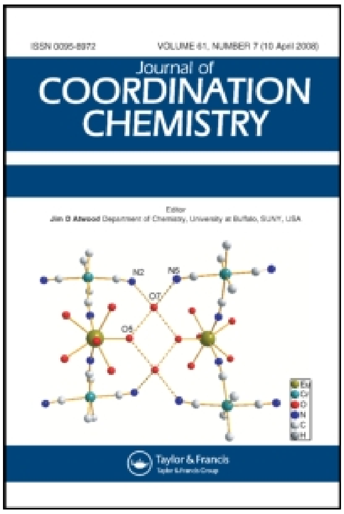

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Mattson, B. M. , Madera, A. E. and Palazzotto, M. C.(1984) 'CARBON-NITROGEN BOND ROTATION IN A DITHIOCARBAMATO COMPLEX OF RHODIUM(III)', Journal of Coordination Chemistry, 13: 4, 321 — 324
To link to this Article: DOI: 10.1080/00958978408073885
URL: http://dx.doi.org/10.1080/00958978408073885

J. Coord. Chem., 1984, Vol. 13, p. 321-324
0095-8972/84/1304-0321 $18.50/0'

CARBON-NITROGEN BOND ROTATION IN A DITHIOCARBAMATO COMPLEX OF RHODIUM(III)

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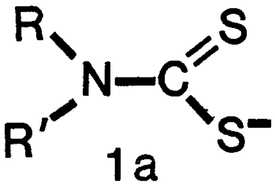
(Received April 15, 1983; in final form March 20, 1984)

The temperature-dependent pmr spectrum of Rh(MePhdtc)$_3$ was examined in CDCl$_3$ solvent over the temperature range −34° to +51°. The complex is stereochemically non-rigid and isomerizes by a C-N bond rotation mechanism. A line shape analysis yielded a value of $\Delta G^{\ddagger} = 61.5 \pm 4.2$ kJ mol^{-1}. This barrier to rotation is large relative to similar complexes of Fe(II) and Fe(III) but similar to values for Fe(IV) and Co(III). Metal-centered optical inversion is slow over the temperature range studied.

INTRODUCTION

Tris(dithiocarbamato), (R$_2$dtc), transition metal complexes exhibit stereochemically nonrigid behavior on the ^{1}H-nmr time scale. In fact, two distinct rearrangement processes, S$_2$C—N bond rotation and optical inversion, occur over similar temperature ranges. The latter process is believed to occur through a metal-centered trigonal twist rearrangement involving a trigonal prismatic transition state.[1] The value of $\Delta G^{\ddagger}$ for this process ranges from *ca* 28 kJ mol^{-1} for certain Fe(III) complexes to over 100 kJ mol^{-1} for Rh(Bz$_2$dtc)$_3$.[1,2] The enthalpy of activation correlates well with the ligand field stabilization energy.

The other nmr-observable dynamic process exhibited by these compounds is that of carbon-nitrogen bond rotation. Relatively high barriers to this rotation are explained by the resonance structures (1a-c). In particular, form (1c) provides a basis for explaining experimental data in terms of partial multiple bond character between carbon and nitrogen.[3] Numerous infrared and x-ray diffraction studies substantiate the importance of (1c) as a contributing resonance form.[4,5]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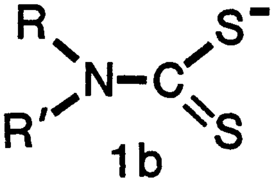
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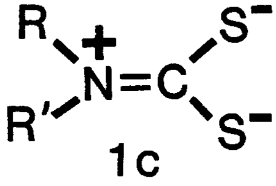
1c

Several investigators have reported $\Delta G^{\ddagger}$ for C—N bond rotation in tris (dtc) complexes. Pignolet reported $\Delta G^{\ddagger}$ values for complexes of Fe(II), Fe(III), and Fe(IV) in the ranges of 34.3 - 36.8, 50.2 - 51.0, and 59.0 - 64.9 kJ mol^{-1}, respectively.[5] Siddall reported a value of $\Delta G^{\ddagger}$ = 62.8 - 83.7 kJ mol^{-1} for Co(MeBzdtc)$_3$.[6] In this paper we report the free energy of activation for C—N bond rotation in Rh(MePhdtc)$_3$. We believe this is the first quantitative report of such a kinetic parameter for a dtc complex of a second row transition metal.[7]

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EXPERIMENTAL

Preparation of Rh(MePhdtc)$_3$

The procedure of Malatesta was followed.[8] The product was purified by column chromatography using silica gel and CH_2Cl_2 eluant. Recrystallization from CH_2Cl_2/heptane by solvent evaporation afforded deep red crystals that were dried under vacuum. Pmr($CDCl_3$): δ = 3.59 (s, Me); 7.39 (m, Ph). Analysis for $Rh_1S_6C_{24}N_3H_{24}\cdot 0.5\ CH_2Cl_2$: Calc.; found: C 42.51, 42.26; H 3.64, 3.71. IR(KBr: ν_{CN} = 1443 cm^{-1}.

Pmr Measurements

A set of spectra were recorded over the temperature range −45° to +63° in $CDCl_3$ solvent. The methyl resonance portion of these spectra is shown in Figure 1. The spectra were recorded on a Varian XL-100-15 nmr spectrometer equipped with a variable temperature probe. Chemical shifts were measured relative to the $CHCl_3$ solvent resonance and are reported relative to TMS. Temperatures were measured by a thermocouple mounted in an nmr tube.

Kinetic Analysis

The complex Rh(MePhdtc)$_3$ exists in solution as a mixture of *cis* and *trans* isomers as well as optical isomers. The kinetic line-shape analysis involves a four site

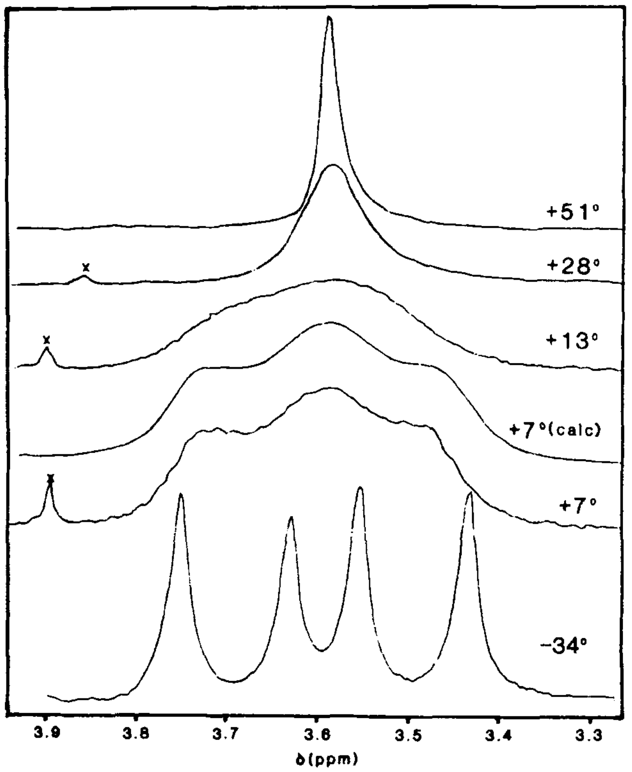


FIGURE 1 Observed pmr spectra of the methyl resonances for Rh(MePhdtc)$_3$ in $CDCl_3$ solution at 100 MHz. Calculated line shape for coalescence spectrum is labelled '+7°(calc)'.

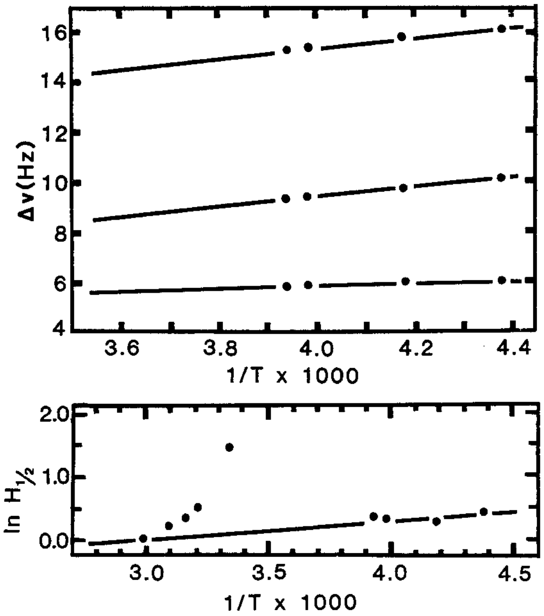


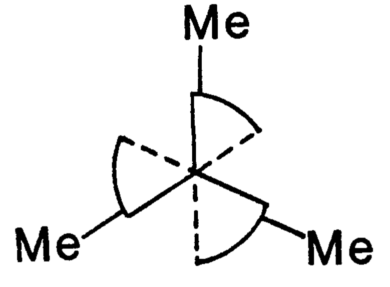
FIGURE 2 ln $H_{1/2}$ *vs* 1/T and $\Delta\nu$ (from high field resonance) *vs* 1/T plots for the N-CH_3 resonances of $Rh(MePhdtc)_3$.

exchange problem; rapid C—N bond rotation results in random scrambling of the four resonances. The line shape of the coalescence spectrum (+7°), was simulated by computer calculation using the Gutowsky-Holm line shape equation and the Binsch DNMR3 program.[9] Linear extrapolations of chemical shift separations, $\Delta\nu$, and line widths at half-height, $H_{1/2} = 1.2$ Hz, used to calculate the line shape, were obtained from slow-exchange spectra and are shown in Figure 2. The assumption that the rate of C—N bond rotation, k, was the same for each dtc ligand yielded the spectrum labelled '+7(calc)' in Figure 1. The value of k we report, 20 ± 2 sec^{-1}, was determined by a visual fit of numerous calculated spectra to that observed at 7°.

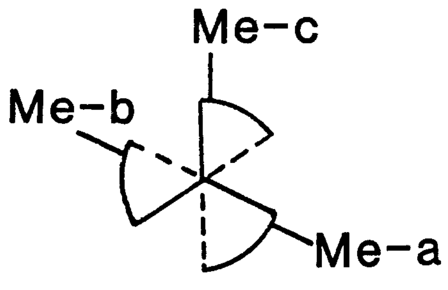
RESULTS AND DISCUSSION

Pmr Resonance Assignment

Two geometric isomers are possible for each enantiomer of $Rh(MePhdtc)_3$, as shown below.



Δ-cis



Δ-trans

In the Δ-*cis* complex, the three methyl groups are mutually *cis* and magnetically equivalent. In the *trans* isomer the three methyl groups are non-equivalent. The exchange matrix used to successfully simulate the observed spectrum at coalescence allows us to partially assign the pmr spectrum. The *cis* isomer gives the Me resonance at $\delta = 3.63$ ppm. Of the three Me resonances observed for the *trans* isomer, only Me-b can be unequivocally assigned ($\delta = 3.55$ ppm). Resonances due to Me-a and Me-c are at $\delta = 3.43$ and 3.75 ppm. At −34° the equilibrium constant is $K = [trans]/[cis] = 3.60 \pm 0.01$. This value does not vary much over the temperature range −19 to −45°; at −19°, $K = 3.12 \pm 0.06$.

Kinetics of C—N Bond Rotation

Either a geometric isomerization such as a C—N bond rotation or a metal-centered rearrangement could result in the observed averaging of the nmr resonances shown in Figure 1.[10] Pignolet reported a value of $\Delta G^{\ddagger} = 105.9$ kJ mol^{-1} for the optical inversion of Rh(Bz$_2$dtc)$_3$.[2] Since Rh(MePhdtc)$_3$ is quite analogous, the barrier to optical inversion is undoubtedly also large for this compound and so this process is assumed to be slow on the pmr timescale over the temperature range employed by us. Thus, the dynamic process we observe for Rh(MePhdtc)$_3$ is undoubtedly C—N bond rotation.

The value of $\Delta G^{\ddagger}$ for C-N bond rotation is obtained from the equation $k = (k_BT/h)\exp(-\Delta G^{\ddagger}/RT)$ and is equal to 61.5 ± 4.2 kJ mol^{-1} at 7° for Rh(MePhdtc)$_3$. This value is comparable to the range of 62.8 - 83.7 kJ mol^{-1} estimated by Siddel for Co(MeBzdtc)$_3$.[6] Compared to dtc complexes of iron, this value is appreciably larger than those for either Fe(II) and Fe(III) but similar to those for Fe(IV) which fall in the range 59.0 - 64.9 kJ mol^{-1}.[5] One would expect that the increased electron affinity of Co(III) and Rh(III) over that of Fe(III) would result in the observed trend by making resonance form (1c) more important for Co and Rh than for Fe. Interestingly, for complexes of Fe(R$_2$dtc)$_3$, the high and low temperature processes are C—N bond rotation and optical inversion, respectively,[5] while the reverse is true for Rh(MePhdtc)$_3$; Rh-centered optical inversion is the high temperature process as deduced from ligand field stabilization arguments.[2]

ACKNOWLEDGEMENTS

This research was supported by grants from the William and Flora Hewlett Foundation of Research Corporation and by the Creighton University Graduate School.

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