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Reactions of 2-Thiopyridone and Related N-, S- and C-Methylated Derivatives with $[Rh_2Cl_2(CO)_4]$: Crystal and Molecular Structure of *fac*-$[Rh(MeC_5H_3NS)_3]$ containing 6-Methyl-2-thiopyridonato Ligands

ANTONY J. DEEMING, M. NAFEES MEAH

Department of Chemistry, University College London, 20 Gordon Street, London WC1H OAJ, U.K.

PAUL A. BATES and MICHAEL B. HURSTHOUSE

Department of Chemistry, Queen Mary College, Mile End Road, London E1 4NS, U.K.

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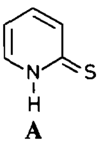
Abstract

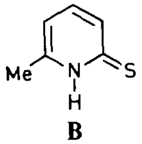
$[Rh_2Cl_2(CO)_4]$ reacts with the ligands L (2-pyridone, 2-thiopyridone, and the isomers 6-methyl-2-thiopyridone, 2-methylmercaptopyridine, and *N*-methylthiopyridone) to give initially, when L/Rh = 1, the bridged-cleaved compounds *cis*-$[RhCl(CO)_2L]$. Further additions of 2-methylmercaptopyridine, *N*-methylthiopyridone, or 2-pyridone caused no further change, but 2-thiopyridone and 6-methyl-2-thiopyridone gave new *cis*-dicarbonyl species (L/Rh = 2) and eventually monocarbonyl species (L/Rh > 3). All these solutions are air-sensitive and air oxidation of a solution of $[Rh_2Cl_2(CO)_4]$ with an excess of 6-methyl-2-thiopyridone gave *fac*-$[Rh(MeC_5H_3NS)_3]$ the X-ray structure of which shows three equivalent chelating 6-methyl-2-thiopyridonato ligands.

Introduction

2-Thiopyridone (alternatively called 2-pyridinethiol or 2-pyridinethione) belongs to a class of heterocycles existing as tautomers [1]. The equilibrium position between the tautomers, 2-thiopyridone and 2-pyridinethiol, is sensitive to the nature of the solvent but the thione form predominates in aqueous solution [2]. In principle metal coordination could be through nitrogen, sulphur, or both. We have examined the reactions of 2-thiopyridone (**A**) and related methyl-substituted ligands ((**B**) to (**D**)) with $[Rh_2Cl_2(CO)_4]$. Methyl substitution at sulphur or nitrogen atoms gives molecules which have previously been used as models for the two tautomeric forms of 2-thiopyridone in studies of physical properties [3, 4]. Methyl substitution at the 6-position would not be expected to modify the free ligand greatly although its coordination chemistry might well differ from that of the unsubstituted form. For comparison, the reaction of 2-pyridone (**E**) with $[Rh_2Cl_2(CO)_4]$ was also studied.



A



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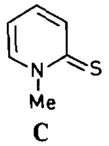
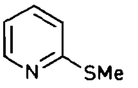


C



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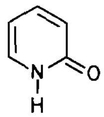

E

Results and Discussion

The addition of 2-thiopyridone (L, pySH) to $[Rh_2Cl_2(CO)_4]$ (L/Rh = 1) in chloroform under nitrogen gives $[RhCl(CO)_2L]$ (ν(CO) 2083 and 2015 cm^{-1}, Table I). The ^1H NMR spectrum of this compound (0.1 mol dm^{-3} in $CDCl_3$) shows multiplets at δ 7.13 (H^5), 7.64 (H^4), 7.66 (H^3), 7.96 (H^6) (Table II), and the downfield shifts relative to those of the free ligand might indicate increased aromaticity of the heterocycle. Protonation of the free ligand gives similar downfield shifts. The lowest field signal at δ 14.5 is typical of an amidic N*H* proton. The indication of $^1J(^{14}NH)$ at high temperatures and at high dilution implies that intermolecular N*H* exchange is slow on the NMR timescale [5]. This is confirmed by the triplet for the H^6 proton (δ 7.90) which collapses to a doublet on exchanging the N*H* proton for deuterium. Thus $^3J(HNCH)$ is clearly apparent. All signals show chemical shift variation with concentration and temperature, implying different solute forms in a temperature variable equilibrium. Possibly these are the intra- and inter-

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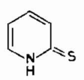
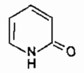
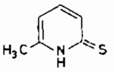
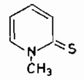
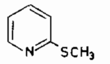
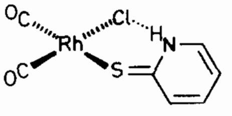
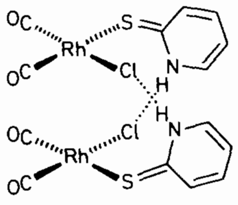
TABLE I. $\nu(CO)$ (cm^{-1}) Data for Chloroform Solutions of $[Rh_2Cl_2(CO_4)]$ on Addition of Ligand L for Various L/Rh Ratios

L	L/Rh			
	1	2	3	4
	2083(s) 2015(s)	2074(s) 2013(s) 1978(m)	2074(w) 2013(w) 1978(s)	2074(w) 2013(w) 1978(s)
	2088(s) 2035(sh) 2013(s)	2088(s) 2013(s)	2088(s) 2013(s)	2088(s) 2013(s)
	2082(s) 2013(s)	2068(s) 2006(s)	2067(s) 2005(s) 1969(m)	2067(s) 2005(s) 1969(m)
	2078(s) 2006(s)	2078(s) 2006(s)	2078(s) 2006(s)	2078(s) 2006(s)
	2089(s) 2016(s)	2089(s) 2016(s)	2089(s) 2016(s)	2089(s) 2016(s)

molecular H-bonded forms **F** and **G**. In crystals of $[Rh_2Cl_2(\mu\text{-}pyS)_2(pySH)_2(CO)_2]$ there is intramolecular H-bonding as shown in **F** [6].



F



G

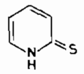
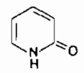
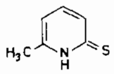
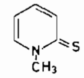
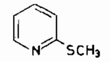
Further additions of pySH (L) to $[RhCl(CO)_2L]$ give different ^1H NMR which we have not interpreted. However, IR spectra show the conversion to another *cis*-dicarbonyl species ($\nu(CO)$ 2074 and 2013 cm^{-1}) when L/Rh = 2. When L/Rh = 3 a monocarbonyl ($\nu(CO)$ 1978 cm^{-1}) is the major species although the second *cis*-dicarbonyl is still present (0.75 mol CO/Rh atom are displaced). An atmosphere of CO partially reverses the last step. Though the exact nature of these species is uncertain (they could not be isolated), conductivity measurements show them to be non-electrolytic.

On leaving such solutions to stand under nitrogen for several days, deep blue–black crystals of $[Rh_2Cl_2(\mu\text{-}pyS)_2(pySH)_2(CO)_2]\cdot 2CHCl_3$ are deposited [6]. However, exposure to air gives orange crystals of the mononuclear complex $[Rh(pyS)_2(pySH)_2]Cl$ [7].

Reaction of $[Rh_2Cl_2(CO)_4]$ with ligands **C** to **E** gave only the bridge-cleaved products $[RhCl(CO)_2L]$ and an excess of L caused no further change in the IR $\nu(CO)$ spectra (Table I). For **C** there can be no doubt as to the identity of the donor atom. However, we cannot be sure whether S or N of **D** is coordinated. The $\nu(CO)$ frequencies are not particularly sensitive to the nature of the *trans* ligands. This can be seen more clearly with **E** where the donor atom is undoubtedly oxygen ($NH = \delta$ 11.64) (see Table I).

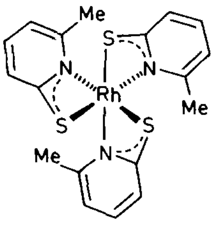
6-Methyl-2-thiopyridone (**B**) reacts with $[Rh_2Cl_2(CO)_4]$ in chloroform under nitrogen to give essentially comparable products as from **A**, the only major difference being that larger excesses of ligand are required to drive the reaction to the monocarbonyl species. Air oxidation of these solutions yields the *tris*-chelate compound $[Rh(MeC_5H_3NS)_3]$ (**H**) as ruby-red crystals which may also be obtained by the

TABLE II. ^1H NMR Data for $[RhCl(CO)_2L]$ Generated *in situ* in $CDCl_3$ ^{a}

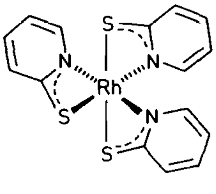
L	Chemical shifts^b						*ortho*-J values (Hz)		
	H^6	H^5	H^4	H^3	NH	$-CH_3$	J_{45}	J_{34}	J_{56}
	7.96	7.13	7.64	7.66	14.35		6.1	6.3	6.3
	7.81	6.68	7.67	6.89	11.64		7.8	8.7	c
		6.83	7.52	7.48		2.54	7.3	7.2	
	8.44	7.13	7.66	8.07		4.16	8.9	6.3	8.3
	8.50	7.16	7.75	7.21		2.59	7.6	8.3	

^{a}200 MHz. ^{b}*ca.* 0.1 mol dm^{-3} concentration and at 24 °C in $CDCl_3$. ^{c}Unresolved.

direct thermal reaction of **B** with $RhCl_3 \cdot nH_2O$. The ^1H NMR spectrum [δ 1.89 (3H, s, Me), 6.65 (1H, d, H^3), 6.53 (1H, d, H^5), and 7.30 (1H, t, H^4)] shows that the ligands are magnetically equivalent which would only be consistent with *fac*-stereochemistry.



H



I

We have confirmed this stereochemistry by a single-crystal X-ray study of $[Rh(MeC_5H_3NS)_3]$. Fractional atomic coordinates are in Table III and selected bond lengths and angles in Table IV. Figure 1 shows that the coordination about the rhodium atom is distorted octahedral (towards trigonal prismatic). The Rh–N and Rh–S distances are of similar values to those found in the literature [7]. The structure contrasts with those of *tris*-chelate complexes of rhodium(III) (**I**) [7] and iron(II) [8] with chelating 2-thiopyridonato ligands which are *mer*, but compares with the related cobalt(III) complex with 4,6-dimethylpyrimidine-2-thiolato ligands which is *fac* [9]. Apparently the steric effect of the methyl-substituent *ortho* to nitrogen stabilizes the *fac* relative to the *mer* configuration. We presume that these differences are of thermodynamic origin because these same isomers (different in each case)

TABLE III. Fractional Atomic Coordinates (X 10^4) for the Complex *fac*-$[Rh(MeC_5H_3NS)_3]$

	x	*y*	*z*
Rh	5362.7(5)	3179.3(3)	7479.1(3)
S(1)	4251(2)	3868(1)	8578(1)
S(2)	3066(2)	2576(1)	6718(1)
S(3)	5466(2)	4435(1)	6574(1)
N(1)	7104(6)	3675(3)	8456(3)
N(2)	4949(6)	1878(3)	7993(3)
N(3)	6568(6)	2840(3)	6472(3)
C(1)	6211(7)	3943(4)	9041(4)
C(2)	6846(9)	4217(5)	9861(4)
C(3)	8440(11)	4196(6)	10088(5)
C(4)	9331(10)	3914(6)	9506(6)
C(5)	8665(8)	3672(5)	8675(5)
C(6)	9582(9)	3387(6)	7994(6)
C(7)	3571(8)	1676(5)	7466(5)
C(8)	2808(10)	866(6)	7543(6)
C(9)	3429(10)	269(6)	8127(6)
C(10)	4878(11)	449(5)	8707(6)
C(11)	5592(8)	1295(4)	8614(4)
C(12)	7052(10)	1576(5)	9187(6)
C(13)	6387(8)	3612(5)	6003(5)
C(14)	6934(9)	3685(6)	5247(5)
C(15)	7725(10)	2942(7)	4978(6)
C(16)	7948(9)	2172(6)	5463(5)
C(17)	7311(8)	2110(5)	6214(5)
C(18)	7442(10)	1261(5)	6764(6)

TABLE IV. Selected Bond Lengths (Å) and Angles (°) for *fac*-$[Rh(MeC_5H_3NS)_3]$

S(1)–Rh	2.341(4)	S(2)–Rh	2.319(4)
S(3)–Rh	2.326(4)	N(1)–Rh	2.089(8)
N(2)–Rh	2.121(8)	N(3)–Rh	2.095(7)
C(1)–S(1)	1.742(10)	C(7)–S(2)	1.765(11)
C(13)–S(3)	1.771(10)	C(1)–N(1)	1.354(10)
C(5)–N(1)	1.349(11)	C(2)–C(1)	1.374(11)
C(3)–C(2)	1.373(14)	C(4)–C(3)	1.347(14)
C(5)–C(4)	1.391(14)	C(6)–C(5)	1.482(13)
C(7)–N(2)	1.367(10)	C(11)–N(2)	1.341(9)
C(8)–C(7)	1.369(11)	C(9)–C(8)	1.311(13)
C(10)–C(9)	1.447(13)	C(11)–C(10)	1.400(10)
C(12)–C(11)	1.483(12)	C(13)–N(3)	1.339(10)
C(17)–N(3)	1.343(9)	C(14)–C(13)	1.354(10)
C(15)–C(14)	1.387(13)	C(16)–C(15)	1.352(13)
C(17)–C(16)	1.388(10)	C(18)–C(19)	1.502(12)
S(2)–Rh–S(1)	96.6(2)	S(3)–Rh–S(1)	100.1(2)
S(3)–Rh–S(2)	95.9(2)	N(1)–Rh–S(1)	69.6(2)
N(1)–Rh–S(2)	164.0(1)	N(1)–Rh–S(3)	94.4(2)
N(2)–Rh–S(1)	89.2(2)	N(2)–Rh–S(2)	70.6(2)
N(2)–Rh–S(3)	164.6(1)	N(2)–Rh–N(1)	100.4(3)
N(3)–Rh–S(1)	167.8(1)	N(3)–Rh–S(2)	91.1(2)
N(3)–Rh–S(3)	69.5(2)	N(3)–Rh–N(1)	103.9(3)
N(3)–Rh–N(1)	102.4(3)	C(1)–N(1)–Rh	100.1(5)
C(1)–S(1)–Rh	80.6(3)	C(7)–S(2)–Rh	81.1(3)
N(1)–C(1)–S(1)	109.4(5)	N(2)–C(7)–S(2)	109.6(6)
C(7)–N(2)–Rh	98.7(5)	C(13)–N(3)–Rh	100.9(5)
C(13)–S(3)–Rh	81.0(3)	N(3)–C(13)–S(3)	108.2(6)

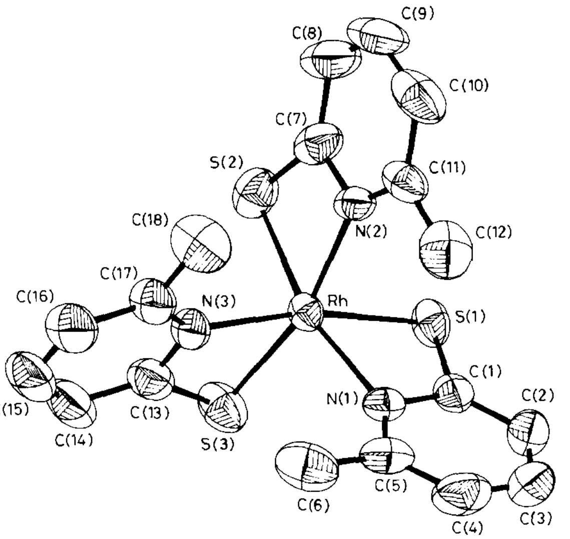


Fig. 1. Molecular structure of *fac*-$[Rh(MeC_5H_3NS)_3]$ containing chelating 6-methyl-2-thiopyridonato ligands.

TABLE V. Rh–N and Rh–S Distances (Å) for *fac* and *mer* Rhodium(III) Complexes of 2-Thiopyridonato and 6-Methyl-2-thiopyridonato

Compound	Rh–N	*trans*-atom	Rh–S	*trans*-atom
mer-[Rh($C_5H_4NS)_3$][a]	2.050(2)	S	2.392(0.5)	S
	2.036(4)	N	2.383(0.5)	S
	2.034(1)	N	2.361(0.5)	N
fac-[Rh($MeC_5H_3NS)_3$][b]	2.095(7)	S	2.341(4)	N
	2.089(8)	S	2.319(4)	N
	2.121(8)	S	2.326(4)	N

[a] Ref. 7. [b] This work.

are formed by oxidation of rhodium(I) complexes or from the reaction of $RhCl_3 \cdot nH_2O$ with the appropriate thiones at high temperatures.

The N–Rh–S angles in the chelate rings (69.5° to 70.6°) are understandably less than 90° and the *trans*-N–Rh–S angles (164.0° to 167.8°) are considerably less than 180°. Also the small bite of the chelating ligand induces some distortion from octahedral to trigonal prismatic geometry [10].

Metal–ligand bond distances for [Rh($C_5H_4NS)_3$] and [Rh($MeC_5H_3NS)_3$] are collected in Table V. The Rh–S bond distances are all longer in *mer*-[Rh($C_5H_4NS)_3$] (av. 2.38 Å) than in the methylated form *fac*-[Rh($MeC_5H_3NS)_3$] (av. 2.33 Å) and conversely the Rh–N distances (av. 2.04 Å) are all shorter than in the methylated compound (av. 2.10 Å). This may reflect the steric effect of the Me group which strengthens Rh–S bonding at the expense of Rh–N bonding. A small but distinct *trans*-influence is superimposed on this overall effect; S having a larger *trans*-influence than N. The longer Rh–N and Rh–S bonds are those *trans* to S relative to those *trans* to N.

Experimental

All reactions were performed under dry nitrogen. 2-Thiopyridone was used as obtained from Aldrich while *N*-methylthiopyridone, 2-(methylmercapto)-pyridine, and 6-methyl-2-thiopyridone were prepared as reported [11].

NMR Studies

Accurately weighed amounts of [$Rh_2Cl_2(CO)_4$] and the ligands were mixed in clean, dry 5 mm NMR tubes and made up to known volumes with dry $CDCl_3$. Spectra were recorded on a Varian XL200 spectrometer.

IR Studies

Accurately weighed amounts of [$Rh_2Cl_2(CO)_4$] were dissolved in $CHCl_3$ and aliquots of ligand solutions in $CHCl_3$ added successively, IR spectra being recorded after each addition.

Preparation of [Rh($MeC_5H_3NS)_3$]

A solution of 6-methyl-2-thiopyridone (0.616 g, 4.9 mmol) and [$Rh_2Cl_2(CO)_4$] (0.195 g, 0.49 mmol) in chloroform (10 cm^3) was stored overnight at room temperature in air. Alumina (2 g) was added and the mixture stirred for 2 h. The burgundy coloured solution after removal of alumina was concentrated and a few drops of diethylether added to precipitate the product. Recrystallization from chloroform/diethylether mixtures gave the product as ruby-red crystals (0.255 g, 54%). *Anal.* Found: C, 43.0; H, 3.6; N, 8.0. Calc. for $C_{18}H_{21}N_3RhS_3 \cdot 0.25CHCl_3$: C, 43.1; H, 4.1; N, 8.0%. The sample for X-ray crystallography was pumped for an extended period and it did not appear to contain chloroform. This complex could also be prepared by reaction of $RhCl_3 \cdot nH_2O$ and the sodium salt of the 6-methyl-2-thiopyridonate ion in refluxing ethanol.

Crystallographic Studies

Crystal data: $C_{18}H_{18}N_3RhS_3$, $M = 475.45$, monoclinic, $a = 8.696(2)$, $b = 14.582(3)$, $c = 15.688(3)$ Å, $\beta = 99.81(2)°$, $U = 1960.2(7)$ Å^3, space group $P2_1/n$, $Z = 4$, $D_c = 1.611$ g cm^{-3}, $F(000) = 960$, $\lambda = 0.71069$ Å, μ(Mo Kα) = 11.7 cm^{-1}, crystal size 0.25 × 0.25 × 0.15 mm).

Data Collection

Unit cell parameters and intensity data were obtained using previously detailed procedure [12], using a CAD4 diffractometer operating in the ω–2θ scan mode, with graphite monochromated Mo Kα radiation. A total of 3734 unique reflections were collected ($3° \leqslant 2\theta \leqslant 50°$). The segment of reciprocal space scanned was: (h) $-10 \rightarrow 10$, (k) $0 \rightarrow 17$, (l) $0 \rightarrow 18$. The reflection intensities were corrected for absorption, using the azimuthal-scan method [13]; maximum transmission factor 1.00, minimum value 0.88.

Structure Solution and Refinement

The structure was solved by routine heavy-atom methods, and refined by full-matrix least-squares (SHELX76 [14]). All non-hydrogen atoms were refined with anisotropic thermal coefficients. The final few cycles of refinement included all hydrogen atoms in calculated positions (C–H 0.96 Å, U = 0.10 Å^2). The final values of R and R_w were 0.049 and 0.054 respectively for the 235 variables and 2898 data for which $F_o \geqslant 3\sigma F_o$. The function minimized was $\Sigma_w(|F_o| - |F_c|)^2$ with the weight, w, being defined as $1/[\sigma^2(F_o) + 0.0004{F_o}^2]$. Atomic scattering factors and anomalous scattering parameters were taken from refs. 15 and 16 respectively. All computations were made on a DEC VAX-11/750 computer.

Supplementary Material

Tables of isotropic hydrogen atom coordinates, anisotropic thermal coefficients, and F_o/F_c values have been deposited as supplementary data.

Acknowledgements

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