Nuclear Magnetic Resonance Measurement of Sulphur Inversion Barriers in *mer*-Tris[bis(trimethylsilylmethyl) sulphide]trichloro-rhodium(III) and -iridium(III)

By **Edward W. Abel, Graham W. Farrow,** and **Keith G. Orrell,*** Chemistry Department, The University, Exeter EX4 4QD

Variable-temperature ^1H n.m.r. studies of *mer*-$[RhCl_3\{S(CH_2SiMe_3)_2\}_3]$ and *mer*-$[IrCl_3\{S(CH_2SiMe_3)_2\}_3]$ have yielded slightly different sulphur inversion barriers for the two different sulphide ligand environments in these complexes. In both complexes the barrier is somewhat lower for the sulphide ligand *trans* to chloride.

DESPITE the fact that n.m.r. studies of inversion at sulphur atoms date back to 1966,[1-3] very few reliable quantitative measurements of inversion barriers at sulphur and other Group 6A atoms have been made. Recently, Cross *et al.*[4-6] examined inversion at sulphur, selenium, and tellurium atoms in complexes of palladium(II) and

---

[1] E. W. Abel, R. P. Bush, F. J. Hopton, and C. R. Jenkins, *Chem. Comm.*, 1966, 58.

[2] P. Haake and P. C. Turley, *J. Amer. Chem. Soc.*, 1967, **89**, 4611.

[3] P. C. Turley and P. Haake, *J. Amer. Chem. Soc.*, 1967, **89**, 4617.

[4] R. J. Cross, I. G. Dalgleish, G. J. Smith, and R. Wardle, *J.C.S. Dalton*, 1972, 992.

[5] R. J. Cross, T. H. Green, and R. Keat, *J.C.S. Chem. Comm.*, 1974, 207.

[6] R. J. Cross, T. H. Green, R. Keat, and J. F. Paterson, *Inorg. Nuclear Chem. Letters*, 1975, **11**, 145.

platinum(II) but only qualitative comparisons of barrier heights were made. Hunter and his co-workers[7,8] examined certain complexes of Pd^{II} and Pt^{II} with various chelate ligands, but there is some doubt as to whether the changes in the n.m.r. spectra are due to total inversion of the five-membered chelate rings or to site inversion at the selenium atoms.

We are currently studying sulphur and selenium inversion in a range of Group 8B transition-metal complexes. The complexes have been chosen for the suitability of their variable-temperature n.m.r. spectra for total band-shape fitting methods. We report here some results for rhodium(III) and iridium(III) complexes[9] with the ligand $S(CH_2SiMe_3)_2$.

EXPERIMENTAL

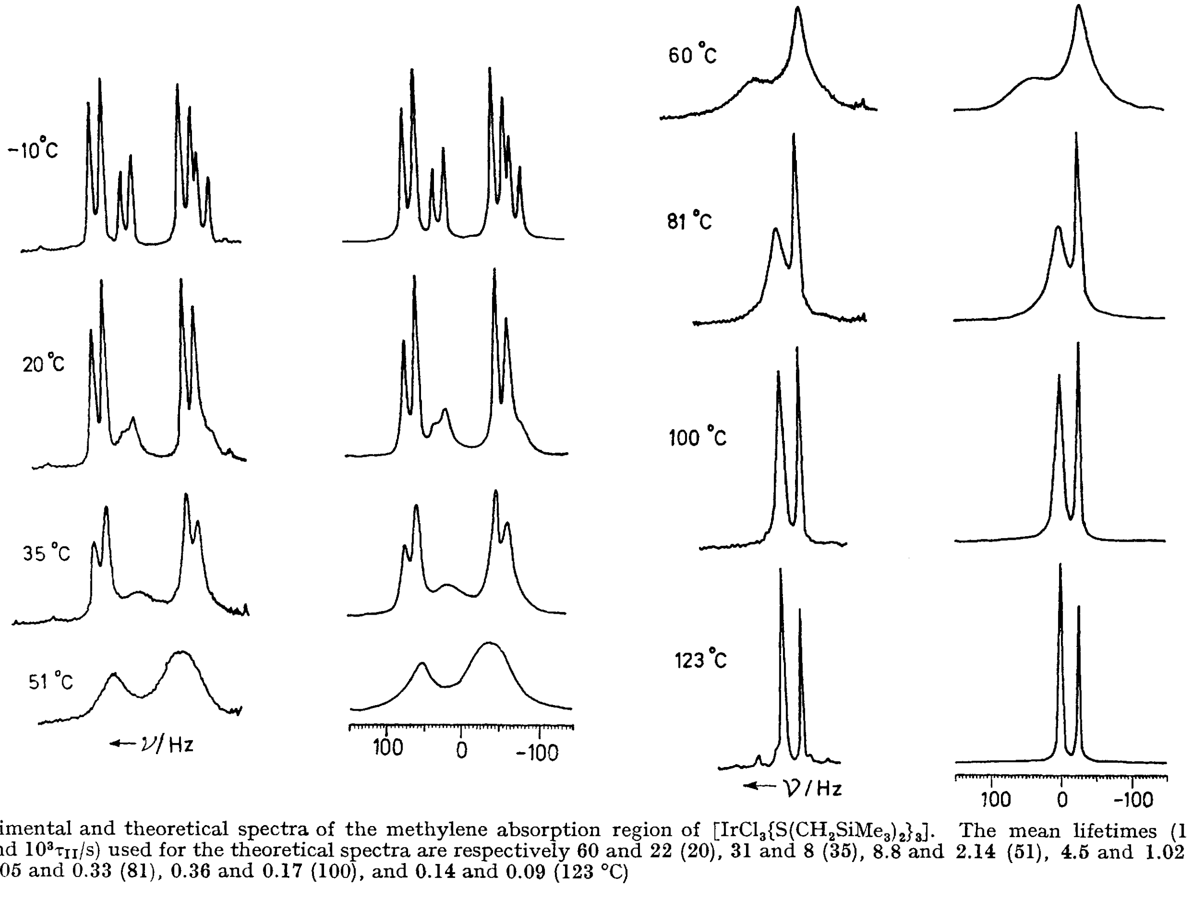
Spectra.—All n.m.r. spectra were recorded on a JEOL MH-100 100-MHz spectrometer operating under internal-field–frequency-lock conditions with the strong $SiMe_3$ absorption being used as the lock signal. N.m.r. line positions were measured with a frequency counter. The JES-VT-3 variable-temperature controller was used for varying the probe temperature. Temperature measurements were made immediately before and after recording the spectra and were accurate to *ca.* ±1 °C over the range studied.

Materials.—mer-*Tris[bis(trimethylsilylmethyl) sulphide]trichlororhodium*(III). Bis(trimethylsilylmethyl) sulphide (0.309 g, 1.5 mmol) was added to a solution of rhodium trichloride (0.132 g, 0.5 mmol for $RhCl_3\cdot 3H_2O$) in n-butyl alcohol (7 cm^3) and stirred under reflux for 1 h. The solvent was then removed *in vacuo* and replaced by methanol (10 cm^3). The addition of a little water initiated crystallization and the solution was cooled to −20 °C to give orange crystals of the product (0.19 g, 43%), m.p. 132 °C (Found: C, 33.65; H, 8.05. Calc. for $C_{24}H_{66}Cl_3RhS_3Si_6$: C, 34.75; H, 7.95%).

mer-*Tris[bis(trimethylsilylmethyl) sulphide]trichloroiridium*(III). A solution of iridium trichloride (0.15 g, 0.5 mmol) and bis(trimethylsilylmethyl) sulphide (0.309 g, 1.5 mmol) in 2-ethoxyethanol (5 cm^3) was stirred under reflux for 1 h. Solvent was removed *in vacuo*, and the resulting residue was recrystallized from ethanol to give orange crystals of the product (0.185 g, 40%), m.p. 140—142 °C (Found: C, 30.75; H, 7.15. Calc. for $C_{24}H_{66}Cl_3IrS_3Si_6$: C, 31.4; H, 7.20%).

RESULTS AND DISCUSSION

Both complexes gave similar spectra and will be discussed together. Spectra of the methylene hydrogens of $[IrCl_3\{S(CH_2SiMe_3)_2\}_3]$ in the range −10 to 123 °C are shown in the Figure.



Experimental and theoretical spectra of the methylene absorption region of $[IrCl_3\{S(CH_2SiMe_3)_2\}_3]$. The mean lifetimes ($10^3\tau_I$/s and $10^3\tau_{II}$/s) used for the theoretical spectra are respectively 60 and 22 (20), 31 and 8 (35), 8.8 and 2.14 (51), 4.5 and 1.02 (60), 1.05 and 0.33 (81), 0.36 and 0.17 (100), and 0.14 and 0.09 (123 °C)

In these complexes each sulphur atom represents a prochiral centre. Attached to these centres are prochiral trimethylsilylmethyl groups in which the pairs of

---

[7] R. Donaldson, G. Hunter, and R. C. Massey, *J.C.S. Dalton*, 1974, 288.

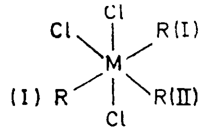
[8] G. Hunter and R. C. Massey, *J.C.S. Dalton*, 1975, 209.

[9] J. Chatt, G. J. Leigh, A. P. Storace, D. A. Squire, and B. J. Starkey, *J. Chem. Soc. (A)*, 1971, 899.

methylene hydrogens are diastereotopic and hence anisochronous, thus giving rise to AB quartet patterns. Sulphur inversion causes the methylene hydrogen environments to be interchanged. In contrast, it should be noted that rotation about the M–S and/or S–CH_2 bonds will not cause any such interchange. In this work such rotations have been assumed to be fast throughout the temperature range studied.

The two distinct environments of the three sulphide ligands in the *mer* complex are exemplified in the low-temperature spectra where two AB quartet patterns were observed in a 2 : 1 intensity ratio. As the sample temperature was increased the two AB quartets broadened at different rates and coalesced at distinctly different temperatures, at *ca.* 50 °C for the weaker quartet and at *ca.* 60 °C for the other. On further warming to *ca.* 130 °C the two bands continued to sharpen but above this temperature they remained essentially unchanged. It should be noted that the different coalescence temperatures of the two AB systems is due primarily, but not solely (see below), to the different internal chemical shifts, δ_{AB}.

Arrhenius energy and activation parameters



M = Rh^{III} or Ir^{III}
R = $S(CH_2SiMe_3)_2$

M	Solvent	R	$E^{\ddagger}$ / kJ mol^{-1}	$\log_{10}A$	$\Delta G^{\ddagger}$ / kJ mol^{-1}	$\Delta H^{\ddagger}$ / kJ mol^{-1}	$\Delta S^{\ddagger}$ / J K^{-1} mol^{-1}
Rh^{III}	$CDCl_3$	I	73.0 ± 1.4	13.6 ± 0.2	68.6 ± 2.8	70.6 ± 1.4	6.5 ± 14.1
		II	70.6 ± 1.6	13.8 ± 0.3	64.9 ± 3.1	68.1 ± 1.6	10.7 ± 15.7
Ir^{III}	C_2Cl_4	I	66.5 ± 0.5	12.8 ± 0.07	66.6 ± 0.9	64.0 ± 0.5	−8.7 ± 4.5
		II	61.1 ± 1.0	12.5 ± 0.15	62.7 ± 1.9	58.6 ± 1.0	−13.8 ± 9.5

Total band-shape fittings of these spectra were made using a modified version of the DNMR program of Binsch.[10] The spectra represent two AB spin systems undergoing mutual exchange. The two systems were computed independently and the sum of both line shapes were plotted. For both complexes the relaxation time T_2* was chosen as 0.318 s for all temperatures. The temperature dependences of the internal chemical shifts of the CH_2 signals were obtained by accurate measurements in the slow-exchange region. The values used were as follows: $[RhCl_3\{S(CH_2SiMe_3)_2\}_3]$ $\delta_{AB}(A)$/Hz = 114.8 + 0.129(θ_c/°C), $\delta_{AB}(B)$/Hz = 97.37 + 0.174(θ_c/°C), $J_{AB}(A)$ 15.4 Hz, and $J_{AB}(B)$ 14.2 Hz; $[IrCl_3\{S(CH_2SiMe_3)_2\}_3]$ $\delta_{AB}(A)$/Hz = 119.6 + 0.067(θ_c/°C), $\delta_{AB}(B)$/Hz = 102.41 + 0.083(θ_c/°C), $J_{AB}(A)$ 15.25 Hz, and $J_{AB}(B)$ 14.2 Hz.

The results of the band-shape fittings are shown in the Table. The errors quoted are based on a least-squares fitting of the Arrhenius equation for seven or eight points. The somewhat larger errors for the complex of Rh^{III} are due to the lower quality (*i.e.* lower S : N ratio) spectra in this case. The most significant finding is that the inversion barriers at sulphur in the two different ligand environments are measurably different with inversion in ligands *trans* to chloride being somewhat more rapid. If the *trans* influence [11] is the dominant factor, this difference in barrier energies must reflect the differing natures of the M–S bonds in the two cases Cl–M–S and S–M–S. Large *trans* influences usually lead to considerable M–S bond weakening. The results imply that the *trans* influence for $S(CH_2SiMe_3)_2$ is slightly less than for chloride. This is somewhat surprising in view of previous data [11] on the relative *trans* influences of S-donor and halide ligands. It would seem more probable that other factors (*viz.* electronic and/or steric) are also operative in the present complexes.

A further unexpected result is that the sulphur barrier energies of the complex of Ir^{III} are significantly lower than in the analogous rhodium(III) complex. This is contrary to the trend observed for related complexes of Pd^{II} and Pt^{II} where inversion barriers in sulphide and selenide ligands [12] appear to be related to the mass and/or size of the transition-metal atom. However, if steric factors are important in determining the stability of the transition state in the inversion process, then such factors may be relieved somewhat in the case of the larger Ir^{III} resulting in a lower energy barrier.

The sulphur inversion barriers reported here are of similar magnitude to those obtained by Haake and Turley [2,3] for complexes of Pd^{II} and Pt^{II}. They suggested a non-dissociative mechanism for the inversion process involving a transition-state structure in which there is bonding to both sulphur lone pairs and with the sulphur atom adopting a tetrahedral rather than a trigonal-planar configuration. Such a mechanism seems very reasonable for the present complexes. However, a dissociative mechanism cannot be completely ruled out since spin interactions with ^{103}Rh, ^{191}Ir, and ^{193}Ir were not detected, thus preventing such couplings from being used to establish whether the M–S bonds remained intact during the inversion process.

The relatively low barriers reported here compared to those in sulphoxides and sulphonium ions are most likely due to the transition state being appreciably stabilized by p_{π}–d_{π} orbital overlap between sulphur and Rh^{III} or Ir^{III}. A further point of note is that the spectra were essentially temperature independent in the approximate range 130—*ca.* 200 °C, indicating that interconversion of the two

---

[10] G. Binsch, *J. Amer. Chem. Soc.*, 1969, **91**, 1304.

[11] T. G. Appleton, H. C. Clark, and L. E. Manzer, *Co-ordination Chem. Rev.*, 1973, **10**, 335.

[12] E. W. Abel, A. K. S. Ahmed, G. W. Farrow, K. G. Orrell, and V. Šik, unpublished work.

types of ligand in the *mer* isomer is too slow to be detected. Additionally, there was no evidence for the existence of any measurable amount of the *fac* isomer in this temperature range.

We thank Mr. E. Underwood for recording the variable-temperature spectra, and Mr. V. Šik for helpful discussions regarding the computations.

[5/2360 *Received, 4th December,* 1975]