Effects of Ligand Configuration upon Rhodium-103 Chemical Shifts

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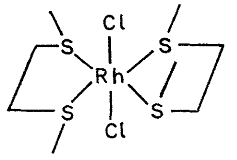
Summary ^{103}Rh chemical-shift differences of up to 83 p.p.m. can arise as a result of different ligand configurations in *cis*- and *trans*-[Rh(MeSCH$_2$·CH$_2$SMe)$_2$Cl$_2$]$^+$Cl$^-$.

THE effects of molecular configuration upon ^{1}H and ^{19}F chemical shifts have been studied extensively,[1] but little is known of the behaviour of heavier nuclei. I now report the measurement by heteronuclear double resonance of some ^{103}Rh (abundance = 100%, $I = \frac{1}{2}$) chemical shifts in octahedral complexes in which variations an order of magnitude larger are found. The technique shows promise as a sensitive probe for the study of homogeneous systems in which rhodium complexes function as stereospecific catalysts.



The 60 MHz. ^{1}H n.m.r. spectrum of the methyl groups of a solution in deuterium oxide of *trans*-[Rh(MeSCH$_2$·CH$_2$SMe)$_2$Cl$_2$]$^+$Cl$^-$ was reported by Walton[2] and is a series of doublets [splitting $^3J(^{103}\text{Rh}\cdots\text{H})$ 1·05 Hz] which arise from species having different ligand configurations. Simultaneous irradiation of the sample at the ^{103}Rh resonant frequency collapses the doublet splitting (Figure), thus confirming the original interpretation,[2] and the precise frequency needed gives the rhodium chemical shift (Table).

^{103}Rh *and* ^{1}H *Chemical shifts in* D$_2$O *solution of* [Rh(MeSCH$_2$·CH$_2$SMe)$_2$Cl$_2$]$^+$Cl$^-$ *at* 22°

^{103}Rh Chemical shift[a] (p.p.m.)	τ (CH$_3$) (p.p.m.)	Assignment
0	7·48	*trans*
+ 22	7·65	*trans*
+ 38	7·40; 7·56; 7·60	*trans*[b]
+ 83	7·50	*trans*
+214	7·35; 7·51$_5$	*cis*
+254	7·35; 7·42; 7·65	*cis*
+296	7·31; 7·60	*cis*

[a] That at lowest field is arbitrarily taken as zero.
[b] See text and displayed formula.

There are only five possible isomers of the *trans*-complex so the observation of at least seven distinct ^{103}Rh frequencies indicates that some *cis*-isomers (ten possibilities) were also present in the solution examined. This is consistent with the changed appearance of the proton spectrum after the sample had been maintained at 100° for some time: some of the weaker lines became stronger, indicating slow equilibrium between the *cis*- and *trans*-isomers. The assignments are based primarily on the assumption that the *trans*-isomer is the predominant species in solution as it is in the solid; the chemical-shift trends are then similar to those found in platinum complexes.[3] In particular, the isomer with rhodium chemical shift + 38 p.p.m. is assigned the configuration shown, because this is the only *trans*-species containing several kinds of methyl group, two of which have identical τ-values (7·56).

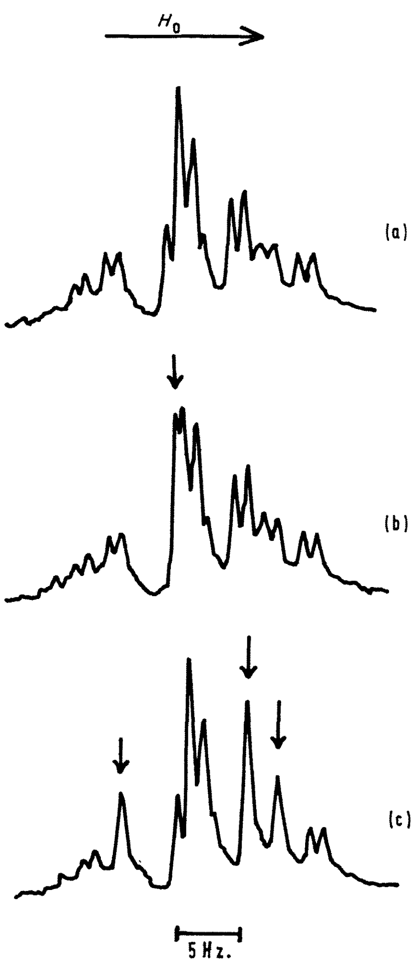


FIGURE. *Frequency-sweep* 60 *MHz. proton spectrum of the methyl groups of* [Rh(MeSCH$_2$·CH$_2$SMe)$_2$Cl$_2$]$^+$Cl$^-$ *in* D$_2$O *at* 22°.

(a) *Normal spectrum.*
(b) ^{103}Rh *irradiated at* 0 *p.p.m.*
(c) ^{103}Rh *irradiated at* +38 *p.p.m.*

Vertical arrows indicate lines that have been collapsed by ^{103}Rh *irradiation.*

The proton spectrum broadens on heating and gives *two* doublets (τ = 7·35 and 7·50; relative intensities *ca.* 1: 3·5) at 108°. The species have rhodium chemical shifts of +163 and −49 p.p.m., and must be the *cis*- and *trans*-isomers undergoing rapid configurational rearrangement. Since the complex is a chelate the retention of $^{103}\text{Rh}\cdots\text{H}$ coupling does not indicate whether the mechanism involves inversion at sulphur or cleavage of an Rh–S bond.[4] Half of the proton resonance from the *cis*-isomer is apparently concealed by the doublet at τ 7·50, and probably arises from methyl groups attached to sulphur atoms that are *trans* to other sulphur atoms. The weighted mean rhodium chemical shift of the *trans*-isomer at 22° is *ca.* + 40 p.p.m., so there is a temperature-dependence of *ca.* $-1\cdot0$ p.p.m./degree. Similar variations occur for ^{59}Co chemical shifts,[5] and arise effectively from changes in the ΔE term of the paramagnetic contribution.

Whilst the spread of proton chemical shifts for the methyl groups can be accounted for by the diamagnetic anisotropy of the sulphur lone-pairs, the range of the rhodium shifts is too great for this. There will be different degrees of steric strain in the various isomers, and this will lead to small variations of bond lengths which will in turn affect ΔE and $\langle r_{4d}^{-3} \rangle$, and so may account for the observed chemical-shift differences. Alternatively, the electrons of the Rh–Cl bonds may be polarised by the sulphur lone-pairs to different extents in the various isomers.

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