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Supplementary Material Available: Listings of refined temperature factors, geometry of the phenyl rings, least-squares planes, calculated coordinates of the hydrogen atoms, and observed and calculated structure factors and a stereoview of the unit cell (Figure 3) (21 pages). Ordering information is given on any current masthead page.

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^{13}C NMR Studies on Diastereotopic Rhodium(III) (±)-2,3-Butanediamine Complexes and the Structure of *lel*,*lel*,*lel*-$[Rh((\pm)\text{-}bn)_3]Br_3$

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The four possible diastereomers of $[Rh((\pm)\text{-}bn)_3]^{3+}$ ("bn" = 2,3-butanediamine, $C_4H_{12}N_2$) have been isolated and the ^{13}C NMR spectra determined. Isomer abundances indicate that the increase in enthalpy per *ob* ring in $[Rh((\pm)\text{-}bn)_3]^{3+}$ diastereomers is only one-third that in $[Co((\pm)\text{-}bn)_3]^{3+}$ complexes. The *lel*,*lel*,*lel* diastereomer of $[Rh((\pm)\text{-}bn)_3]^{3+}$ does not exhibit the broadened methyl group ^{13}C NMR resonance found earlier for *lel*,*lel*,*lel*-$[Co((\pm)\text{-}bn)_3]^{3+}$ even though a crystal structure of the former complex as the bromide salt ($[Rh(C_4H_{12}N_2)_3]Br_3$, trigonal system, space group $P\bar{3}1c$, a = 12.549 (2) Å, c = 8.195 (1) Å, Z = 2) shows a decreased intra-ring methyl group contact distance. These observations rule out steric interactions proposed earlier as a source of the anomalous broadening and indicate that the broadening involves the ^{59}Co atom. ^{13}C NMR spectra of corresponding rhodium(III) and cobalt(III) tris((±)-2,3-butanediamine) diastereomers are virtually identical. The possible contribution of magnetic anisotropy of the metal ion to ^{13}C NMR chemical shift differentiation of diastereotopic carbon atoms in these complexes is discussed.

Introduction

Past studies[1-3] from our group have demonstrated the utility of ^{13}C NMR spectroscopy in differentiating and identifying diastereomeric complexes of diamagnetic metal ions—particularly diastereomers arising from the presence of sinambic[4] ligands. From this work there has arisen an increasingly intriguing question: What is the ultimate origin of ^{13}C NMR chemical shift differences between diastereotopic carbon atoms in such complexes?

Previous work has indicated that, relative to rigid chelates, diastereomers containing flexible chelate rings are more easily differentiated by ^{13}C NMR spectroscopy and that diastereotopic atoms lying in conformationally distinct environments within such complexes have enhanced ^{13}C chemical shift differences.[1,2] Thus, we can readily interpret chemical shift variations between diastereotopic methyl carbon atoms in *ms*-2,3-butanediamine complexes as arising from steric compression shifts[5] associated with axial/equatorial differences in the chelate ring.[1] Moreover, we can explain the striking differentiability of *ms*-2,3-butanediamine diastereomeric complexes as due to the conformational flexibility of the ligand allowing different time-averaged conformations for symmetry-nonequivalent chelate rings.[1] Unfortunately, such explanations are not easily extended to chelate ring carbon atoms where steric compression shifts are not expected, nor are they readily applied to complexes such as $[Co((\pm)\text{-}bn)_3]^{3+}$ ("bn" = 2,3-butanediamine) whose diastereomers are easily distinguished by ^{13}C NMR even though the three chelate rings are expected to be rigid and to have very similar conformations.[1] Equally disconcerting is recent work showing exceptionally large chemical shift differences between diastereotopic carbon atoms in complexes of *cis*-1,2-cyclopentanediamine, a ligand expected to give rigid chelate rings with relatively fixed conformations.[6]

In order to determine what influence subtle electronic and steric effects might play in chemical shift differentiation of diastereotopic carbon atoms in complexes, we have separated the diastereomers of $[Rh((\pm)\text{-}bn)_3]^{3+}$ and have determined their ^{13}C NMR spectra for comparison with (redetermined) spectra of $[Co((\pm)\text{-}bn)_3]^{3+}$ isomers. A crystal structure of *lel*,*lel*,*lel*-$[Rh((\pm)\text{-}bn)_3]Br_3$ has also been determined in order to compare the geometry of the cation with that found for $[Co((\pm)\text{-}bn)_3]^{3+}$.[7]

Experimental Section

Synthesis. 2,3-Butanediamine was obtained commercially, and the meso and racemic isomers were separated as described elsewhere.[1] The racemic material as the dihydrochloride salt (9.66 g, 60 mmol) was dissolved in 50 mL of 80% aqueous methanol and was allowed to react with NaOH (4.8 g, 120 mmol) dissolved in a minimum of water. The NaCl precipitate was filtered off and the solution was added to aqueous $RhCl_3 \cdot 3H_2O$ (2.63 g, 10 mmol). The mixture was heated on a steam bath and two more 60-mmol portions of (±)-2,3-butanediamine were added. After additional NaCl had precipitated, the solution was allowed to cool and isopropyl alcohol was added. The NaCl was removed by filtration, the solution was concentrated in vacuo with heating, and acetone was added to precipitate a mixture of $[Rh((\pm)\text{-}bn)_3]Cl_3$ and excess ligand as the hydrochloride salt.

An aqueous solution of the precipitated mixture was chromatographed on SP Sephadex C-25 cation exchange resin on a 2.7 cm × 50 cm column using 0.5 M aqueous Na_2SO_4 eluent with a flow rate of 1 mL min^{-1}. Elution curves plotted from the spectral absorbances at 300 nm showed the presence of four chromatographic bands, which were identified as the *lel*,*lel*,*lel*, *lel*,*lel*,*ob*, *lel*,*ob*,*ob*, and *ob*,*ob*,*ob*

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Table I. Crystal and Data Collection Parameters for $[Rh((\pm)\text{-}NH_2CH(CH_3)CH(CH_3)NH_2)_3]Br_3$

fw	607.1
F_{000}	600
a, Å	12.549 (2)
c, Å	8.195 (1)
V, Å^3	1117.7 (3)
Z	2
ρ(calcd), g cm^{-3}	1.80
space group	$P\bar{3}1c$
crystal dimens, mm	0.13 × 0.13 × 0.22
radiation	Mo Kα (λ = 0.710 69 Å)
monochromator	graphite
abs coeff, μ(Mo Kα), cm^{-1}	60.7
scan speed, deg min^{-1}	variable, 4.0–30.0
scan range, deg	1.0° below 2θ (Kα_1) to 1.0° above 2θ (Kα_2)
2θ limits, deg	1.0–55.0
reflcns collected	$h, \pm k, \pm l$
backgrd counting time	0.5 × scan time
stds monitored	3 stds every 192 reflcns
reflcns collected	4747
unique reflcns	877
unique data used	751 with $F^2 > 2.5\sigma(F^2)$
no. of variables refined	59
w^{-1}	$\sigma^2(F_O) + (gF_O)^2$, $g = 0.0032$
$R(F) = \Sigma\|\|F_O\| - \|F_C\|\|/\Sigma\|F_O\|$	0.033
$R_w(F) = [\Sigma w(\|F_O\| - \|F_C\|)^2/\Sigma w\|F_O\|^2]^{1/2}$	0.024

Table II. Fractional Coordinates and Thermal Parameters for *lel,lel,lel*-$[Rh((\pm)\text{-}bn)_3]Br_3$

atom	x	y	z	U,[a] Å^2
Rh	0.66667 (0)	0.33333 (0)	0.75000 (0)	0.0287 (2)
Br	0.54600 (2)	−0.54600 (2)	0.25000 (0)	0.0614 (3)
N	0.6777 (3)	0.2019 (3)	0.6132 (4)	0.041 (2)
C(1)	0.7928 (3)	0.2005 (3)	0.6571 (4)	0.042 (2)
C(2)	0.7915 (5)	0.0884 (4)	0.5851 (6)	0.062 (2)
H(1)	0.679 (3)	0.216 (3)	0.525 (4)	0.051 (12)
H(2)	0.610 (2)	0.130 (3)	0.638 (4)	0.037 (9)
H(11)	0.864 (2)	0.278 (3)	0.610 (4)	0.039 (8)
H(21)	0.783 (4)	0.087 (4)	0.452 (5)	0.089 (13)
H(22)	0.726 (4)	0.011 (4)	0.627 (5)	0.094 (15)
H(23)	0.866 (4)	0.093 (3)	0.603 (5)	0.081 (14)

[a] $U = U_{eq}$ for non-hydrogen atoms and U_{iso} for hydrogen atoms. $U_{eq} = 1/3(U_{11} + U_{22} + U_{33})$ with the U_{ii}'s in an orthonormal coordinate system. The anisotropic thermal parameters used were of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. See: Willis, B. T. M.; Pryor, A. W. "Thermal Vibrations in Crystallography"; Cambridge University Press: Cambridge, 1975; pp 101–102.

Table III. Observed Isomer Abundances, %

isomer	$[Rh((\pm)\text{-}bn)_3]^{3+}$	$[Co((\pm)\text{-}bn)_3]^{3+}$ [a]
lel,lel,lel	27	60
lel,lel,ob	38	28
lel,ob,ob	29	12
ob,ob,ob	6	<1

[a] Reference 1.

isomers in order of elution.[8] The isomers were assigned from a comparison of expected[1] and observed abundances and from the ^{13}C NMR spectra (vide infra).

Addition of methanol to the chromatographic fractions permitted the removal of sodium sulfate. The methanolic solutions were evaporated to dryness under a stream of air to give the solid diastereomers as sulfate salts for use in the ^{13}C NMR spectral determinations. Addition of NaBr to aqueous solutions of the sulfate salts gave well-developed crystals of the bromide salts. Anal. Calcd for $[Rh(C_4H_{12}N_2)_3]Br_3$: C, 23.72; H, 5.93. Found (*lel,lel,lel*): C, 23.90; H, 6.12. Calcd for $[Rh(C_4H_{12}N_2)_3]Br_3\cdot H_2O$: C, 23.04; H, 6.08; N, 13.44. Found (*lel,lel,ob*): C, 23.26; H, 6.17; N, 13.31. Found (*lel,ob,ob*): C, 23.43; H, 6.07; N, 13.50. Found (*ob,ob,ob*): C, 23.37; H, 6.12.

Diastereomers of $[Co((\pm)\text{-}bn)_3]_2(SO_4)_3$ were obtained as described elsewhere.[1] As found earlier,[1] the *ob,ob,ob* isomer was present in too low an abundance to isolate. Addition of NaBr to aqueous solutions of the sulfate salts gave compounds that analyzed as anhydrous for the *lel,lel,lel* diastereomer and as monohydrated for the other two isomers. Anal. Calcd for $[Co(C_4H_{12}N_2)_3]Br_3$: C, 25.60; H, 6.44; N, 14.92. Found (*lel,lel,lel*): C, 25.73; H, 6.66; N, 14.97. Calcd for $[Co(C_4H_{12}N_2)_3]Br_3\cdot H_2O$: C, 24.80; H, 5.59; N, 14.46. Found (*lel,lel,ob*): C, 24.83; H, 6.69. Found (*lel,ob,ob*): C, 25.06; H, 6.80; N, 14.45.

Physical Measurements. Proton-decoupled, natural abundance ^{13}C NMR data were collected on solutions of 100 mg of the sulfate salts dissolved in 1.5 mL of D_2O. The solutions were contained in a 10-mm tube with the external Me_4Si standard in a coaxial 5-mm tube. Spectra were obtained at ca. 40 °C on a Varian FT-80 spectrometer with an observe frequency of 20.0 MHz, a 4000-Hz sweep width, 0.5-s acquisition time, 10-μs pulse width (equivalent to a 50° pulse), noise-modulated proton decoupling, and no pulse delay. Sulfates, rather than halide salts, were employed for the ^{13}C NMR studies owing to their greater solubility.

IR spectra of the bromide salts of $[Rh((\pm)\text{-}bn)_3]^{3+}$ and $[Co((\pm)\text{-}bn)_3]^{3+}$ were collected on a Perkin-Elmer Model 621 grating spectrophotometer using KBr pellets.

Crystal Structure Determination. A colorless crystal of *lel,lel,lel*-$[Rh((\pm)\text{-}bn)_3]Br_3$ with a hexagonal prismatic habit was grown by evaporation of an aqueous solution and was sealed in a glass capillary. Lattice parameters, obtained by a least-squares fit to the settings for 25 automatically centered reflections, and intensity data were determined by using a Syntex P3/F diffractometer system at ambient temperature (~23 °C). Empirical absorption corrections based on ψ scans were applied.[9] The estimated minimum and maximum transmission coefficients were 0.46 and 0.53. No extinction corrections were made. Scattering factors for Rh^{3+} and Br^- were used, and anomalous dispersion corrections were applied to all non-hydrogen atoms. The crystal and data collection parameters are tabulated in Table I.

Equivalent reflections were merged with an agreement factor of 1.8%. From the systematic absences of $hh\bar{2h}l$, $l = 2n + 1$, and from the subsequent satisfactory refinement, the space group was assigned as $P\bar{3}1c$. The only exception to the expected absences was that of the $44\bar{3}$ reflection, whose average intensity of $2.83\sigma(F^2)$ was marginally above the cut-off of $2.5\sigma(F^2)$. The structure was solved by direct methods, and the non-hydrogen atoms were refined anisotropically to give $R = 0.044$. Hydrogen atoms, located from a difference map, were then added and the positions and thermal parameters (isotropic for the hydrogen atoms) of all atoms were refined. The final difference map showed the two highest peaks to be 0.98 e Å^{-3} (0.1 Å from Rh) and 0.55 e Å^{-3} (0.87 Å from Br). All other peaks had intensities of 0.47 e Å^{-3} or less. The final positions and thermal parameters (U_{eq} or U_{iso}) are given in Table II.

Results

Characterization. The synthesis of *lel,lel,lel*-$[Rh((\pm)\text{-}bn)_3]^{3+}$ has been reported previously.[10] There are no reports of prior isolation of the other three diastereomers. The relative abundances of all four $[Rh((\pm)\text{-}bn)_3]^{3+}$ diastereomers as determined from the spectral absorbances at 300 nm measured by using fractions combined from several chromatographic runs with absorption coefficients assumed identical are listed in Table III along with values found for $[Co((\pm)\text{-}bn)_3]^{3+}$.[1] Our presentation of these results is not meant to imply that we have evidence that equilibrium was attained during synthesis of

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(8) See footnote 9 in ref 1 for a discussion of the isomer nomenclature.

(9) All calculations and plots were carried outusing the SHELXTL79 package: Sheldrick, G. M. "Nicolet SHELXTL Operations Manual;" Nicolet XRD Corp.: Cupertino, CA, 1979. SHELXTL uses anomalous dispersion and scattering factor data from: "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4, pp 99–101, 149, 150.

(10) Woldbye, F.; Borch, G. In "Some New Physical Methods in Structural Chemistry"; Bonnett, R., Davis, J. G., Eds.; United Trade Press, Ltd.: London, 1967; pp 192–200.

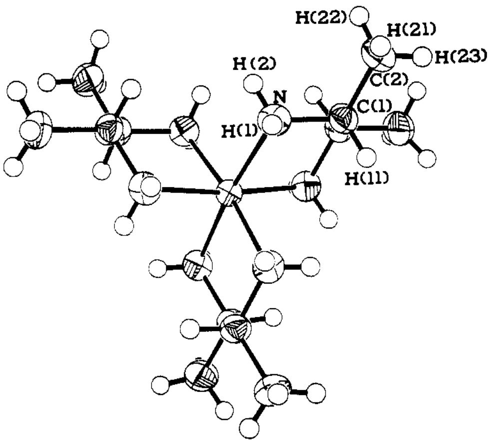

Figure 1. Atom numbering scheme for the cation *lel,lel,lel*-Δ-[Rh-(R,R-bn)$_3$]$^{3+}$, shown with thermal ellipsoids at the 50% probability level.

either [Rh((±)-bn)$_3$]$^{3+}$ or [Co((±)-bn)$_3$]$^{3+}$. However, assuming equilibrium is attained in both systems, one can conclude a significantly decreased *lel/ob* energy difference in the Rh(III) series of isomers compared to the Co(III) series. One example of this is found in our ready isolation of the *ob,ob,ob* diastereomer of [Rh((±)-bn)$_3$]$^{3+}$ compared to our inability to isolate *ob,ob,ob*-[Co((±)-bn)$_3$]$^{3+}$, apparently owing to its negligible abundance. Similarly, though *lel,lel,ob*-[Rh-((±)-bn)$_3$]$^{3+}$ is expected to have a higher enthalpy than the *lel,lel,lel* diastereomer,[1] the observed abundance of the former species is actually greater than that of the latter. This "reversal" which is due to a symmetry-dependent entropy contribution of R ln 3 for the C_2-symmetry *lel,lel,ob* and *lel,ob,ob* isomers, is not observed for [Co((±)-bn)$_3$]$^{3+}$.[1] A similar reversal is found for [Co(en)$_3$]$^{3+}$ ("en" = 1,2-ethanediamine) in solution.[11] One can use the data in Table III to calculate an average enthalpy contribution of 0.4 kcal mol^{-1} per *ob* ring in the Rh(III) system compared to 1.1 kcal mol^{-1} per *ob* ring in the Co(III) system assuming equilibrium is attained. For these calculations a temperature of 60 °C (approximately that used in the syntheses[1]) was assumed.

IR spectra of the diastereomeric [M((±)-bn)$_3$]Br$_3$ salts are quite similar though, as might be expected, spectral bands found for the higher symmetry (D_3) *lel,lel,lel* and *ob,ob,ob* isomers are markedly sharper than those determined for the lower symmetry (C_2) *lel,lel,ob* and *lel,ob,ob* compounds. The *lel,lel,lel* diastereomers do exhibit characteristic IR bands at 763 cm^{-1} (Rh(III)) or 760 cm^{-1} (Co(III)) and at 1262 cm^{-1} (Rh(III)) or 1270, 1260 cm^{-1} (Co(III)). These bands, which almost certainly correspond to NH$_2$ rock and impure-twist modes[12] (they shift to 632 cm^{-1} and approximately 1160 cm^{-1}, respectively, for *lel,lel,lel*-[Rh((±)-bn)$_3$]Br$_3$ recrystallized from D$_2$O), are missing in spectra of the *ob*-containing isomers, which exhibit a new, broad band near 1240 cm^{-1}. That these bands are characteristic of the *lel,lel,lel* salts is probably due to the other diastereomeric compounds being hydrated and thus experiencing increased hydrogen bonding involving the amine protons.

Other than quite minor shifts in band frequencies, the only difference between IR spectra of corresponding diastereomers of [Co((±)-bn)$_3$]Br$_3$ and [Rh((±)-bn)$_3$]Br$_3$ is found for the *lel,lel,lel* species. Here the IR spectrum of the Co(III) compound shows a distinct splitting of a sharp single peak found at 1262 cm^{-1} for the Rh(III) derivative. The otherwise striking similarities indicate that corresponding diastereomers of the Co(III) and Rh(III) complexes as the bromide salts are likely isostructural, as found by X-ray diffraction for the *lel,lel,lel* diastereomers with different halide counterions (vide infra).

Table IV. Selected Interatomic Distances (Å) and Angles (deg) Involving Non-Hydrogen Atoms for the Cationic Complex in *lel,lel,lel*-[Rh((±)-bn)$_3$]Br$_3$

Rh-N	2.055 (4)	C(1)-C(2)	1.518 (7)
N-C(1)	1.497 (6)	C(1)-C(1)′	1.526 (6)
N-Rh-N′	82.2 (2)	N-C(1)-C(2)	110.8 (3)
Rh-N-C(1)	109.3 (2)	C(2)-C(1)-C(1)′	114.3 (3)
N-C(1)-C(1)′	105.4 (2)		

[a] Positions of primed atoms are generated by $1 - y$, $1 - x$, $1.5 - z$.

Table V. Chelate Ring Dihedral Angles (deg) for *lel,lel,lel*-[Rh((±)-bn)$_3$]Br$_3$ and *lel,lel,lel*-[Co((±)-bn)$_3$]Cl$_3$[a]

	[Rh((±)-bn)$_3$]$^{3+}$	[Co((±)-bn)$_3$]$^{3+}$ [b]
N-C(1)-C(1)′-N	−57.3 (4)	55.1 (4)
C(2)-C(1)-C(1)′-C(2)′	58.7 (4)	−60.5 (2)
C(2)-C(1)-C(1)′-N′	−179.3 (3)	177.3 (2)
M-N-C(1)-C(1)′	44.1 (3)	−42.9 (2)

[a] Primed atoms are generated by $1 - y$, $1 - x$, $1.5 - z$ for the Rh(III) structure and by $y - x$, y, $^1/_2 - z$ for the Co(III) structure. [b] From ref 7.

Table VI. ^{13}C NMR Chemical Shifts for Diastereomers of [M((±)-bn)$_3$]$_2$(SO$_4$)$_3$

		δ	
diastereomer	assignt	Rh(III)	Co(III)
lel,lel,lel	CH$_3$	19.52	19.06[a]
	CH	59.63	59.17
lel,lel,ob	CH$_3$	19.33	18.83, 19.10[b]
	CH	58.35, 59.14, 59.73	58.03, 58.81, 59.18
lel,ob,ob	CH$_3$	19.29, 19.45[b]	18.93, 19.06, 19.19
	CH	58.50,[b] 59.43	58.00, 58.15, 58.95
ob,ob,ob	CH$_3$	19.44	
	CH	58.84	

[a] Broad. [b] Area of resonance indicates the presence of two overlapping peaks.

Crystal Structure Results. A racemic mixture of Δ-[Rh-(R,R-bn)$_3$]$^{3+}$ and Λ-[Rh(S,S-bn)$_3$]$^{3+}$ enantiomers having crystallographic D_3 symmetry is present in *lel,lel,lel*-[Rh-((±)-bn)$_3$]Br$_3$. A stereoview of the Λ enantiomer has been deposited as supplementary material. Selected interatomic distances and angles involving non-hydrogen atoms are given in Table IV, and the atom labeling scheme is indicated in Figure 1.

The bromide salt of *lel,lel,lel*-[Rh((±)-bn)$_3$]$^{3+}$ is isostructural with the corresponding diastereomer of [Co((±)-bn)$_3$]$^{3+}$ as the chloride salt.[7] The Rh-N distance of 2.055 (4) Å can be compared to the Co-N distance of 1.958 (2) Å and the N-Rh-N′ angle of 82.2 (2)° with the N-Co-N′ angle of 85.0 (1)°. Bond lengths and bond angles not involving the metal ions are nearly identical for the two structures; however, the chelate ring in *lel,lel,lel*-[Co((±)-bn)$_3$]$^{3+}$ is slightly flattened relative to the Rh(III) complex (Table V). This slight flattening, which gives a slightly larger methyl carbon separation within a chelate ring for the Co(III) structure (3.107 (4) Å) compared to the Rh(III) complex (3.095 (7) Å), indicates greater steric interactions in the former structure than in the latter, a difference which is also reflected in the *lel/ob* energy differences for the Rh(III) and Co(III) systems.

A good representation of the unit cell contents for the Rh(III) compound can be seen in the packing diagram reported for *lel,lel,lel*-[Co((±)-bn)$_3$]Cl$_3$.[7] In the Rh(III) structure, each bromide ion is at a site of C_2 symmetry with four hydrogen-bonding contacts with amine groups. There are two H(1)-Br contacts of 2.77 (3) Å and two H(2)-Br

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(11) Sudmeier, J. L.; Blackmer, G. L.; Bradley, C. H.; Anet, F. A. L. *J. Am. Chem. Soc.* **1972**, *94*, 757.

(12) Rasmussen, K.; Larsen, J. *Commentat. Phys.-Math.* **1978**, *48*, 103.

contacts of 2.65 (4) Å. The respective N–H–Br angles are 137 (3)° and 164 (3)°. These hydrogen-bonding interactions are probably quite weak, and this accounts for the sharp and unshifted NH_2 IR bands observed for the *lel,lel,lel* diastereomer.

^{13}C NMR. NMR data for $[Rh((\pm)\text{-bn})_3]^{3+}$ and $[Co((\pm)\text{-bn})_3]^{3+}$ diastereomers as the sulfate salts are presented in Table VI. The chemical shifts determined for the Co(III) compounds are about 0.5 ppm higher than those found for the chloride salts in an earlier investigation.[1] The difference is probably due to the use of different references. For the present study, all spectra have been run under identical conditions so that chemical shifts can be compared with confidence.

Except for a shift to lower field (larger δ) of 0.35 ppm average for methyl carbon resonances and 0.43 ppm (av) for methine carbon resonances upon going from Co(III) to Rh(III), the spectra determined for corresponding diastereomers in two systems are strikingly similar. The relatively uniform shift observed is probably primarily due to a bulk susceptibility difference between the Co(III) and Rh(III) complexes. A difference in volume susceptibility of 0.4×10^{-6} owing to a larger second-order paramagnetism for Co(III) would account for the observed shift.[13] The important point is that chemical shift differences between both intramolecularly and intermolecularly diastereotopic carbon atoms are virtually the same for the two metal systems. After adjustment for the average shift differences noted above, the average absolute difference between corresponding NMR resonance positions for all carbon atoms is only 0.09 ppm, with a maximum observed difference of 0.15 ppm. Since there is, at best, a 0.05 ppm precision in the location of single, sharp ^{13}C NMR peaks and, perhaps, a 0.10 ppm precision for peaks appearing as shoulders, the observed differences fall within the limits of experimental error. Thus, the small differences in steric environments of the carbon atoms in the two systems are not reflected in measurable differences in chemical shift differentiation of diastereotopic carbon atoms even though they are sufficient to cause significant differences in *lel/ob* energy variations. In both systems, there is a shift of about 1 ppm toward higher field for the ^{13}C NMR resonance of a methine carbon on going from *lel* to *ob* but there is very little change in the methyl group chemical shift.

A possibility that second-order paramagnetism of the metal ion might account for a significant portion of the chemical shift differences between diastereotopic carbon atoms in the complexes we have been investigating—primarily tris(diamine) chelates of cobalt(III)—has been suggested to us.[6] Anisotropy in the second-order paramagnetism at the metal ion could give a directional contribution to the shielding, σ, which for an axial system, would have the form[14]

$$\sigma = \frac{\chi_\parallel - \chi_\perp}{3R^3}(1 - 3\cos^2\theta) \qquad (1)$$

Here R is the length of the vector $\mathbf{R}$ between the metal ion and the NMR-active atom, θ is the angle between the principal axis and $\mathbf{R}$, and $\chi_\parallel - \chi_\perp$ is the difference in magnetic susceptibility parallel and perpendicular to the principal axis. Since diastereotopic carbon atoms in a tris chelate may well occupy positions with different values of R and θ, a shielding contribution as in eq 1 could give rise to chemical shift differences from a remote effect only.

For Co(III) in a trigonal field, $\chi_\parallel - \chi_\perp$ can be related to the difference in the energies of the $E(D_3)$ and $A_2(D_3)$ states that arise from the lower energy T_{1g} excited cubic state. For tris(diamine)cobalt(III) complexes, the energy separation is very small—70 cm^{-1} or less in $[Co(en)_3]^{3+}$.[15,16] This seems too small to significantly affect the ^{13}C NMR chemical shifts in the present complexes. In fact, owing to the small trigonal splitting expected for the excited states of tris(diamine) complexes, such compounds are poor choices for studies of possible contributions by magnetic anisotropy. ^{13}C chemical shift contributions from Co(III) magnetic anisotropy in lower symmetry complexes have been reported to be significant by some.[17]

That the ^{13}C NMR spectra of corresponding isomers of $[Co((\pm)\text{-bn})_3]^{3+}$ and $[Rh((\pm)\text{-bn})_3]^{3+}$ are virtually identical also indicates no significant contribution to chemical shift differentiation from second-order paramagnetism except in the very unlikely event that the magnetic anisotropies of Co(III) and Rh(III) in these complexes are the same. Unfortunately the relative anisotropies are unknown, though there is good evidence that Rh(III) anisotropy in general is significantly less than that of Co(III). First, a reported calculation (which is admittedly questioned by the authors of that paper) indicates this to be the case.[18] Second, the observation of cis/trans ^{1}H NMR chemical shift differences for NH_3 groups in $[Co(NH_3)_5X]^{2+}$ complexes but not in $[Rh(NH_3)_5X]^{2+}$ complexes indicates a decreased magnetic anisotropy in the latter case.[19]

There is one striking difference between ^{13}C NMR spectra of $[Co((\pm)\text{-bn})_3]^{3+}$ and $[Rh((\pm)\text{-bn})_3]^{3+}$ diastereomers. As observed previously,[1,20] the methyl carbon resonance of *lel,lel,lel*-$[Co((\pm)\text{-bn})_3]^{3+}$ is severely broadened (width at half-height, 26 Hz). On the other hand, there is no similar broadening in the spectrum of *lel,lel,lel*-$[Rh((\pm)\text{-bn})_3]^{3+}$ (width of methyl peak at half-height, 5 Hz). A broadened methyl resonance in a Co(III) complex seems characteristic of a *lel* chelate ring.[20] Unfortunately, unambiguous determination of the presence or absence of broadening in spectra of *lel,lel,ob*- and *lel,ob,ob*-$[Co((\pm)\text{-bn})_3]^{3+}$ is not possible owing to overlap of peaks from nonequivalent carbon atoms.

We have proposed a lowering of the symmetry of the *lel,lel,lel* diastereomer of $[Co((\pm)\text{-bn})_3]^{3+}$ owing to methyl group meshing as an explanation of methyl resonance broadening.[1] If this explanation were correct, one would expect a greater methyl group separation in the Rh(III) complex since this species shows no unusually broad resonances; however, we have seen that the crystal structure results indicate a slightly smaller methyl group separation for this complex. If the structures do not change significantly in solution, this observation refutes our proposal of a contribution from methyl group interaction. In fact, the striking similarity in the geometries of the *lel,lel,lel*-$[M((\pm)\text{-bn})_3]^{3+}$ complexes indicates that the broadening is not steric in origin.

It has been proposed that the broadening in the *lel* rings of Co(III) complexes is due to a relaxation effect involving a geometry-dependent scalar coupling between rapidly relaxing ^{59}Co and methyl group carbon atoms.[21] For such an effect, the contribution to the transverse relaxation rate of the ^{13}C nucleus is directly proportional to the square of the ^{59}Co–^{13}C coupling constant, $J(^{59}\text{Co}-^{13}\text{C})$, and inversely proportional to the longitudinal ^{59}Co relaxation rate, $R_1(^{59}\text{Co})$. Though our results are compatible with such an explanation (^{103}Rh, 100% abundance, has no quadrupole moment and, therefore, is not expected to experience the relaxation rate at which scalar

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coupling provides an effective relaxation mechanism for a coupled ^{13}C nucleus), there is expected to be little difference in ^{59}Co–^{13}C coupling in *lel* and *ob* rings. Differences are expected to arise from a dependence of $J(^{59}\text{Co}-^{13}\text{C})$ on dihedral angle. The functional relationship for such a dependence should be symmetrical, to a first approximation, about a value of 180° for this angle.[22] Values calculated for Co–N–C–C dihedral angles in *lel* and *ob* rings generated in molecular mechanics calculations[1] are, respectively, +160° and −158° (for *lel,lel,lel*-Δ- and *ob,ob,ob*-Δ-$[\text{Co}((\pm)\text{-bn})_3]^{3+}$). The former value is in relatively good agreement with the value of 166.9° observed for the *lel,lel,lel* Co(III) complex.[7] Since the angles expected for *lel* and *ob* rings are spaced nearly equally on either side of 180°, little difference in the coupling constant is expected. On the other hand, it may be that variations in the ^{59}Co quadrupole coupling constant, and hence in $R_1(^{59}\text{Co})$, with geometry differences between isomers, could lead to the observed effect of geometry on methyl group resonance broadening. Studies are now in progress in our laboratory on ^{13}C relaxation in these and related complexes.

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Registry No. $[\text{Rh}((\pm)\text{-bn})_3]_2(\text{SO}_4)_3$, 88667-97-4; $[\text{Co}((\pm)\text{-bn})_3]_2(\text{SO}_4)_3$, 88589-49-5; $[\text{Rh}((\pm)\text{-bn})_3]\text{Br}_3$, 88667-98-5; $[\text{Co}((\pm)\text{-bn})_3]\text{Br}_3$, 88589-50-8.

Supplementary Material Available: A stereoview of *lel,lel,lel*-$[\text{Rh}((\pm)\text{-bn})_3]^{3+}$, listings of final anisotropic thermal parameters and observed and calculated structure factors, and a complete table of interatomic distances and angles (9 pages). Ordering information is given on any current masthead page.

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Reductive Intramolecular Hydrogen Transfer in a d^8 Metal Hydride Promoted by CO Addition. An Experimental Study and Its Theoretical Implications

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The nickel(II) hydride $[(\text{np}_3)\text{NiH}]\text{BPh}_4$, np$_3$ = tris(2-(diphenylphosphino)ethyl)amine, reacts in both the solid state and solution with carbon monoxide, under mild conditions, to yield the nickel(0) carbonyl derivative $[(\text{Hnp}_3)\text{NiCO}]\text{BPh}_4$. The molecular structure of $[(\text{Hnp}_3)\text{NiCO}]\text{BPh}_4\cdot0.5\text{C}_4\text{H}_8\text{O}$ has been established by single-crystal X-ray diffraction methods. The crystals are triclinic, space group $P\bar{1}$, with the following cell parameters: $a = 18.917$ (8), $b = 16.341$ (7), $c = 10.151$ (5) Å; $\alpha = 94.31$ (6), $\beta = 94.27$ (6), $\gamma = 96.94$ (6)°; $Z = 2$. The structure has been solved by three-dimensional Patterson and Fourier syntheses and refined by least-squares techniques to final R and R_w factors of 0.073 and 0.073, respectively. The nickel atom is tetrahedrally coordinated by the three phosphorus atoms of the np$_3$ ligand and by the carbonyl group. A hydrogen atom lies collinear with the nickel and the apical nitrogen atom of the np$_3$ ligand. The N–H distance, 1.15 (9) Å, indicates a bonding between these two atoms, but the Ni–H distance of 1.95 (9) Å does not exclude some interaction between the hydrogen and the metal atom. The ^{1}H NMR spectra of $[(\text{Hnp}_3)\text{NiCO}]\text{BPh}_4$ are indicative of N–H bonding, whereas the IR data suggest at least a weak residual Ni–H interaction. Molecular orbital studies of the extended Hückel type indicate that the N–H bond is energetically favored over a possible Ni–H bond and that the Ni–H overlap population drops to zero as the hydrogen approaches the nitrogen atom along the threefold axis of the complex. A Ni–H interaction of electrostatic nature may be predicted from calculated atomic charges. Calculations have been also performed to evaluate a possible migration path of the hydrogen atom from one apical position of the trigonal bipyramid in $[(\text{np}_3)\text{NiH}]^+$ to the position where is bonded to nitrogen in the carbonyl derivative.

Introduction

Metal hydrides are involved as reagents in the reduction of a wide variety of organic functional groups and as intermediates in numerous catalytic processes. Thus the hydrogen transfer from metal hydrides to organic substrates is a process of general interest.[1]

The results of the reaction of carbon monoxide with hydride complexes can be summarized as follows: (i) CO coordinates to the metal that does not simultaneously affect the metal–hydrogen bond; in this case either the increase in the coordination number or the replacement of the other coligands ensues.[2] (ii) CO coordinates to the metal with cleavage of the metal–hydrogen bond; usually a reductive process occurs with elimination of hydridic hydrogen from the coordination sphere and displacement of H$_2$ or HX molecules.[3] Sometimes an intramolecular transfer of H$^+$ to the ligand was observed[4] whereas in a few cases the fate of the hydrogen remained unknown. (iii) CO inserts[5] into the hydrogen–metal bond with

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