Rhodium(III) complexes with sterically-hindered thiolate ligands. Crystal structures of [$Rh(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_3$] and [$Rh(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_2(C_5Me_5)$]·$CH_3CN$

Eric Block, Gabriel Ofori-Okai
Department of Chemistry, State University of New York at Albany, Albany, NY 12222 (USA)

Hyunkyu Kang, Qin Chen and Jon Zubieta*
Department of Chemistry, Syracuse University, Syracuse, NY 13244 (USA)

(Received June 27, 1991)

Abstract

The complex [$Rh(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_3$] (**1**) may be prepared by the reaction of $Rh(NO_3)_3$ with $2\text{-}HSC_5H_3N\text{-}3\text{-}SiMe_3$ in ethanol. The structure of **1** is similar to that of [$Rh(2\text{-}SC_5H_4N)_3$]. The reaction of [$Rh(C_5Me_5)Cl_2]_2$ with $2\text{-}HSC_5H_3N\text{-}3\text{-}SiMe_3$ in acetonitrile yields [$Rh(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_2(C_5Me_5)$]·$CH_3CN$ (**2**), whose structure exhibits two distinct types of pyridinethiolato ligation: monodentate through the S donor and bidentate through S and N donors. Crystal data: **1**, orthorhombic, *Pbca*, $a=23.444(4)$, $b=21.138(4)$, $c=13.348(2)$ Å, $V=6615.1(12)$ Å^3, $Z=8$; **2**, monoclinic, *C2/c*, $a=18.978(3)$, $b=14.437(2)$, $c=24.309(5)$ Å, $\beta=100.09(1)°$, $V=6557.4(11)$ Å^3, $Z=8$.

Introduction

The versatility of the 2-pyridinethione ligand, $2\text{-}HSC_5H_4N$, is demonstrated by the variety of bonding modes which it may adopt in its coordination compounds [1–28]. As the conjugate anion, 2-pyridinethiolate, $^-SC_5H_4N$, this ligand may coordinate as a monodentate group through the sulfur donor, as a bidentate chelating moiety through the sulfur and nitrogen donors, or as a bridging ligand through both donor groups. As part of our investigations of the chemistry of sterically-hindered thiolate ligands [29–39], we have prepared Rh(III) complexes of the 3-(triorganosilyl)pyridine-2-thiol ligand.

Here we report the X-ray structures of the tris-chelate compound [$Rh(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_3$] (**1**) and of the pentamethylcyclopentadienyl derivative [$Rh(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_2(C_5Me_5)$]·$CH_3CH$ (**2**).

Experimental

The ligand $2\text{-}HSC_5H_3N\text{-}3\text{-}SiMe_3$ was prepared as previously described [36]. Dichloromethane was technical grade and was distilled from $CoCl_2$ and P_4O_{10}. The following instruments were used in the study: IR, Perkin-Elmer 283B IR spectrophotometer; X-ray crystallography, Rigaku AFC-5S four-circle diffractometer.

[$Rh(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_3$] (1)

An ethanol solution containing $Rh(NO_3)_3$ (0.289 g, 1.0 mmol) and $2\text{-}HSC_5H_3N\text{-}3\text{-}SiMe_3$ (0.549 g, 3.0 mmol) was stirred for 2 h at room temperature. The resultant red solution was treated with diethyl ether to give a turbid mixture which was stored at 4 °C overnight. The red solid was collected, washed with ethanol/ether (1:2 vol./vol.) and dissolved in CH_2Cl_2. This solution was carefully layered with diethyl ether and allowed to stand for 5 days, whereupon ruby red crystals of **1** deposited in 65% yield. *Anal.* Calc. for $C_{24}H_{36}N_3Si_3S_3Rh$: C, 44.4; H, 5.55; N, 6.48. Found: C, 43.9; H, 5.44; N, 6.56%.

[$Rh(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_2(C_5Me_5)$]·$CH_3CN$ (2)

An acetonitrile suspension (20 ml) of [$Rh(C_5Me_5)Cl_2]_2$ (0.124 g, 0.2 mmol) and $2\text{-}HSC_5H_3N\text{-}3\text{-}SiMe_3$ (0.073 g, 0.4 mmol) was stirred for 8 h at room temperature. After concentrating the solution to 10 ml, diethyl ether was added carefully and the two solvents allowed to diffuse for 5 days. Red crystals of **2** were isolated in 56% yield. *Anal.* Calc. for $C_{28}H_{42}N_3Si_2S_2Rh$: C, 52.3; H, 6.53; N, 6.53. Found: C, 51.9; H, 6.32; N, 6.55%.

---

*Author to whom correspondence should be addressed.

0020-1693/91/$3.50

[Rh(2-SC$_5$H$_3$N-3-SiMe$_3$)(2-SC$_5$H$_3$NH-3-SiMe$_3$)(C$_5$Me$_5$)]Cl (3)

A solution of HCl in CH$_2$Cl$_2$ (0.40 ml of a 0.13 M solution) was added to a solution of **2** (0.064 g, 0.1 mmol) in CH$_2$Cl$_2$ (5 ml) and stirred overnight at room temperature. The solvent was removed and the residue dissolved in CH$_2$Cl$_2$. Addition of diethyl ether yielded a bright red precipitate of **3**. *Anal.* Calc. for $C_{28}H_{43}N_3Si_2S_2ClRh$: C, 49.5; H, 6.33; N, 6.18. Found: C, 49.3; H, 6.30; N, 6.00%.

TABLE 1. Summary of crystal data and experimental conditions for the X-ray studies of [Rh(2-SC$_5$H$_3$N-3-SiMe$_3$)$_3$] (**1**) and [Rh(2-SC$_5$H$_3$N-3-SiMe$_3$)$_2$(C$_5$Me$_5$)]·CH$_3$CH (**2**)

Crystal		
Empirical formula	$C_{24}H_{36}N_3Si_3S_3Rh$	$C_{28}H_{42}N_3Si_2S_2Rh$
Color, habit	red block	red needle
Crystal size (mm)	0.32×0.35×0.31	0.20×0.32×0.24
Crystal system	orthorhombic	monoclinic
Space group	*Pbca*	*C2/c*
Unit cell dimensions		
a (Å)	23.444(4)	18.978(3)
b (Å)	21.138(4)	14.437(2)
c (Å)	13.348(2)	24.309(5)
β (°)		100.09(1)
Volume (Å^3)	6615.1(12)	6557.4(11)
Z	8	8
Formula weight	649.91	640.77
Density (calc.) (g cm^{-3})	1.305	1.298
Density (exp.) (g cm^{-3})	1.31(1)	1.28(1)
Absorption coefficient (cm^{-1})	8.31	7.26
F(000)	2496	2688
Data collection		
Diffractometer	Rigaku AFC5S	
Radiation	Mo Kα (λ=0.71073 Å)	
Temperature (K)	293	
Monochromator	highly oriented graphite	
2θ range (°)	2–45	
Scan speed (°/min)	8	
Scan range (°)	(1.50+0.30 tan θ)	
Background measurement	stationary background counts at each side of the reflections	
Standard reflections	3 monitored every 250 reflections	
Reflections collected	6240	6321
Observed reflections with $I_o \geq 3\sigma(I_o)$	2788	4563
Absorption correction	based on Ψ scans for 5 reflections with χ angles near 90° or 270°	
Solution and refinement		
System used	TEXSAN solution package	
Solution	Patterson	
Refinement method	full-matrix least squares	
Quantity minimized	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$	
Hydrogen atoms	idealized positions	
Weighting scheme	$4F_o^2/\sigma^2(F_o^2)$	
Final R indices (obs. data) R	0.057	0.038
R_w	0.069	0.052
Goodness of fit	1.96	2.21
Largest and mean Δ/σ	0.06	0.11
Data to parameter ratio	9.1:1	14.7:1
Largest difference peak (e$^-$ Å^3)	0.52	0.22
Largest difference hole (e^{-3} Å^3)	−0.47	−0.43

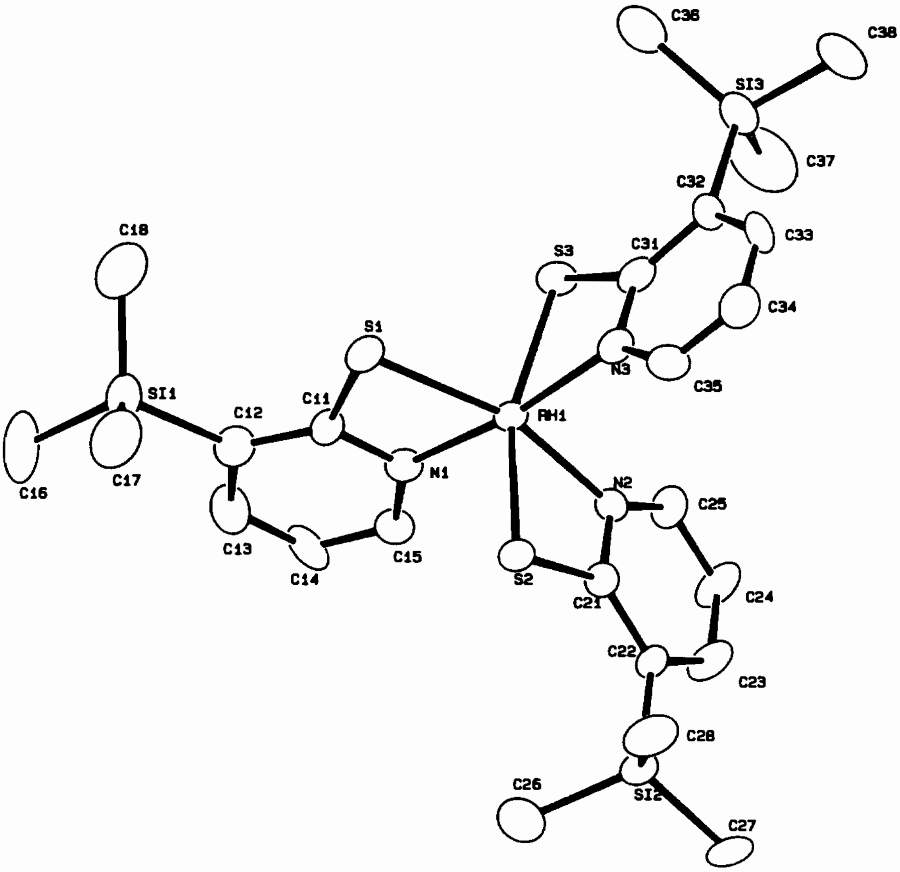

Fig. 1. ORTEP view of the structure of $[Rh(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_3]$ (**1**).

X-ray structure determinations

Full details of the crystallographic methodologies may be found in ref. 40. The crystal data and experimental conditions are summarized in Table 1.

In no instance was an extinction correction applied to the data. Idealized hydrogen atom positions were used throughout the analysis, with the C–H distances set at 0.96 Å. All non-hydrogen atoms of both structures were refined anisotropically.

Results and discussion

The attachment of bulky organic substituents to thiolate ligands not only affords enhanced solubility to their metal complexes but also allows some steric control of coordination geometry and oligomerization processes. The ligand $2\text{-}HSC_5H_3N\text{-}3\text{-}SiMe_3$ reacts with $Rh(NO_3)_3$ in organic solvents to give $[Rh(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_3]$ (**1**), a species structurally analogous to the previously described $[Rh(2\text{-}SC_5H_4N)_3]$ [3]. However, $[Rh(2\text{-}SC_5H_4N)_3]$ reacts with excess $2\text{-}HSC_5H_4N$ to give the complex $[Rh(2\text{-}SC_5H_4N)_3(2\text{-}SC_5H_4NH)]$, in which two ligands adopt the chelating mode, one the monodentate thiolato S-donor mode, and one the monodentate 2-(1*H*)-pyridenthione mode. In contrast, **1** does not react with excess $2\text{-}HSC_5H_3N\text{-}3\text{-}SiMe_3$ or with $2\text{-}HSC_5H_4N$, presumably as a consequence of the steric constraints imposed by the triorganosilyl groups. Attempts to protonate **1** with HCl or HBF_4 were likewise unsuccessful.

The binuclear pentamethylcyclopentadienyl species $[Rh(C_5Me_5)Cl_2]_2$ also reacts readily with $2\text{-}HSC_5H_3N\text{-}3\text{-}SiMe_3$ to give $[Rh(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_2(C_5Me_5)]\cdot CH_3CN$ (**2**). In contrast to **1**, complex **2** reacts with proton sources to give a complex analyzing for $[Rh(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)(2\text{-}SC_5H_3NH\text{-}3\text{-}SiMe_3)(C_5Me_5)]Cl$ (**3**), which suggested that one of the thiolate ligands of **2** has a pyridine nitrogen readily accessible to protonating reagents. The IR spectrum of **3** revealed the presence of ν(N–H) at 3250 cm^{-1}, a feature absent from the spectra of **1** and **2**.

The structure of **1**, shown in Fig. 1, consists of discrete mononuclear species with the rhodium center in a distorted octahedral $[RhS_3N_3]$ geometry with

TABLE 2. Atomic positional parameters for [Rh(2-SC_5H_3N-3-$SiMe_3)_3$] (**1**)

Atom	x	y	z	B_{eq}
Rh1	0.23159(4)	0.25374(4)	0.04247(6)	2.74(4)
S1	0.2892(1)	0.3307(1)	−0.0404(2)	3.7(1)
S2	0.2897(1)	0.1627(1)	0.0209(2)	3.4(1)
S3	0.1504(1)	0.3216(1)	0.0594(2)	3.6(2)
Si1	0.4093(2)	0.4233(2)	0.0403(3)	5.2(2)
Si2	0.3001(2)	0.0150(2)	0.1444(3)	3.6(2)
Si3	0.0104(2)	0.3201(2)	−0.0440(3)	4.8(2)
N1	0.2883(4)	0.2907(4)	0.1369(7)	3.2(5)
N2	0.2060(4)	0.1821(4)	0.1359(7)	3.0(4)
N3	0.1681(4)	0.2297(4)	−0.0547(7)	3.2(5)
C11	0.3187(5)	0.3316(6)	0.0798(8)	3.2(6)
C12	0.3652(6)	0.3672(6)	0.117(1)	4.3(7)
C13	0.3771(6)	0.3562(7)	0.219(1)	5.0(8)
C14	0.3469(5)	0.3149(7)	0.2756(9)	4.6(7)
C15	0.3028(5)	0.2815(6)	0.2336(8)	3.9(6)
C16	0.4660(8)	0.457(1)	0.125(2)	11(1)
C17	0.4459(7)	0.3775(8)	−0.059(1)	8(1)
C18	0.3661(7)	0.4877(8)	−0.011(1)	8(1)
C21	0.2445(5)	0.1366(5)	0.1165(8)	3.0(5)
C22	0.2460(5)	0.0794(5)	0.1695(8)	3.0(5)
C23	0.2052(6)	0.0742(6)	0.245(1)	4.6(7)
C24	0.1666(6)	0.1215(6)	0.266(1)	5.2(8)
C25	0.1671(5)	0.1752(6)	0.210(1)	4.0(7)
C26	0.3713(6)	0.0421(8)	0.185(1)	8(1)
C27	0.2785(6)	−0.0550(5)	0.219(1)	4.6(7)
C28	0.3025(7)	−0.0036(6)	0.008(1)	5.6(8)
C31	0.1251(5)	0.2692(5)	−0.0308(8)	3.5(6)
C32	0.0707(5)	0.2665(6)	−0.0760(8)	3.2(6)
C33	0.0652(5)	0.2162(6)	−0.144(1)	3.9(6)
C34	0.1089(7)	0.1748(7)	−0.166(1)	4.7(7)
C35	0.1597(6)	0.1820(6)	−0.120(1)	3.7(7)
C36	0.0285(6)	0.4025(8)	−0.080(2)	9(1)
C37	−0.0040(8)	0.316(1)	0.092(1)	10(1)
C38	−0.0519(6)	0.2942(8)	−0.116(1)	8(1)

TABLE 3. Selected bond lengths (Å) and angles (°) for [Rh(2-SC_5H_3N-3-$SiMe_3)_3$] (**1**)

Rh–S1	2.386(3)
Rh–S2	2.377(3)
Rh–S3	2.395(3)
Rh–N1	1.992(9)
Rh–N2	2.051(9)
Rh–N3	2.038(9)
S1–Rh–S2	99.9(1)
S1–Rh–S3	94.9(1)
S1–Rh–N1	69.4(3)
S1–Rh–N2	161.9(3)
S1–Rh–N3	106.7(2)
S2–Rh–S3	162.4(1)
S2–Rh–N1	90.6(3)
S2–Rh–N2	69.1(3)
S2–Rh–N3	98.0(3)
S3–Rh–N1	103.7(3)
S3–Rh–N2	98.8(3)
S3–Rh–N3	68.3(3)
N1–Rh–N2	95.7(4)
N1–Rh–N3	171.1(4)
N2–Rh–N3	89.4(3)
Rh–S1–C11	78.8(4)
Rh–S2–C21	79.5(4)
Rh–S3–C31	79.9(4)

(*continued*)

TABLE 4. Atomic positional parameters for [Rh(2-SC_3H_5N-3-$SiMe_3)_2(C_5Me_5)] \cdot CH_3CN$ (**2**)

Atom	x	y	z	B_{eq}
Rh	0.12840(2)	0.03468(2)	0.15452(1)	2.78(1)
S(1)	0.16224(6)	0.10017(7)	0.24647(4)	3.22(4)
S(2)	0.24604(6)	0.07199(8)	0.14305(5)	3.80(5)
Si(1)	0.26310(8)	0.01972(8)	0.37434(5)	3.88(5)
Si(2)	0.39987(7)	0.1096(1)	0.09874(5)	4.05(6)
N(1)	0.1695(2)	−0.0642(2)	0.2143(1)	3.0(1)
N(2)	0.2427(2)	−0.0957(3)	0.0968(2)	4.3(2)
C(1)	0.0218(2)	0.0954(3)	0.1330(2)	3.6(2)
C(2)	0.0648(2)	0.1214(3)	0.0924(2)	3.5(2)
C(3)	0.0824(3)	0.0382(3)	0.0656(2)	4.0(2)
C(4)	0.0535(3)	−0.0377(3)	0.0905(2)	4.2(2)
C(5)	0.0157(2)	−0.0028(3)	0.1328(2)	3.8(2)
C(6)	−0.0104(2)	0.1618(4)	0.1683(2)	4.6(2)
C(7)	0.0811(3)	0.2185(3)	0.0778(2)	5.2(2)
C(8)	0.1209(3)	0.0349(4)	0.0168(2)	5.9(3)
C(9)	0.0592(3)	−0.1365(4)	0.0736(3)	6.4(3)
C(10)	−0.0255(3)	−0.0604(4)	0.1674(3)	6.2(3)
C(11)	0.1891(2)	−0.0138(3)	0.2612(2)	2.9(2)
C(12)	0.2256(2)	−0.0523(3)	0.3114(2)	3.2(2)
C(13)	0.2344(3)	−0.1474(3)	0.3108(2)	4.2(2)
C(14)	0.2102(3)	−0.2002(3)	0.2630(2)	4.5(2)
C(15)	0.1803(3)	−0.1559(3)	0.2149(2)	3.9(2)
C(16)	0.3255(3)	0.1071(4)	0.3546(2)	6.0(3)
C(17)	0.1905(3)	0.0804(4)	0.4017(2)	5.9(3)
C(18)	0.3094(4)	−0.0592(4)	0.4290(2)	7.8(3)
C(21)	0.2805(2)	−0.0163(3)	0.1060(2)	3.3(2)
C(22)	0.3479(2)	−0.0020(3)	0.0894(2)	3.4(2)
C(23)	0.3754(3)	−0.0773(3)	0.0643(2)	4.4(2)
C(24)	0.3381(3)	−0.1600(3)	0.0533(2)	5.3(2)
C(25)	0.2721(3)	−0.1648(3)	0.0713(2)	5.2(2)
C(26)	0.3462(3)	0.2095(3)	0.0674(2)	5.1(2)
C(27)	0.4358(3)	0.1323(5)	0.1739(2)	6.6(3)
C(28)	0.4768(3)	0.0975(4)	0.0614(3)	5.9(3)

the ligands adopting the *mer* configuration. Atomic coordinates are given in Table 2 and selected bond lengths and angles in Table 3. The major distortions from octahedral geometry are consequences of the constraints imposed by the four-membered chelate rings and the consequent small ligand bite and N–Rh–S internal chelate angles. The effects of chelation are also dramatically illustrated by the Rh–S–C angles which average 79.5(6)° compared to a Rh–S–C angle of 109.9(2)° for the monodentate form of the ligand in **2**. The structure of **1** is essentially identical to that of [Rh(2-$SC_5H_4N)_3$] if the presence of the triorganosilyl groups is ignored.

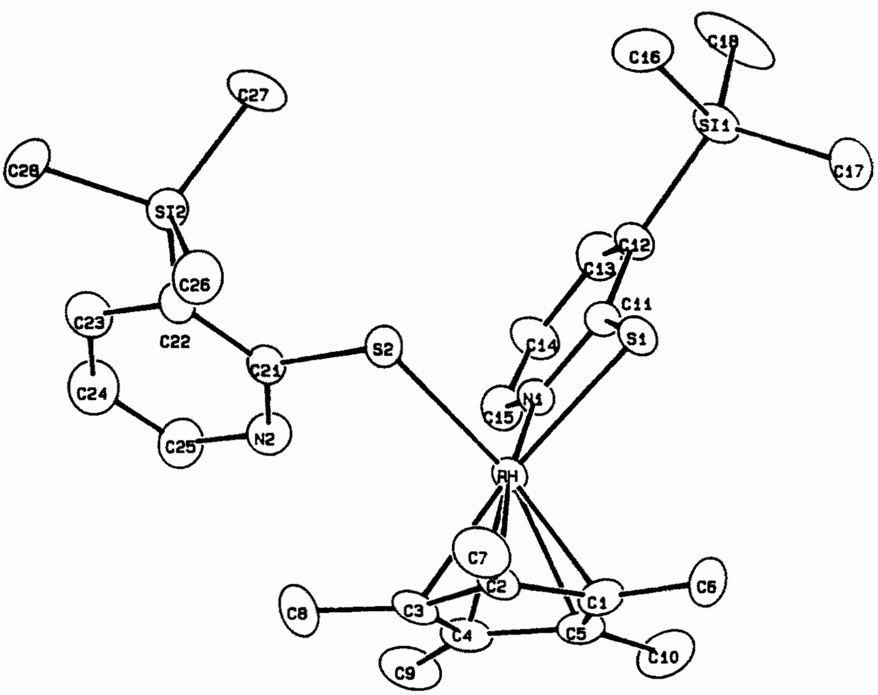

Fig. 2. ORTEP view of the structure of [Rh(2-SC_5H_3N-3-$SiMe_3$)$_2$(C_5Me_5)] (2).

TABLE 5. Selected bond lengths (Å) and angles (°) for [Rh(2-SC_5H_3N-3-$SiMe_3$)$_2$(C_5Me_5)]·CH_3CN (2)

Rh–S1	2.408(2)
Rh–S2	2.360(2)
Rh–N1	2.089(4)
Rh–N2	3.361(5)
Rh–C1	2.183(5)
Rh–C2	2.158(5)
Rh–C3	2.183(5)
Rh–C4	2.183(5)
Rh–C5	2.172(5)
S1–C11	1.742(4)
S2–C21	1.751(4)
S1···N1	2.512(4)
S2···N2	2.666(5)
S1–Rh–S2	85.19(5)
S1–Rh–N1	67.44(9)
S2–Rh–N1	89.6(1)
Rh–S1–C11	80.9(1)
Rh–N1–C11	103.5(2)
Rh–N1–C15	136.2(3)
Rh–S2–C21	109.9(2)

The structure of **2** is illustrated in Fig. 2, the atomic positional parameters are listed in Table 4 and selected bond lengths and angles are collected in Table 5. The pentamethylcyclopentadienyl residue adopts the usual η^5 coordination mode with ring carbons essentially equidistant from the Rh center. The two pyridinethiolate ligands are inequivalent, one adopting the bidentate chelating mode while the second is monodentate, coordinating through the sulfur donor. The Rh–S2 distance of 2.360(2) Å is significantly shorter than Rh–S1, 2.408(2) Å, indicating more effective metal–sulfur overlap for the monodentate coordination mode. The Rh–S2–C21 angle of 109.9(2)° is close to the anticipated tetrahedral limit, and may be compared to Rh–S–C angles of *c.* 80° and 115° for the chelated form of the pyridinethiolate ligand and for the monodentate 2-1(*H*)-pyridinethione form, respectively [3]. The X-ray crystallography revealed the presence of all hydrogen atoms associated with **2** on the final difference Fourier map. The absence of a peak associated with a hydrogen bonded to N2 confirmed that the ligand is present in its deprotonated form. The reactivity of **2** toward protonating reagents reflects the relative accessibility of the lone pair of electrons of N2.

Acknowledgement

Support from the National Institutes of Health (GM22566) is gratefully acknowledged.

References

1 B. P. Kennedy and A. B. P. Lever, *Can. J. Chem.*, *50* (1972) 3488.

2 E. Binamira-Soriaga, M. Lundeen and K. Seff, *Acta Crystallogr., Sect. B, 35* (1979) 2875.

3 A. J. Deeming, K. I. Hardcastle, M. N. Meah, P. A. Bates, H. M. Dawes and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, (1988) 227.

4 S. C. Kokkou, P. Rentzeperis and P. Karagiannides, *Acta Crystallogr., Sect. C., 39* (1983) 178; S. C. Kokkou, V. Schramm and P. Karagiannides, *Acta Crystallogr., Sect. C, 41* (1985) 1040.

5 G. Valle. R. Ettore, U. Vettori, V. Peruzzo and G. Plazzogna, *J. Chem. Soc., Dalton Trans.*, (1987) 818.

6 E. S. Raper, *Coord. Chem. Rev., 61* (1985) 115.

7 J. A. Broomhead, R. Greenwood, W. Pienkowski and M. Sterns, *Aust. J. Chem., 36* (1986) 1985.

8 P. Mura, B. G. Olby and S. D. Robinson, *J. Chem. Soc., Dalton Trans.*, (1985) 2101, and refs. therein.

9 A. J. Deeming and N. M. Meah, *Inorg. Chim. Acta, 117* (1986) L13.

10 S. G. Rosenfield, H. P. Berends, L. Gelmini, D. W. Stephan and P. K. Mascharak, *Inorg. Chem., 26* (1987) 2792.

11 P. Mura and S. D. Robinson, *Acta Crystallogr., Sect. C; 41* (1984) 1798.

12 P. Mura, B. G. Olby and S. D. Robinson, *Inorg. Chim. Acta, 98* (1985) L21.

13 K. S. Nagaraja and M. R. Udupa, *Bull. Chem. Soc. Jpn., 57* (1984) 1705.

14 F. A. Cotton, P. E. Fanwick and J. W. Fitch III, *Inorg. Chem., 17* (1978) 3254.

15 S. G. Rosenfield, S. A. Swedberg, S. K. Arora and P. K. Mascharak, *Inorg. Chem., 25* (1986) 2109.

16 A. J. Deeming, M. N. Meah, H. M. Dawes and M. B. Hursthouse, *J. Organomet. Chem., 299* (1986) C25.

17 M. A. Ciriano, F. Viguri, L. A. Ora, A. Tiripicchio and M. Tiripicchio-Camelini, *Angew. Chem., Int. Ed. Engl., 26* (1987) 444.

18 N. Zhang, S. R. Wilson and P. A. Shapley, *Organometallics, 7* (1988) 1126.

19 K. Umakoshi, I. Kinoshuta, A. Ichimura and S. Ooi, *Inorg. Chem., 26* (1987) 3551.

20 E. M. Padilla, J. M. Yamamoto and C. M. Jensen, *Inorg. Chim. Acta, 174* (1990) 209.

21 S. Kitagawa, M. Munckoto, H. Shimono, S. Matsuyama and H. Masuda, *J. Chem. Soc., Dalton Trans.*, (1990) 2105.

22 L. A. Oro, M. A. Ciriano, F. Viguri, A. Tiripicchio-Camellini and F. J. Lahoz, *Nouv. J. Chim., 10* (1986) 75.

23 A. J. Deeming, M. N. Meah, P. A. Bates and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, (1988) 235.

24 A. J. Deeming, M. Karim, P. A. Bates and M. B. Hursthouse, *Polyhedron, 7* (1988) 1401.

25 E. C. Constable, C. A. Palmer and I. A. Tocher, *Inorg. Chim. Acta, 176* (1990) 57.

26 P. Karagiannides, P. Aslanidis, S. Papastefanou, D. Mentzafos, A. Hountas and A. Terzis, *Polyhedron, 9* (1990) 2833.

27 A. J. Deeming, M. Karim, N. I. Powell and K. I. Hardcastle, *Polyhedron, 9* (1990) 623.

28 B. Cockerton, A. J. Deeming, M. Karim and K. I. Hardcastle, *J. Chem. Soc., Dalton Trans.*, (1991) 431.

29 K. Tang, M. Aslam, E. Block, T. Nicholson and J. A. Zubieta, *Inorg. Chem., 26* (1987) 488.

30 E. Block, M. Gernon, H. Kang, S. Liu and J. A. Zubieta, *J. Chem. Soc., Chem. Commun.*, (1988) 1031.

31 E. Block, M. Gernon, H. Kang, G. Ofori-Okai and J. A. Zubieta, *Inorg. Chem., 28* (1989) 1263.

32 E. Block, M. Gernon, H. Kang and J. A. Zubieta, *Angew. Chem., Int. Ed. Engl., 27* (1988) 1342.

33 E. Block, H. Kang, G. Ofori-Okai and J. A. Zubieta, *Inorg. Chim. Acta, 166* (1990) 155.

34 E. Block, H. Kang, G. Ofori-Okai and J. A. Zubieta, *Inorg. Chim. Acta, 167* (1990) 147.

35 E. Block, D. Macheroni, S. N. Shaikh and J. A. Zubieta, *Polyhedron, 9* (1990) 1429.

36 E. Block, M. Brito, M. Gernon, D. McGowty, H. Kang and J. A. Zubieta, *Inorg. Chem., 29* (1990) 3172.

37 E. Block, M. Gernon, H. Kang, G. Ofori-Okai and J. A. Zubieta, *Inorg. Chem., 30* (1991) 1767.

38 E. Block, H. Kang and J. Zubieta, *Inorg. Chim. Acta, 181* (1991) 227.

39 E. Block, M. Gernon, H. Kang, S. Liu and J. Zubieta, *Inorg. Chim. Acta, 167* (1990) 143.

40 C. E. Pfluger, J. Kallmerten and D. J. Plata, *Acta Crystallogr., Sect. C, 45* (1989) 1031.