.3839	0.065
H28C	0.2864	0.2622	0.4551	0.065

Table 1c. Crystallographic Experimental Details for **5**.

A. Crystal Data

formula	$C_{20}H_{25}MnNO_3PS$
formula weight	445.38
crystal dimensions (mm)	$0.46 \times 0.39 \times 0.32$
crystal system	monoclinic
space group	$P2_1/c$ (No. 14)
unit cell parameters[a]	
a (Å)	9.688 (2)
b (Å)	15.570 (4)
c (Å)	13.898 (3)
β (deg)	91.494 (4)
V (Å^3)	2095.8 (8)
Z	4
ρ_{calcd} (g cm^{-3})	1.412
μ (mm^{-1})	0.825

B. Data Collection and Refinement Conditions

diffractometer	Bruker PLATFORM/SMART 1000 CCD[b]
radiation (λ [Å])	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	–80
scan type	ω scans (0.3°) (15 s exposures)
data collection 2θ limit (deg)	52.78
total data collected	16327 ($-12 \leq h \leq 12$, $-19 \leq k \leq 19$, $-17 \leq l \leq 17$)
independent reflections	4273 ($R_{int} = 0.0252$)
number of observed reflections (*NO*)	3966 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	Patterson search/structure expansion (*DIRDIF–99[c]*)
refinement method	full-matrix least-squares on F^2 (*SHELXL–93[d]*)
absorption correction method	multi-scan (*SADABS*)
range of transmission factors	0.7781–0.7027
data/restraints/parameters	4273 [$F_o^2 \geq -3\sigma(F_o^2)$] / 0 / 244
goodness-of-fit (*S*)[e]	1.043 [$F_o^2 \geq -3\sigma(F_o^2)$]
final *R* indices[f]	
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0273
wR_2 [$F_o^2 \geq -3\sigma(F_o^2)$]	0.0764
largest difference peak and hole	0.364 and –0.252 e Å^{-3}

[a]Obtained from least-squares refinement of 7660 reflections with $4.96° < 2\theta < 52.78°$.

[b]Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

Table 1c. Crystallographic Experimental Details for **5**. (continued)

[c]Beurskens, P. T.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Garcia Granda, S.; Gould, R. O.; Israel, R.; Smits, J. M. M. (1996). The *DIRDIF-96* program system. Crystallography Laboratory, University of Nijmegen, The Netherlands.

[d]Sheldrick, G. M. *SHELXL-93*. Program for crystal structure determination. University of Göttingen, Germany, 1993. Refinement on F_o^2 for all reflections (all of these having $F_o^2 \geq -3\sigma(F_o^2)$). Weighted R-factors wR_2 and all goodnesses of fit S are based on F_o^2; conventional R-factors R_1 are based on F_o, with F_o set to zero for negative F_o^2. The observed criterion of $F_o^2 > 2\sigma(F_o^2)$ is used only for calculating R_1, and is not relevant to the choice of reflections for refinement. R-factors based on F_o^2 are statistically about twice as large as those based on F_o, and R-factors based on ALL data will be even larger.

[e]$S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0401P)^2 + 0.9334P]^{-1}$ where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$).

[f]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Table 2c. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for **5**.

Atom	x	y	z	U_{eq}, Å^2
Mn	0.06815(2)	0.099911(14)	0.306505(16)	0.02317(8)*
S	0.31575(5)	-0.07947(3)	0.14839(4)	0.04335(13)*
P	0.38519(4)	0.01383(2)	0.23071(3)	0.02378(10)*
O11	-0.04313(15)	-0.06912(8)	0.24892(11)	0.0494(3)*
O12	0.13100(15)	0.04632(12)	0.50537(10)	0.0584(4)*
O13	-0.20489(14)	0.16081(12)	0.36398(13)	0.0639(5)*
N	0.34625(13)	0.18218(8)	0.39201(9)	0.0258(3)*
C1	0.14592(16)	0.22685(9)	0.28541(12)	0.0280(3)*
C2	0.25821(14)	0.17224(9)	0.30975(10)	0.0226(3)*
C3	0.26328(15)	0.10292(8)	0.23924(10)	0.0211(3)*
C3A	0.15826(15)	0.12409(9)	0.16515(11)	0.0237(3)*
C4	0.11889(17)	0.08601(10)	0.07500(11)	0.0298(3)*
C5	0.01190(18)	0.12137(12)	0.02217(12)	0.0358(4)*
C6	-0.06117(18)	0.19420(12)	0.05457(14)	0.0401(4)*
C7	-0.02684(18)	0.23310(11)	0.13917(14)	0.0370(4)*
C7A	0.08602(15)	0.19900(9)	0.19571(12)	0.0276(3)*
C11	0.00171(17)	-0.00439(10)	0.27097(12)	0.0322(3)*
C12	0.10476(17)	0.06551(12)	0.42715(13)	0.0370(4)*
C13	-0.09917(17)	0.13613(12)	0.34092(13)	0.0378(4)*
C21	0.54608(16)	0.06146(11)	0.18435(11)	0.0315(3)*
C22	0.6378(2)	-0.00594(15)	0.13697(15)	0.0496(5)*
C23	0.5143(2)	0.13472(13)	0.11375(13)	0.0424(4)*
C24	0.42284(17)	-0.02219(10)	0.35535(11)	0.0298(3)*
C25	0.3246(2)	-0.09365(13)	0.38473(17)	0.0501(5)*
C26	0.5715(2)	-0.05270(14)	0.37152(14)	0.0450(4)*
C27	0.48224(18)	0.21501(13)	0.36935(14)	0.0435(4)*
C28	0.28801(19)	0.23584(12)	0.46704(13)	0.0394(4)*

Anisotropically-refined atoms are marked with an asterisk (*). The form of the anisotropic displacement parameter is: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$.

Table 3c. Selected Interatomic Distances (Å) for **5**.

Atom1	Atom2	Distance	Atom1	Atom2	Distance
Mn	C1	2.1381(15)	N	C27	1.455(2)
Mn	C2	2.1579(14)	N	C28	1.461(2)
Mn	C3	2.1312(15)	C1	C2	1.415(2)
Mn	C3A	2.2030(15)	C1	C7A	1.429(2)
Mn	C7A	2.1899(15)	C2	C3	1.4595(19)
Mn	C11	1.8109(17)	C3	C3A	1.466(2)
Mn	C12	1.7869(18)	C3A	C4	1.429(2)
Mn	C13	1.7930(18)	C3A	C7A	1.431(2)
S	P	1.9575(6)	C4	C5	1.370(2)
P	C3	1.8277(14)	C5	C6	1.416(3)
P	C21	1.8566(17)	C6	C7	1.356(3)
P	C24	1.8481(16)	C7	C7A	1.432(2)
O11	C11	1.136(2)	C21	C22	1.534(2)
O12	C12	1.150(2)	C21	C23	1.531(2)
O13	C13	1.147(2)	C24	C25	1.527(2)
N	C2	1.4169(19)	C24	C26	1.528(2)

Table 4c. Selected Interatomic Angles (deg) for **5**.

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
C1	Mn	C2	38.45(5)	C2	C1	C7A	108.58(13)
C1	Mn	C3	66.41(5)	Mn	C2	N	124.70(10)
C1	Mn	C3A	64.56(6)	Mn	C2	C1	70.02(8)
C1	Mn	C7A	38.53(6)	Mn	C2	C3	69.12(8)
C1	Mn	C11	156.30(7)	N	C2	C1	124.77(13)
C1	Mn	C12	110.11(7)	N	C2	C3	126.33(12)
C1	Mn	C13	94.02(7)	C1	C2	C3	108.85(13)
C2	Mn	C3	39.78(5)	Mn	C3	P	126.43(7)
C2	Mn	C3A	64.64(5)	Mn	C3	C2	71.09(8)
C2	Mn	C7A	64.15(6)	Mn	C3	C3A	72.89(8)
C2	Mn	C11	140.43(7)	P	C3	C2	129.64(11)
C2	Mn	C12	89.34(6)	P	C3	C3A	124.25(11)
C2	Mn	C13	127.38(7)	C2	C3	C3A	105.69(12)
C3	Mn	C3A	39.50(5)	Mn	C3A	C3	67.61(8)
C3	Mn	C7A	65.72(5)	Mn	C3A	C4	127.45(10)
C3	Mn	C11	102.31(7)	Mn	C3A	C7A	70.50(8)
C3	Mn	C12	105.16(7)	C3	C3A	C4	133.40(14)
C3	Mn	C13	158.21(7)	C3	C3A	C7A	108.10(13)
C3A	Mn	C7A	38.01(5)	C4	C3A	C7A	118.50(14)
C3A	Mn	C11	93.23(7)	C3A	C4	C5	118.96(16)
C3A	Mn	C12	144.53(7)	C4	C5	C6	121.92(16)
C3A	Mn	C13	124.48(7)	C5	C6	C7	121.32(15)
C7A	Mn	C11	118.30(7)	C6	C7	C7A	118.47(16)
C7A	Mn	C12	148.61(7)	Mn	C7A	C1	68.77(9)
C7A	Mn	C13	93.13(7)	Mn	C7A	C3A	71.49(8)
C11	Mn	C12	92.72(8)	Mn	C7A	C7	125.03(11)
C11	Mn	C13	92.15(8)	C1	C7A	C3A	108.41(13)
C12	Mn	C13	90.16(8)	C1	C7A	C7	130.80(15)
S	P	C3	112.85(5)	C3A	C7A	C7	120.79(15)
S	P	C21	111.86(6)	Mn	C11	O11	178.35(16)
S	P	C24	112.28(6)	Mn	C12	O12	177.34(17)
C3	P	C21	105.61(7)	Mn	C13	O13	178.49(18)
C3	P	C24	106.36(7)	P	C21	C22	112.11(14)
C21	P	C24	107.43(8)	P	C21	C23	111.30(11)
C2	N	C27	113.14(13)	C22	C21	C23	110.10(15)
C2	N	C28	113.75(12)	P	C24	C25	111.26(12)
C27	N	C28	108.80(13)	P	C24	C26	113.24(12)
Mn	C1	C2	71.53(8)	C25	C24	C26	109.03(15)
Mn	C1	C7A	72.70(8)				

Table 5c. Torsional Angles (deg) for **5**.

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
C2	Mn	C1	C7A	117.12(13)	C7A	Mn	C3	C3A	-35.74(8)
C3	Mn	C1	C2	-37.02(9)	C11	Mn	C3	P	-40.34(11)
C3	Mn	C1	C7A	80.10(9)	C11	Mn	C3	C2	-166.16(9)
C3A	Mn	C1	C2	-80.57(9)	C11	Mn	C3	C3A	79.98(9)
C3A	Mn	C1	C7A	36.55(8)	C12	Mn	C3	P	55.95(11)
C7A	Mn	C1	C2	-117.12(13)	C12	Mn	C3	C2	-69.87(10)
C11	Mn	C1	C2	-102.42(18)	C12	Mn	C3	C3A	176.27(9)
C11	Mn	C1	C7A	14.7(2)	C13	Mn	C3	P	-170.79(15)
C12	Mn	C1	C2	61.27(11)	C13	Mn	C3	C2	63.4(2)
C12	Mn	C1	C7A	178.39(10)	C13	Mn	C3	C3A	-50.5(2)
C13	Mn	C1	C2	152.91(10)	C1	Mn	C3A	C3	83.12(9)
C13	Mn	C1	C7A	-89.97(10)	C1	Mn	C3A	C4	-148.53(15)
C1	Mn	C2	N	119.09(15)	C1	Mn	C3A	C7A	-37.04(9)
C1	Mn	C2	C3	-120.43(12)	C2	Mn	C3A	C3	40.36(8)
C3	Mn	C2	N	-120.47(15)	C2	Mn	C3A	C4	168.71(15)
C3	Mn	C2	C1	120.43(12)	C2	Mn	C3A	C7A	-79.80(9)
C3A	Mn	C2	N	-160.54(13)	C3	Mn	C3A	C4	128.35(17)
C3A	Mn	C2	C1	80.36(10)	C3	Mn	C3A	C7A	-120.16(12)
C3A	Mn	C2	C3	-40.07(8)	C7A	Mn	C3A	C3	120.16(12)
C7A	Mn	C2	N	157.13(13)	C7A	Mn	C3A	C4	-111.49(17)
C7A	Mn	C2	C1	38.03(9)	C11	Mn	C3A	C3	-105.50(9)
C7A	Mn	C2	C3	-82.40(9)	C11	Mn	C3A	C4	22.85(14)
C11	Mn	C2	N	-98.95(14)	C11	Mn	C3A	C7A	134.35(10)
C11	Mn	C2	C1	141.96(11)	C12	Mn	C3A	C3	-6.22(15)
C11	Mn	C2	C3	21.52(13)	C12	Mn	C3A	C4	122.13(16)
C12	Mn	C2	N	-5.47(13)	C12	Mn	C3A	C7A	-126.38(13)
C12	Mn	C2	C1	-124.56(11)	C13	Mn	C3A	C3	159.67(9)
C12	Mn	C2	C3	115.00(10)	C13	Mn	C3A	C4	-71.98(16)
C13	Mn	C2	N	84.22(14)	C13	Mn	C3A	C7A	39.51(12)
C13	Mn	C2	C1	-34.87(13)	C1	Mn	C7A	C3A	119.16(12)
C13	Mn	C2	C3	-155.31(10)	C1	Mn	C7A	C7	-125.72(18)
C1	Mn	C3	P	161.63(11)	C2	Mn	C7A	C1	-37.95(9)
C1	Mn	C3	C2	35.81(8)	C2	Mn	C7A	C3A	81.20(9)
C1	Mn	C3	C3A	-78.05(9)	C2	Mn	C7A	C7	-163.67(16)
C2	Mn	C3	P	125.82(13)	C3	Mn	C7A	C1	-82.05(9)
C2	Mn	C3	C3A	-113.86(11)	C3	Mn	C7A	C3A	37.11(8)
C3A	Mn	C3	P	-120.32(13)	C3	Mn	C7A	C7	152.24(16)
C3A	Mn	C3	C2	113.86(11)	C3A	Mn	C7A	C1	-119.16(12)
C7A	Mn	C3	P	-156.06(11)	C3A	Mn	C7A	C7	115.13(18)
C7A	Mn	C3	C2	78.12(9)	C11	Mn	C7A	C1	-173.35(9)

Table 5c. Torsional Angles for **5**. (continued)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
C11	Mn	C7A	C3A	-54.19(11)	C3	P	C21	C22	-158.10(12)
C11	Mn	C7A	C7	60.94(16)	C3	P	C21	C23	-34.28(14)
C12	Mn	C7A	C1	-2.91(17)	C24	P	C21	C22	88.68(13)
C12	Mn	C7A	C3A	116.25(15)	C24	P	C21	C23	-147.50(12)
C12	Mn	C7A	C7	-128.62(17)	S	P	C24	C25	-32.28(14)
C13	Mn	C7A	C1	92.53(10)	S	P	C24	C26	90.95(13)
C13	Mn	C7A	C3A	-148.32(10)	C3	P	C24	C25	91.61(14)
C13	Mn	C7A	C7	-33.19(16)	C3	P	C24	C26	-145.16(12)
C1	Mn	C11	O11	-96(5)	C21	P	C24	C25	-155.67(13)
C2	Mn	C11	O11	-168(5)	C21	P	C24	C26	-32.45(14)
C3	Mn	C11	O11	-154(5)	C27	N	C2	Mn	165.48(11)
C3A	Mn	C11	O11	-116(5)	C27	N	C2	C1	-105.97(17)
C7A	Mn	C11	O11	-85(5)	C27	N	C2	C3	77.14(18)
C12	Mn	C11	O11	99(5)	C28	N	C2	Mn	-69.70(16)
C13	Mn	C11	O11	9(5)	C28	N	C2	C1	18.8(2)
C1	Mn	C12	O12	-3(4)	C28	N	C2	C3	-158.04(14)
C2	Mn	C12	O12	30(4)	Mn	C1	C2	N	-119.01(14)
C3	Mn	C12	O12	67(4)	Mn	C1	C2	C3	58.35(10)
C3A	Mn	C12	O12	71(4)	C7A	C1	C2	Mn	-63.70(10)
C7A	Mn	C12	O12	-1(4)	C7A	C1	C2	N	177.29(13)
C11	Mn	C12	O12	171(4)	C7A	C1	C2	C3	-5.36(17)
C13	Mn	C12	O12	-97(4)	Mn	C1	C7A	C3A	-60.78(10)
C1	Mn	C13	O13	-37(8)	Mn	C1	C7A	C7	118.56(18)
C2	Mn	C13	O13	-16(8)	C2	C1	C7A	Mn	62.95(10)
C3	Mn	C13	O13	-62(8)	C2	C1	C7A	C3A	2.17(17)
C3A	Mn	C13	O13	-99(8)	C2	C1	C7A	C7	-178.49(16)
C7A	Mn	C13	O13	-76(8)	Mn	C2	C3	P	-122.10(12)
C11	Mn	C13	O13	166(8)	Mn	C2	C3	C3A	65.22(9)
C12	Mn	C13	O13	73(8)	N	C2	C3	Mn	118.41(14)
S	P	C3	Mn	67.33(10)	N	C2	C3	P	-3.7(2)
S	P	C3	C2	162.41(11)	N	C2	C3	C3A	-176.38(13)
S	P	C3	C3A	-26.12(13)	C1	C2	C3	Mn	-58.89(10)
C21	P	C3	Mn	-170.16(9)	C1	C2	C3	P	179.01(11)
C21	P	C3	C2	-75.09(14)	C1	C2	C3	C3A	6.32(15)
C21	P	C3	C3A	96.38(13)	Mn	C3	C3A	C4	-121.04(17)
C24	P	C3	Mn	-56.20(11)	Mn	C3	C3A	C7A	59.04(10)
C24	P	C3	C2	38.87(15)	P	C3	C3A	Mn	122.83(11)
C24	P	C3	C3A	-149.66(12)	P	C3	C3A	C4	1.8(2)
S	P	C21	C22	-34.97(14)	P	C3	C3A	C7A	-178.13(10)
S	P	C21	C23	88.85(13)	C2	C3	C3A	Mn	-63.99(9)

Table 5c. Torsional Angles for **5**. (continued)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
C2	C3	C3A	C4	174.98(15)	C4	C3A	C7A	Mn	122.81(13)
C2	C3	C3A	C7A	-4.95(15)	C4	C3A	C7A	C1	-178.11(13)
Mn	C3A	C4	C5	85.07(18)	C4	C3A	C7A	C7	2.5(2)
C3	C3A	C4	C5	178.74(15)	C3A	C4	C5	C6	-0.3(2)
C7A	C3A	C4	C5	-1.3(2)	C4	C5	C6	C7	1.0(3)
Mn	C3A	C7A	C1	59.08(10)	C5	C6	C7	C7A	0.1(3)
Mn	C3A	C7A	C7	-120.34(15)	C6	C7	C7A	Mn	-89.9(2)
C3	C3A	C7A	Mn	-57.25(10)	C6	C7	C7A	C1	178.86(16)
C3	C3A	C7A	C1	1.83(16)	C6	C7	C7A	C3A	-1.9(2)
C3	C3A	C7A	C7	-177.59(14)					

Table 6c. Least-Squares Planes for **5**.

Plane	Coefficients[a]				Defining Atoms with Deviations (Å)[b]

Plane		Coefficients[a]			Defining Atoms with Deviations (Å)[b]
1	6.346(4)	9.055(7)	-6.941(5)	0.9955(16)	

C1	0.0035(12)	C2	0.0527(11)
C3	-0.0534(11)	C3A	-0.0139(13)
C4	0.0172(12)	C5	0.0251(13)
C6	-0.0040(14)	C7	-0.0211(13)
C7A	-0.0061(14)		
<u>Mn</u>	-1.7858(8)	<u>P</u>	-0.0274(18)
<u>N</u>	0.1304(18)		

[a]Coefficients are for the form $ax+by+cz = d$ where x, y and z are crystallographic coordinates.
[b]Underlined atoms were not included in the definition of the plane.

Table 7c. Anisotropic Displacement Parameters (U_{ij}, Å^2) for **5**.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mn	0.01762(12)	0.02378(13)	0.02805(13)	0.00005(8)	-0.00052(9)	-0.00234(8)
S	0.0462(3)	0.0317(2)	0.0512(3)	-0.01946(19)	-0.0177(2)	0.01067(18)
P	0.02365(19)	0.02203(18)	0.02543(19)	-0.00339(14)	-0.00396(14)	0.00527(14)
O11	0.0505(8)	0.0306(7)	0.0665(9)	-0.0011(6)	-0.0090(7)	-0.0149(6)
O12	0.0454(8)	0.0931(12)	0.0363(7)	0.0205(7)	-0.0085(6)	-0.0283(8)
O13	0.0245(7)	0.0851(12)	0.0827(11)	-0.0200(9)	0.0111(7)	0.0044(7)
N	0.0222(6)	0.0238(6)	0.0311(6)	-0.0065(5)	-0.0038(5)	-0.0009(5)
C1	0.0242(7)	0.0198(7)	0.0400(8)	-0.0017(6)	-0.0015(6)	0.0007(5)
C2	0.0192(7)	0.0189(6)	0.0297(7)	-0.0004(5)	0.0009(5)	-0.0017(5)
C3	0.0182(7)	0.0193(6)	0.0255(7)	0.0005(5)	-0.0008(5)	-0.0001(5)
C3A	0.0208(7)	0.0222(7)	0.0280(7)	0.0043(6)	-0.0012(5)	-0.0019(5)
C4	0.0302(8)	0.0308(8)	0.0281(8)	0.0025(6)	-0.0027(6)	-0.0041(6)
C5	0.0360(9)	0.0401(9)	0.0308(8)	0.0091(7)	-0.0090(7)	-0.0096(7)
C6	0.0307(9)	0.0401(9)	0.0486(10)	0.0177(8)	-0.0146(7)	-0.0023(7)
C7	0.0291(8)	0.0281(8)	0.0534(10)	0.0093(7)	-0.0086(7)	0.0043(6)
C7A	0.0232(7)	0.0216(7)	0.0379(8)	0.0045(6)	-0.0030(6)	-0.0003(5)
C11	0.0290(8)	0.0309(8)	0.0366(9)	0.0049(6)	-0.0036(7)	-0.0038(6)
C12	0.0245(8)	0.0489(10)	0.0375(9)	0.0049(7)	-0.0004(7)	-0.0146(7)
C13	0.0237(8)	0.0457(10)	0.0440(10)	-0.0068(8)	0.0005(7)	-0.0042(7)
C21	0.0238(8)	0.0425(9)	0.0282(8)	-0.0001(7)	0.0011(6)	0.0062(6)
C22	0.0387(10)	0.0667(13)	0.0438(10)	-0.0043(9)	0.0086(8)	0.0215(9)
C23	0.0375(10)	0.0535(11)	0.0367(9)	0.0113(8)	0.0072(7)	0.0039(8)
C24	0.0371(9)	0.0241(7)	0.0281(7)	0.0024(6)	-0.0034(6)	0.0044(6)
C25	0.0504(12)	0.0394(10)	0.0603(13)	0.0219(9)	-0.0050(10)	-0.0019(8)
C26	0.0424(10)	0.0529(11)	0.0391(10)	0.0111(8)	-0.0125(8)	0.0084(8)
C27	0.0249(8)	0.0559(11)	0.0499(10)	-0.0198(9)	0.0011(7)	-0.0108(8)
C28	0.0356(9)	0.0435(10)	0.0390(9)	-0.0176(8)	-0.0007(7)	-0.0016(7)

The form of the anisotropic displacement parameter is:

$$\exp[-2\pi^2(h^2 a^{*2} U_{11} + k^2 b^{*2} U_{22} + l^2 c^{*2} U_{33} + 2klb^*c^* U_{23} + 2hla^*c^* U_{13} + 2hka^*b^* U_{12})]$$

Table 8c. Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms for **5**.

Atom	x	y	z	U_{eq}, Å^2
H1	0.1182	0.2791	0.3220	0.034
H4	0.1662	0.0369	0.0521	0.036
H5	-0.0140	0.0963	-0.0379	0.043
H6	-0.1357	0.2162	0.0163	0.048
H7	-0.0765	0.2818	0.1604	0.044
H21	0.5994	0.0861	0.2404	0.038
H22A	0.6577	-0.0524	0.1828	0.060
H22B	0.7244	0.0209	0.1180	0.060
H22C	0.5897	-0.0293	0.0798	0.060
H23A	0.4561	0.1775	0.1448	0.051
H23B	0.4656	0.1118	0.0566	0.051
H23C	0.6008	0.1617	0.0947	0.051
H24	0.4079	0.0278	0.3990	0.036
H25A	0.2290	-0.0744	0.3749	0.060
H25B	0.3411	-0.1077	0.4528	0.060
H25C	0.3406	-0.1447	0.3454	0.060
H26A	0.6352	-0.0070	0.3531	0.054
H26B	0.5876	-0.1038	0.3322	0.054
H26C	0.5872	-0.0668	0.4396	0.054
H27A	0.5381	0.2209	0.4288	0.052
H27B	0.4726	0.2712	0.3381	0.052
H27C	0.5276	0.1750	0.3259	0.052
H28A	0.3536	0.2396	0.5217	0.047
H28B	0.2015	0.2104	0.4883	0.047
H28C	0.2699	0.2935	0.4414	0.047