

The Reversible and Stereoselective N- to C-bonded Rearrangement of Tris(2-pyridylmethyl)-1,4,7-triazacyclononane cobalt(III)

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The hexaamminecobalt(III) complex $[\text{Co}(\text{tmptacn})]^{3+}$ ($\text{tmptacn} = 1,4,7\text{-tris}(2'\text{-pyridylmethyl})\text{-}1,4,7\text{-triazacyclononane}$) undergoes a novel base-catalyzed N- to C-bonded rearrangement in which a tacn nitrogen is displaced by the α -carbon which deprotonates and binds to the metal ion as a carbanion. The X-ray structure establishes the configuration for the regio- and stereoselectively (100%) formed product. The reaction involves both ring expansions and ring contraction. The carbanion is part of a strained four-membered ring. The kinetics are reported for the N- to C-rearrangement, shown to be retentive for the optically resolved (+)- $[\text{Co}(\text{tmptacn})]^{3+}$ reactant, and also the kinetics for a competitive and somewhat faster base-catalyzed racemization reaction of this complex. The reaction is completely but very slowly reversed in acid, also with retention, and in $\text{D}_2\text{O}/\text{D}^+$ there is 1:1 D-incorporation into the two sets of inequivalent tacn carbons. Extensive 1D and 2D NMR studies establish mechanistic details, and alternative mechanisms are proposed for the forward and reverse reactions. In neutral solution, there is a competitive oxidation reaction for the reverse C- to N-bonded process, involving the regio- and stereoselective (100%) incorporation of an α -OH substituent into the tacn ring.

Introduction

It was demonstrated recently^{1,2} that the α -CH₂ protons in complexes such as $[\text{Co}(\text{dmptacn})\text{Cl}]^{2+}$ (**1**) or $[\text{Co}(\text{dmpmetacn})\text{Cl}]^{2+}$ (**2**) (Figures 1 and 2) are acidic. Further, on deprotonation at such a center, a pseudo-aminato ion is generated at the metal ion which labilizes the Co–Cl bond and the leaving group ion is expelled faster than reprotonation of this $-\text{CH}^-$ center.² Thus, $[\text{Co}(\text{pentaamine})\text{OH}]^{2+}$ is generated by rate-limiting deprotonation at the carbon center, a new mechanism for the base-catalyzed ligand-substitution reaction.

It was anticipated that the tmptacn complex (Figures 1 and 2) might behave similarly (Figure 3, upper reaction).

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(1) Jackson, W. G.; Dickie, A. J.; Bhula, R.; McKeon, J. A.; Spiccia, L.; Brudenell, S. J.; Hockless, D. C. R.; Willis, A. C. *Inorg. Chem.* **2004**, *43*, 6549.

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Pyridine N-donors do not bind Co(III) as strongly as an amine,³ and the tris complex was anticipated to dissociate one 'arm' via activation by an aminato generated by deprotonation at another 'arm' in basic solution, resulting in a hydroxopentaamine complex with a 'dangling' pyridine arm. Indeed, it was found that the yellow hexaamine complex slowly became red-brown in aqueous OH[−], but the acid/base properties of the isolated product were inconsistent with a simple hydroxo complex. Moreover, this material did not yield a purple chloropentaamine complex on heating in aqueous HCl, the expectation for an aqua product with the dangling pyridyl arm which is prevented from recoordination through protonation. A tentative structural assignment for the product had a pyridylmethylene 'arm' which had switched bonding from N to C with loss of a proton (Figure 3, lower), in a manner similar to that described for the reaction of the tris(bipyridine)Ir(III) cation in basic solution,^{4,5}

(3) The complexes $\text{cis-}[\text{Co}(\text{en})_2(\text{py})_2]^{3+}$ and $[\text{Co}(\text{NH}_3)_5\text{py}]^{3+}$ slowly liberate free py in aqueous base, whereas the corresponding NH₃ complexes $\text{cis-}[\text{Co}(\text{en})_2(\text{NH}_3)_2]^{3+}$ and $[\text{Co}(\text{NH}_3)_6]^{3+}$ are completely stable under the same conditions (Jackson, W. G., unpublished observations).

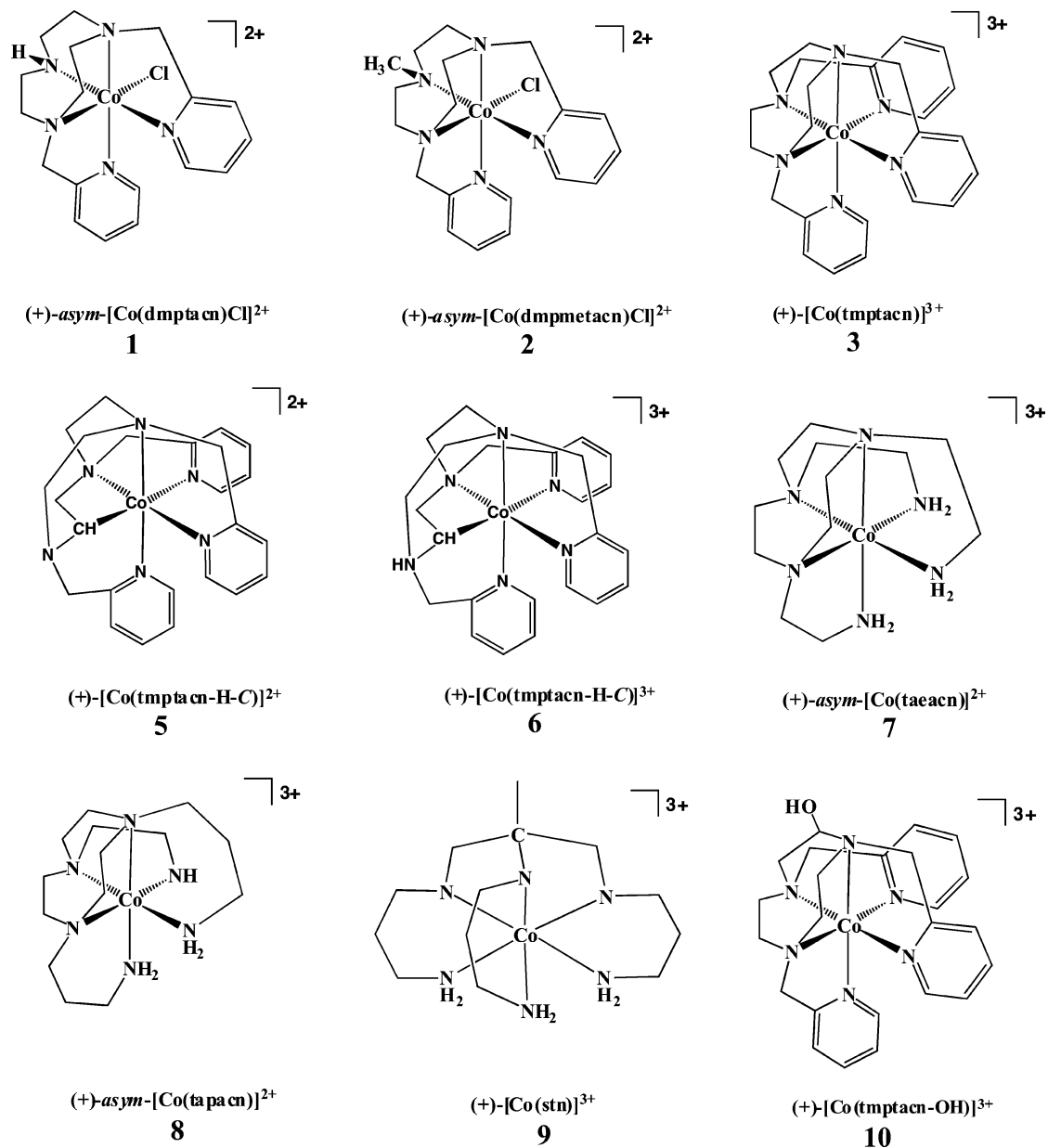


Figure 1. Cobalt(III) complexes of tacn-derived penta- and hexadentate ligands. All are chiral and (+)-isomers are shown arbitrarily.

but an N- to C-bonded rearrangement involving a tacn rather than a pyridyl carbon. However, a detailed structural analysis of 1D and 2D NMR data reported herein indicated that something quite unexpected had occurred, confirmed by a single-crystal X-ray structure of the unique product. The kinetics for this base-catalyzed rearrangement are reported, as well as various isotopic substitution studies which define the mechanism. Also reported are the optical resolution of the tmptacn complex and the kinetics of base-catalyzed racemization, a competitive reaction. Also described are deuterium incorporation experiments which reveal the mechanism for the unusual reverse process which regenerates the [Co(tmptacn)]³⁺ complex in acidic conditions.

(4) Watts, R. J.; Harrington, J. S.; Van Houten, J., *J. Am. Chem. Soc.* **1977**, *99*, 2179.

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Experimental Section

All chemicals were AnalaR or an equivalent grade and used as received. Triflic acid (CF₃SO₃H) obtained from the MMM company was used as received. 1D ¹³C, ¹H, ²H, ¹H DEPT and 2D NMR spectra (DQCOSY, NOESY, TNOCSY, HMQC, and HETCOR) were recorded on Varian XL-300 and Unity Plus 400 MHz instruments at 20 °C. Mix times of 0.01, 0.05, and 0.1 s were employed for the TNOCSY NMR experiments. Solvents used were D₂O with dioxane as the internal reference (¹³C, 69.27 ppm relative to DSS), and Me₂SO-*d*₆ with the central peak of the CD₃ septet as the reference (¹³C, 39.37 ppm relative to TMS). UV-visible absorption spectra (300–600 nm) were recorded on a HP8453 diode-array UV-visible spectrophotometer. Optical rotations were obtained with use of a Perkin-Elmer PE241 instrument (25.0 ± 0.1 °C). The kinetics for the rearrangement and racemization reactions (in NaOH/NaCl media; *I* = 1.0 M) at 25.0 ± 0.1 °C were determined spectrophotometrically and polarimetrically, the former using full absorption spectra (300–600 nm) and global

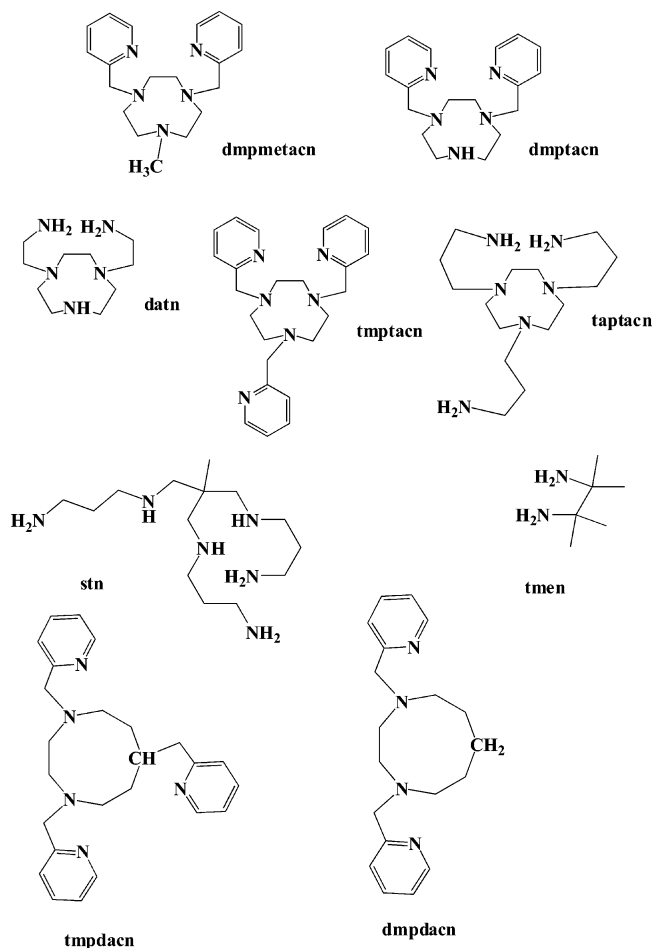


Figure 2. Ligand structures. Full names are given in the Experimental Section.

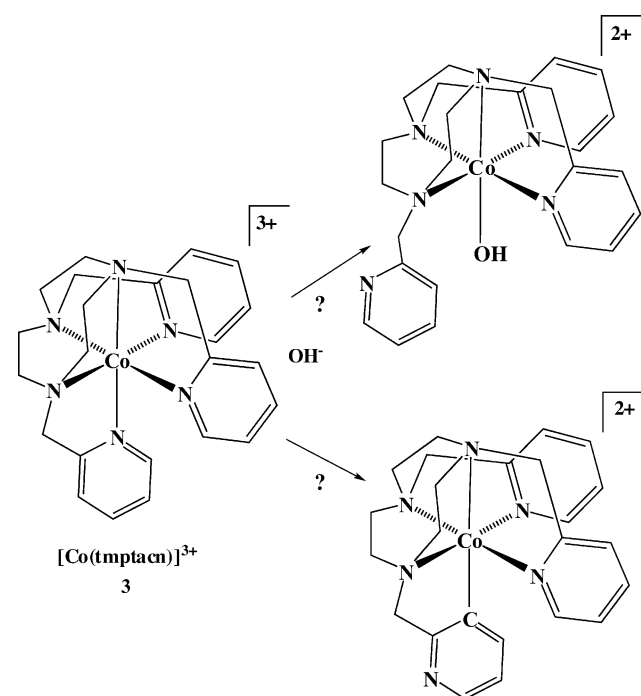


Figure 3. Two possible reaction modes for $[\text{Co}(\text{tmptacn})]^{3+}$ in basic solution.

spectral analysis employing Specfit, and the latter using simple optical rotation versus time plots (578, 436 nm) and conventional

weighted nonlinear least-squares analysis (Kaleidagraph).⁶ The kinetics for the rearrangement of the monodeuterated tris complex $d_1\text{-}[\text{Co}(\text{tmptacn})](\text{ClO}_4)_3$ (**4**) were studied in parallel with that for the protic compound **3** in 0.50 M NaOH at 25 °C. Cation exchange media used were Dowex 50Wx2 (H^+ form, 200–400 mesh; Biorad) and SP-Sephadex C25 (Na^+ form; Pharmacia). Elemental analyses were performed in the microanalytical laboratories at the Research School of Chemistry, ANU.

Syntheses. Caution: Perchlorate salts of metal complexes containing organics are potentially explosive. They should be handled only in small quantities and never be heated in the solid state nor in solutions of neat organic solvents especially in the presence of concentrated HClO_4 .

Ligand abbreviations: dmptacn = 1,4-bis(2'-pyridylmethyl)-1,4,7-triazacyclononane; dmpmetacn = 1,4-bis(2'-pyridylmethyl)-7-methyl-1,4,7-triazacyclononane; tmptacn = 1,4,7-tris(2'-pyridylmethyl)-1,4,7-triazacyclononane; taetacn = 1,4,7-tris(1'-aminoethyl)-1,4,7-triazacyclononane; taptacn = 1,4,7-tris(1'-aminopropyl)-1,4,7-triazacyclononane; tmpdacn = 1,4,7-tris(2'-pyridylmethyl)-1,4-diazacyclononane; dmpdacn = 1,4-bis(2'-pyridylmethyl)-1,4-diazacyclononane; stn = 2-(5'-amino-2'-aza-pentyl)-4,8-diazaundecane-1,11-diamine; tmen = 1-dimethyl-2-dimethyl-ethane-1,2-diamine.

$[\text{Co}(\text{tmptacn})](\text{ClO}_4)_3$ (**3**). This was prepared by H_2O_2 oxidation of a 1:1 mixture of $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and amine^{7–9} in water/methanol containing activated charcoal.⁸ The yellow product was purified by chromatography on Dowex, and crystallized as ClO_4^- and ZnCl_4^{2-} salts from water. The more soluble Cl^- salt was obtained from the less soluble perchlorate using the water/acetone/HCl technique described previously.^{1,2} The three salts were spectroscopically identical (^1H and ^{13}C NMR, D_2O).⁷ Anal. Calcd for $\text{CoC}_{24}\text{H}_{30}\text{N}_6\text{Cl}_3\text{O}_{12}$: C, 37.94; H, 3.98; N, 11.06; Cl, 14.00. Found: C, 38.22; H, 4.01; N, 11.00; Cl, 13.86%. UV–visible spectrum (H_2O): $\epsilon_{473}(\text{max})$ 293, $\epsilon_{347}(\text{max})$ 265 $\text{M}^{-1} \text{cm}^{-1}$. (Lit.^{8,9} $\epsilon_{473}(\text{max})$ 292, $\epsilon_{347}(\text{max})$ 255; $\epsilon_{474}(\text{max})$ 296, $\epsilon_{343}(\text{max})$ 284 $\text{M}^{-1} \text{cm}^{-1}$).

Optical Resolution of 3. A sample of $[\text{Co}(\text{tmptacn})]\text{Cl}_3$ (0.5 g) in water (200 mL) was absorbed on a segmented column of Sephadex (1 m \times 3 cm), washed with water, and then eluted with $\text{KSbO}(+)\text{tart}$ (0.2 M) in ascending mode driven by a peristaltic pump. The major yellow band separated after a few cycles into two bands, overlapped, which were physically removed from the segmented column in three sections. The complex was recovered from each using 1 M NaCl, and the eluates separately reabsorbed on Dowex (Na^+ form) and recovered after washing (0.1 M HCl to remove Na^+) using 3 M HCl. The eluates were rotary-evaporated to dryness and then crystallized from water using 5 M NaClO_4 as the precipitant. Further crops were obtained from the filtrates using 2 M ' H_2ZnCl_4 ' ((2 M ZnCl_2 in 5 M HCl)/*i*-PrOH) as precipitant. The various salts were exhaustively refracted from water using the same two precipitants, and the crystalline products checked using the α_{365}/D_{472} values as the criterion for maximal activity. Maximum rotations were, for crystals derived from band 1: $(+)_{589}$, $[\text{M}]_{436} = 4730$, $[\text{M}]_{365} = 5520$; for the central overlapped band, $(-)_{589}$, $[\text{M}]_{436} = -4740$, $[\text{M}]_{365} = -5800$, and band 2, also $(-)_{589}$, $[\text{M}]_{436} = -4670$ and $[\text{M}]_{365} = -5560 \text{ deg mol}^{-1} \text{ dm}^2$. The two crops with essentially equal and opposite rotations suggest full resolution.

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d_6 -[Co(tmptacn)](ClO₄)₃ (**5**). A saturated solution of the hexamine complex **3** (0.2 g) in 0.1 M NaOD was allowed to react for 1 min and then acid quenched (32% DCl, 5 mL). A fifth volume of HClO₄ (70%) was added and the resultant yellow crystals collected and washed with ethanol and ether and air-dried.

[Co(tmptacn-H-C)](ClO₄)₂ (**6**).¹⁰ A suspension of **3** (1.0 g) in 2 M NaOH (20 mL) was stirred at ambient temperature until all had dissolved and the yellow solution had become a clear red-brown (ca. 3 h). After the solution stood a further 2 h, 5 M NaClO₄ (10 mL) was added and red-brown crystals deposited essentially quantitatively. These were collected, washed with ethanol and ether, and air-dried. Recrystallization was from a concentrated Me₂SO solution using 5 M aqueous NaClO₄ as precipitant. Anal. Calcd for CoC₂₄H₂₉N₆Cl₂O₈: C, 43.72; H, 4.43; N, 12.75; Cl, 10.75. Found; C, 43.40; H, 4.38; N, 12.58; Cl, 10.58%. UV-visible spectrum: $\epsilon_{473}(\text{max})$ 237 M⁻¹ cm⁻¹ (H₂O); $\epsilon_{465}(\text{max})$ 206 M⁻¹ cm⁻¹ (2.5 M HCl). A bronze-colored ZnCl₄²⁻ salt (dihydrate) was also crystallized, using 2 M 'H₂ZnCl₄' as precipitant instead of NaClO₄ ($\epsilon_{473}(\text{max})$ 235 M⁻¹ cm⁻¹ (H₂O)).

[Co(tmptacn-H-C)](ClO₄)₃ (**7**). A suspension of the red-brown perchlorate salt (0.5 g) in water (5 mL) on treatment with HCl (11.7 M, 5 mL) and HClO₄ (70%, 5 mL) resulted in the dissolution and rapid reprecipitation of yellow crystals. On collection and washing with ethanol and ether, some regeneration of the red-brown complex resulted. The yellow form can be retained by copious washing with ether alone and air-drying.

d_6 -[Co(tmptacn-H-C)](ClO₄)₂ (**8**). Reaction of **3** in NaOD. The reaction described under the heading above for **6** was carried out using 1 M NaOD/D₂O instead of protic media.

Regeneration of **3** from **5**. A solution of **5** in 3–5 M H₂SO₄, HCl, or CF₃SO₃H is yellow and represents the N-protonated form since it is instantly reversed on addition of sufficient base. On heating at 95 °C for 15–30 min, it remains yellow,¹¹ but the red-brown compound is no longer instantly regenerated by addition of base. On a preparative scale (1.0 g in 20 mL of 3 M H₂SO₄), the product was recovered after heating by dilution with water and chromatography on Dowex (2–3 M HCl). Initial elution with 2 M NaCl (0.01 M in Tris) was required to separate any residual red-brown **6** from yellow **3**. After rotary-evaporation of the HCl, the yellow complex **3** was recovered quantitatively from water using 5 M NaClO₄ as precipitant.

d_1 -[Co(tmptacn)](ClO₄)₃ (**4**). The above procedure was repeated using D₂O and D₂SO₄ rather than protic reagents. A control experiment was carried out on a sample of fully protic **3** to observe if there was D incorporation into either the pyridyl or tacn methylenes.

d_7 -[Co(tmptacn)](ClO₄)₃ (**9**). The method above was again followed but using **5** (perdeuterated α -pyridyl methylenes) in D₂O/D₂SO₄ to observe if there was any D loss under the conditions of workup.

Attempted Resolution of **5**. Synthesis of [Co(tmptacn-OH)](ClO₄)₃ (**10**). The chromatographic resolution method described for the tmptacn complex **3** was followed using 0.1 M Na₂(+)-tart as eluant. Over a period of several hours, the initial band spread but never clearly separated. It was stopped well short of the time frame used in the resolution of the tmptacn complex because the red-brown material had become yellow. The band was segmented into three portions, front, middle, and tail, and the cobalt recovered from Dowex, as described for the tmptacn complex **3**, as crystalline ClO₄⁻ salts.

(10) Dmptacn-H-C denotes the tmptacn ligand deprotonated at C and bonded through the carbanion.

(11) In HCl, the product is green-yellow rather than a pure yellow and contains some Co(II) arising from reduction by Cl⁻.

Table 1. Crystal Data for [Co(tmptacn-H-C)](ClO₄)₂^a

formula	C ₂₄ H ₂₉ Cl ₂ CoN ₆ O ₈
fw	659.37
cryst syst	monoclinic
space group	P2 ₁ /n (14)
<i>a</i> /Å	16.078(4)
<i>b</i> /Å	9.323(6)
<i>c</i> /Å	17.752(5)
β /°	97.89(2)
<i>V</i> /Å ³	2636(2)
<i>Z</i>	4
<i>T</i> /K	193.2
λ (Cu K α)/Å	1.5418
<i>D_c</i> /g cm ⁻³	1.661
μ /cm ⁻¹	75.19
no. of obsd/unique data	4376/3929 (1995, <i>I</i> > 3 σ (<i>I</i>))
no. of refined params	370
<i>R</i>	0.0448
<i>R_w</i>	0.0452

^a *R* factors are conventional.

Independent Synthesis of the Oxidized form of [Co(tmptacn-H-C)](ClO₄)₂ (11**) (deuterated **10**). Reaction of **6** in Weakly Basic Solution.** A sample of the tmptacn complex **3** in D₂O containing dried NaOAc (1 M) was heated 2 h on a steam bath and then the complex was crystallized with anhydrous NaClO₄. The product was chromatographed on SP-Sepahex C-25 (Na⁺ form) using NaCl as eluant (0.5–0.75 M), and two closely spaced but separated yellow bands developed. Crystals were derived from each by reducing the volume and adding NaClO₄. Band 1 proved to be the oxidized tmptacn complex **11**, band 2 the (deuterated) unoxidized tmptacn complex **5**.

Base–Acid Cycle for (+)₅₈₉-3**.** A sample of (+)₅₈₉-**3** (0.3 g) was dissolved in 1.00 M NaOH (10 mL) and allowed to react at 25 °C for 5*t*_{1/2} (ca. 85 min). The reaction mixture was acid-quenched (concentrated H₂SO₄, 5 mL) and then heated on a steam bath for 30 min. After cooling, it was diluted with water (300 mL), adsorbed on a short (10 × 3 cm²) column of Sephadex, and well washed. Elution with 1 M NaCl cleanly separated the (trace) faster-running residual reactant from the yellow product. Readsorption of the product on Dowex and recovery using 2 M HCl, after washing (0.1 M HCl) to remove NaCl, yielded partly active **3**. The eluate was reduced to dryness on a rotary evaporator and the product crystallized from water using 5 M NaClO₄ as precipitant. The UV-visible spectrum (1 cm cell) and optical rotations (1 dm) were recorded for an aqueous solution at an arbitrary concentration ($\alpha_{436} = 0.110$, $D_{472} = 0.283$; $\alpha_{436}/D_{472} = 0.389$). The same measurements were made on a sample of starting material ($\alpha_{436} = 0.561$, $D_{472} = 1.281$; $\alpha_{436}/D_{472} = 1.282$). These results translate to 30% retained activity for the tmptacn reactant **3**. A repeat experiment yielded a 29% retained activity result; these results are independent of the optical purity of the reactant tmptacn complex.

Crystallography. Red-brown crystals of **6** suitable for X-ray crystallographic analysis were grown by slow evaporation of an aqueous solution at ca. 20 °C. A platelet having the approximate dimensions of 0.12 × 0.10 × 0.04 mm³ was mounted on a quartz fiber. All measurements were made at 193 K on a Rigaku AFC6R diffractometer with graphite-monochromated Cu K α radiation. Crystal data are given in Table 1.

The structure was solved by direct methods.¹² Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included at geometrically determined positions and were not refined. All calculations were performed using

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the teXsan crystallographic software package of Molecular Structure Corporation.¹³

Results and Discussion

The $[\text{Co}(\text{tmptacn})]^{3+}$ ion, known since the middle 1980s,^{8,9} has been synthesized by direct reaction of the free tmptacn ligand with *trans*- $[\text{Co}(\text{py})_4\text{Cl}_2]\text{Cl}\cdot 6\text{H}_2\text{O}$ in methanol or via aerial or H_2O_2 oxidation of $\text{Co}(\text{II})/\text{tmptacn}$ (1:1). Spiccia et al.¹⁴ obtained the material as a sideproduct in the synthesis of the pentaamine derivative **1**.^{14,15} The tmptacn complex **3** has also been obtained through oxidation of the isolated $\text{Co}(\text{II})$ derivative.⁹ The complex is structurally related to $[\text{Co}(\text{taetacn})]^{3+}$ (**12**)⁷ and $[\text{Co}(\text{taptacn})]^{3+}$ (**13**) (Figure 1),¹⁶ but unlike these ions, it has not been characterized by X-ray crystallography. The UV–visible spectral properties of the complex were in essential agreement with the reported data.^{8,9}

3 has been optically resolved using the chromatographic method described for the analogous **12** with $(\text{SbO}(+)\text{tart})_2^{2-}$ as the discriminating anion;⁷ $\text{Na}_2(+)\text{-tartrate}$ was also tried, but this was much less effective. Incomplete, but nonetheless significant, separation of the enantiomers on the Sephadex resin was achieved, and the enantiomers were ultimately obtained pure through fractional crystallization of their salts, yielding equal and opposite rotations. The absolute configurations for these follow by analogy with the chiroptical properties of resolved **12**, the structure of which can be deduced from the X-ray study of the resolved capped cage complex;⁷ the capping reaction proceeds with retention of the cobalt configuration.

The $\text{Mn}(\text{II})$ and $\text{Fe}(\text{II})$ complexes of tmptacn are trigonally distorted,^{8,9} and it is likely the $\text{Co}(\text{III})$ complex is also. While the luteo complex is a characteristic hexaamincobalt(III) species ($\lambda(\text{max})$ 472 and 348 nm (sh)), it has been noted⁸ that the molar extinction coefficients for **3** are about three times greater than usual, indicative of such a distortion. However, the octahedral configuration is obviously accessible in solution on the NMR time scale because the ^1H and ^{13}C spectra clearly reflect the C_3 symmetry. It has also been noted that,¹⁷ for the Δ configuration of the related complex **12**, the preferred five-membered ring conformations are $\lambda\lambda\lambda$ for the tacn but $\delta\delta\delta$ for the three ‘arms’, leading to an $(\text{ob})_3$ configuration which is observed in the crystal.¹⁸ The tmptacn complex **3** is likely to be similar but with flatter ‘arms’ because of the aromatic pyridine donors. It should be noted, however, that irrespective of ring conformations, the two carbons in each of the tae ($\text{NH}_2\text{CH}_2\text{CH}_2-$) ‘arms’ are intrinsically diastereotopic, and their inequivalence in the ^{13}C NMR spectrum does not comment on the preferred ring conformations.

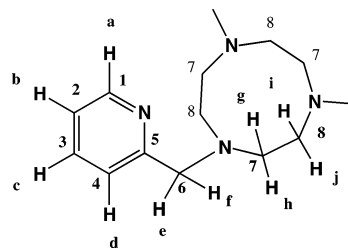


Figure 4. Proton and carbon atom-numbering scheme used for the discussion of the NMR spectra for the tmptacn ligand in the $[\text{Co}(\text{tmptacn})]^{3+}$ complex. The sequential C7 and C8 labeling in the tacn ring is a consequence of the C_3 symmetry of the tmptacn complex **3**.

The atom numbering scheme for the tmptacn ligand in the complex **3** is shown in Figure 4. The simple eight-line ^{13}C NMR spectrum (Figure 5) is consistent with the C_3 symmetry, and the pyridyl carbons were assigned as described previously.^{1,2} For the remaining three signals around 60 ppm, the lowest-field peak is the $-\text{CH}_2-$ α to the pyridyl, and the other two are the tacn methylenes.

The ^1H NMR spectrum is shown in Figure 5. The characteristic AB quartet centered at 4.75 ppm is assigned to the diastereotopic methylene protons H^e , H^f α to the pyridyls; this is absent in the spectrum of the complex **5** (unreported). The four pyridyl proton multiplets (inner H triplets, outer H doublets) were assigned unambiguously using the HETCOR or HMQC $^{13}\text{C}-^1\text{H}$ correlated spectra (Figures 1S and 2S), since the carbons to which they are attached are already assigned.

Proton **a** (Figure 4) is shielded by virtue of its location over the π system of an adjacent pyridine ring and appears at higher field than usual (ca. 7 ppm).² The two lowest-field tacn CH_2 proton multiplets in the range 2.7–4.4 ppm correspond to the two protons attached to C7, H^g , and H^h , respectively, while the remaining correspond to H^i and H^j attached to C8 (the protons, from low to high field, are H^g , H^h , H^i , and H^j). The COSY spectrum (Figure 3S) confirmed these assignments, and showed also the gem and (weaker) vicinal coupling, except for H^h and H^i on adjacent tacn carbons ($J_{hi} \approx 0$). Selective spin-decoupling experiments were carried out, and they confirmed these observations and enabled the evaluation of all the tacn $-\text{CH}_2-$ coupling constants: $J_{gi} = 8$, $J_{gh} = 18$, $J_{gj} = 16$, $J_{ij} = 16$, and $J_{hj} = 8$ Hz. The TOCSY spectrum (Figure 4S) showed the expected correlations among all four pyridine CH protons and all four tacn CH_2 protons. In addition, the α -pyridyl methylene showed a correlation with proton **d** on the pyridine in the same ‘arm’, a four-bond distance. The NOESY spectrum (Figure 5S) showed a weak through-space interaction of one of the α -pyridyl CH_2 protons with proton **a** on an adjacent arm. Drieding molecular models revealed which two protons these were, and therefore, we could assign the separate CH_2 protons on the pyridyl methylene. Finally, this same **a** pyridyl methylene proton showed a through-space correlation with tacn proton H^h , enabling the assignment of both H^g and H^h on that carbon, C7. Only the H^i and H^j protons on C8 remained unassigned.

Reaction of **3 in OH^- .** The compound was surprisingly unstable in basic solution, with a smooth yellow-to-red-brown

(13) teXsan, Single-Crystal Structure Analysis Software, Version 1.7; Molecular Structure Corporation: The Woodlands, TX, 1992–1997.

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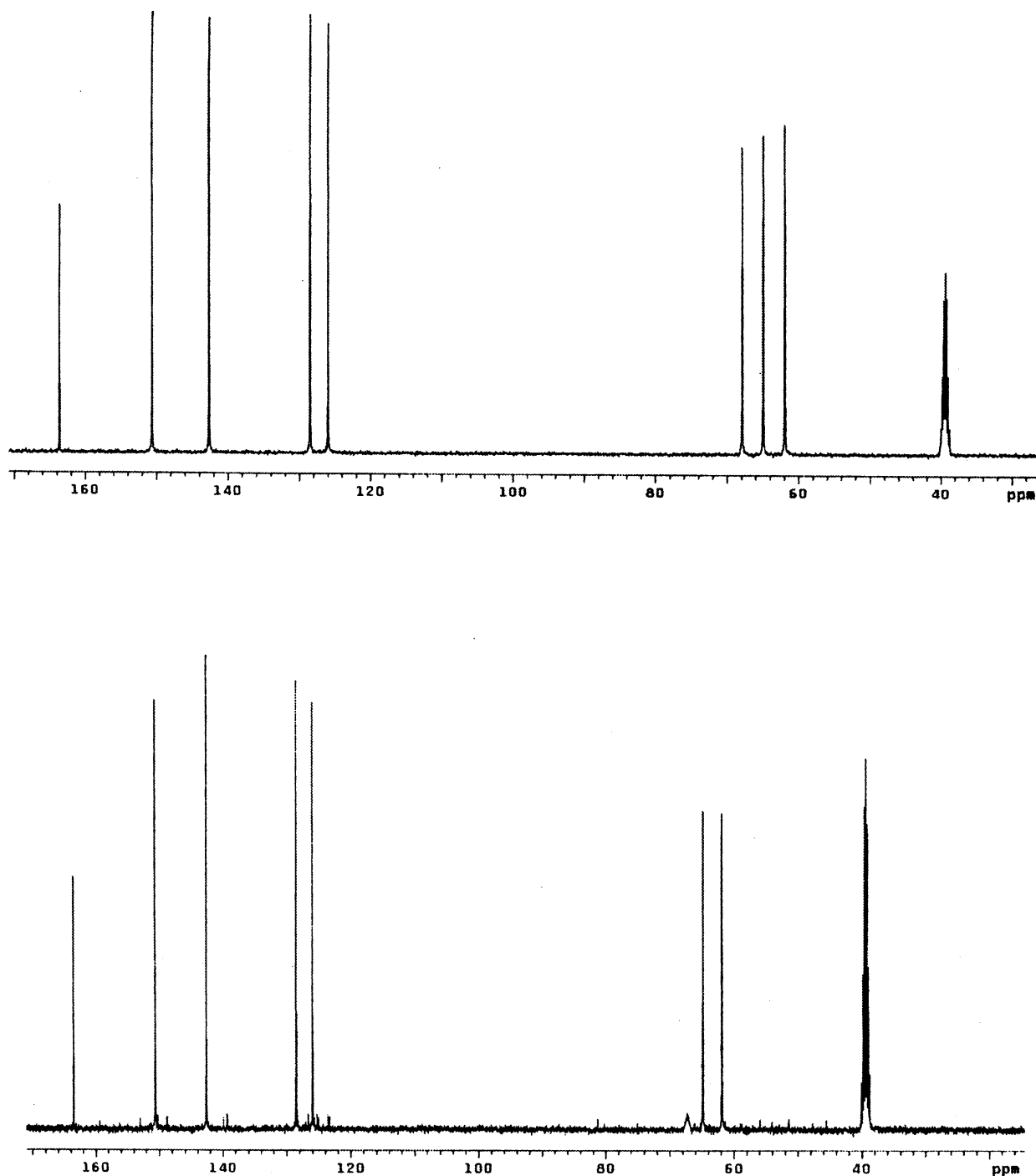


Figure 5. ^{13}C NMR spectra for $[\text{Co}(\text{tmptacn})](\text{ClO}_4)_3$ (upper) and $d_6\text{-}[\text{Co}(\text{tmptacn})](\text{ClO}_4)_3$ (lower) in $\text{Me}_2\text{SO}-d_6$, showing the collapse of the α -pyridyl methylene carbons (ca. 67 ppm) on perdeuteration.

transformation ensuing in 1 M OH^- in less than an hour at 25 $^\circ\text{C}$ ($t_{1/2} = 17.5$ min). The product was crystallized readily, and it is stable indefinitely under ambient conditions. Given the initial belief that one methylenepyridyl arm was being dissociated to generate the hydroxo complex $[\text{Co}(\text{tmptacn})\text{-OH}]^{2+}$, the reaction was repeated in basic 1 M NaN_3 , and we looked for the competition product $[\text{Co}(\text{tmptacn})\text{N}_3]^{2+}$ which normally¹⁹ would be a low-level product accompanying $[\text{Co}(\text{tmptacn})\text{OH}]^{2+}$ formation if the reaction were a base-catalyzed substitution process. None was observed using the usual ion-exchange method.¹⁹

We studied the title reaction by NMR spectroscopy (^1H and ^{13}C). The first and faster process was the exchange of the α -pyridyl methylenes. This was complete before any further reaction. We exploited this large rate difference by acid quenching using HClO_4 at the end ($5t_{1/2}$) of the first stage and isolating the hexadeuterated complex as the perchlorate salt. The ^2H NMR spectrum of this material (Figure 6S) showed a singlet at 4.8 ppm in $\text{Me}_2\text{SO}-d_6$, at the same position for the protic complex for which a sharp

(19) Buckingham, D. A.; Olsen, I. I.; Sargeson, A. M. *J. Am. Chem. Soc.* **1966**, *88*, 5443–5447.

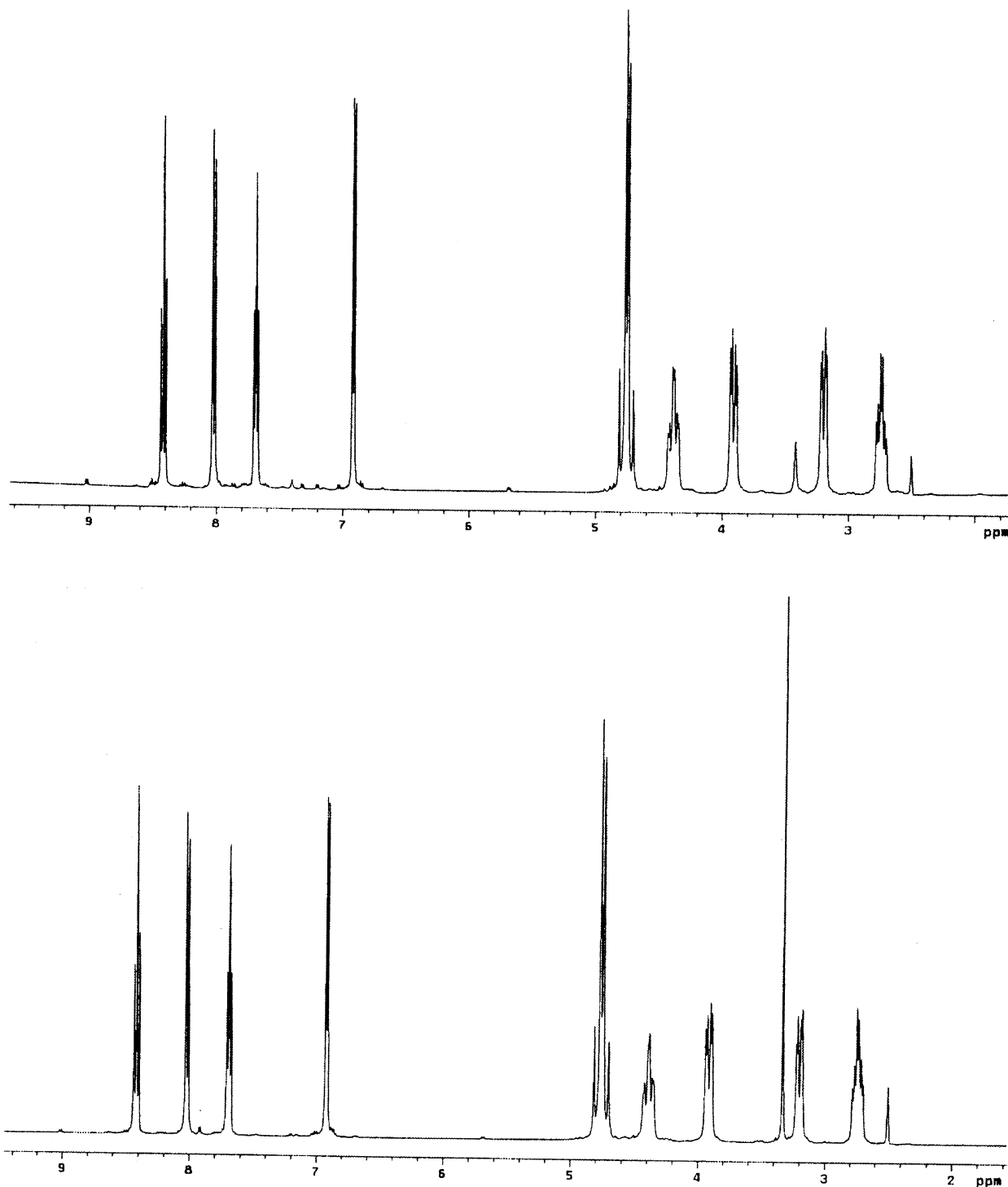


Figure 6. ^1H NMR spectra for $[\text{Co}(\text{tmptacn})](\text{ClO}_4)_3$ (**3**) in $\text{Me}_2\text{SO}-d_6$. The lower spectrum is for the monodeuterated species (discussed later), with 0.5D in the 4.4 ppm multiplet (2.5H) and 0.5D in the 3.2 ppm multiplet (2.5H). All other signals integrate for 3H except the 4.75 ppm AB quartet (6H) which are the α -pyridyl methylenes. Signals at 3.3–3.4 and 2.5 ppm are H_2O and solvent $\text{Me}_2\text{SO}-d_5$, respectively.

AB quartet is observed (Figure 7); the ^2H signal is broadened both by D–D coupling and through the normal quadrupolar broadening process.

The ^1H (Figure 7, upper) and ^{13}C NMR spectra (Figure 8) of the red-brown product of prolonged reaction in NaOH showed that the C_3 symmetry of the starting material was completely lost; an eight-line ^{13}C spectrum had become a 24-line spectrum. The same material derived from

NaOD showed 21 rather than 24 lines, thereby identifying the three inequivalent α - CD_2 centers (Figure 9; CH_2 region only). Similarly, the three AB quartets seen in the ^1H NMR could be identified (Figure 7). The ^2H spectrum for the α - CD_2 complex (Figure 10) shows six CD resonances, broadened and partly overlapped, corresponding in position to the proton chemical shifts comprising the three AB CH_2 quartets in the ^1H NMR spectrum. This spectrum

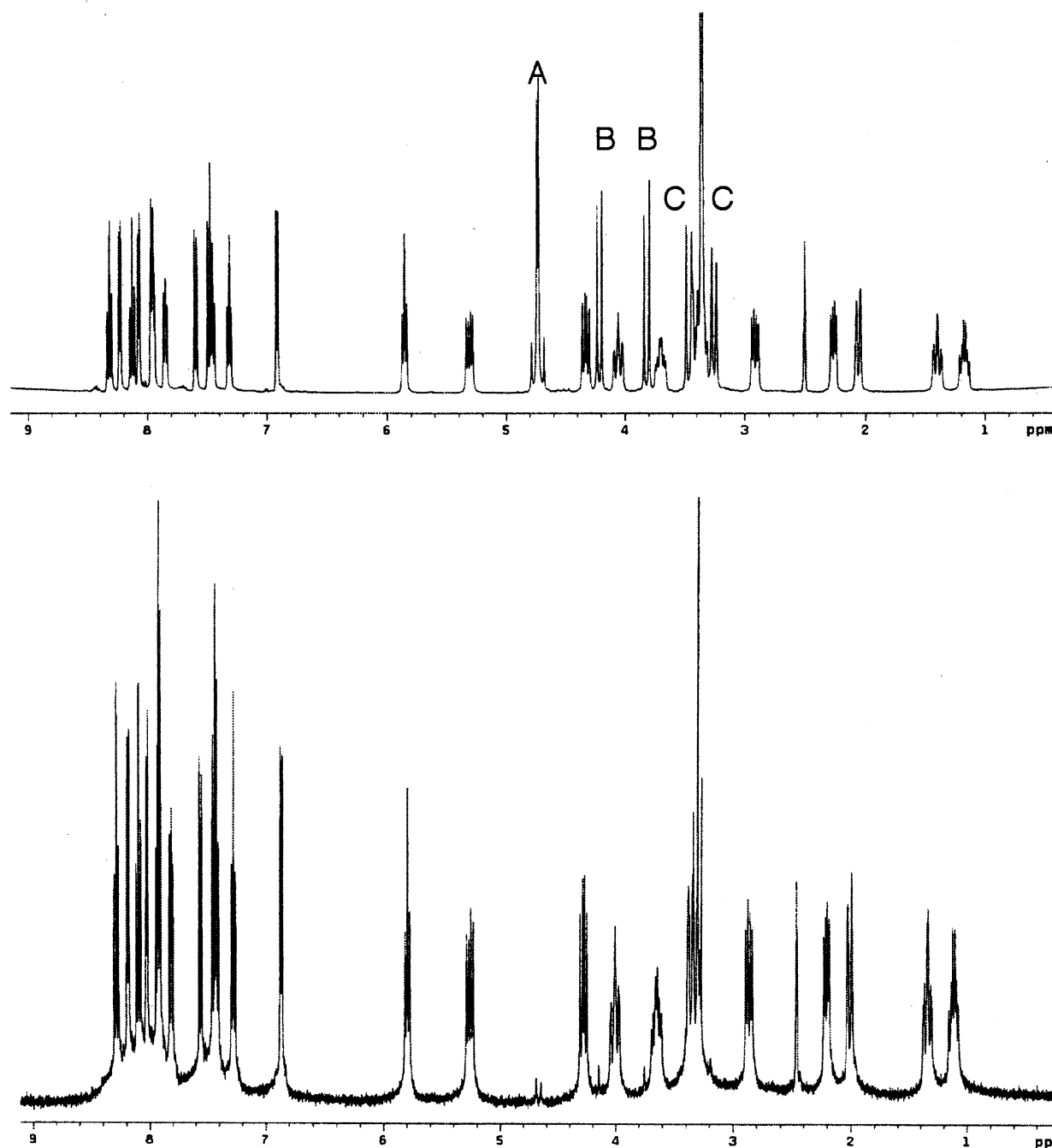


Figure 7. ^1H NMR spectra for $h_6\text{-[Co(tmptacn-H-C)]}^{2+}$ (upper) and $d_6\text{-[Co(tmptacn-H-C-d}_6\text{)]}^{2+}$ (lower) in $\text{Me}_2\text{SO-d}_6$; deuteration is at the six α -pyridyl methylenes, as seen in the collapse of the three 'AB quartets' (at sites A, B, and C).

also confirms that no other site, tacn CH_2 or pyridyl CH, is deuterated.

With the six α -pyridyl CH_2 proton exchanged, one can see (Figure 6, lower) the 11 distinct CH proton multiplets, between 5.85 and 1.2 ppm, corresponding to the 11 tacn protons—one is missing, but not because it is deuterated, but rather because a hydrogen (ion) has been abstracted (vide infra).

Figure 7S is a blow-up of the pyridyl region of Figure 8, and it shows that none of the three α -CH pyridyl carbons have exchanged, which a rearrangement such as that shown in Figure 2 might permit. Furthermore, for the spectrum

recorded of an ca. 1:1 mixture of protic and deuterated materials (not reported), all three of the lowest-field tertiary carbons are doubled, with the signals attributable to the deuterated material appearing ca. 25 Hz upfield. This is the usual isotopic shift for a carbon having two β -D as opposed to two β -H substituents, i.e., C^a in $-\text{C}^a\text{-CD}_2-$ is at higher field than C^a in $-\text{C}^a\text{-CH}_2-$.^{20,21} (A similar doubling of the tertiary pyridyl carbon for a mixture of **3** and **5** has been demonstrated (not reported).) The results are consistent with complete deuteration for the α - CH_2 pyridyl protons in NaOD.

(20) Jackson, W. G. *Inorg. Chem.* **1991**, *30*, 1570–4.

(21) Jackson, W. G. *Inorg. Chem.* **1993**, *32*, 4168.

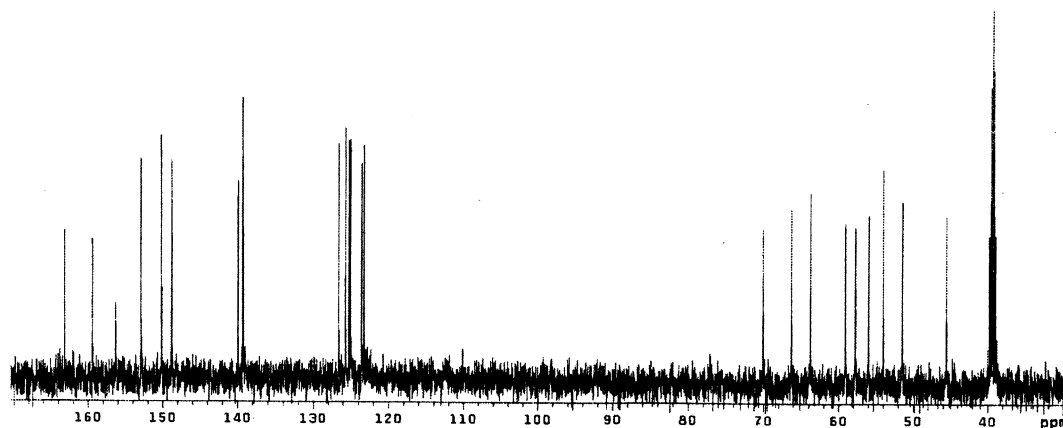


Figure 8. ^{13}C NMR spectrum for $[\text{Co}(\text{tmptacn-H-C})]^{2+}$ in $\text{Me}_2\text{SO-}d_6$.

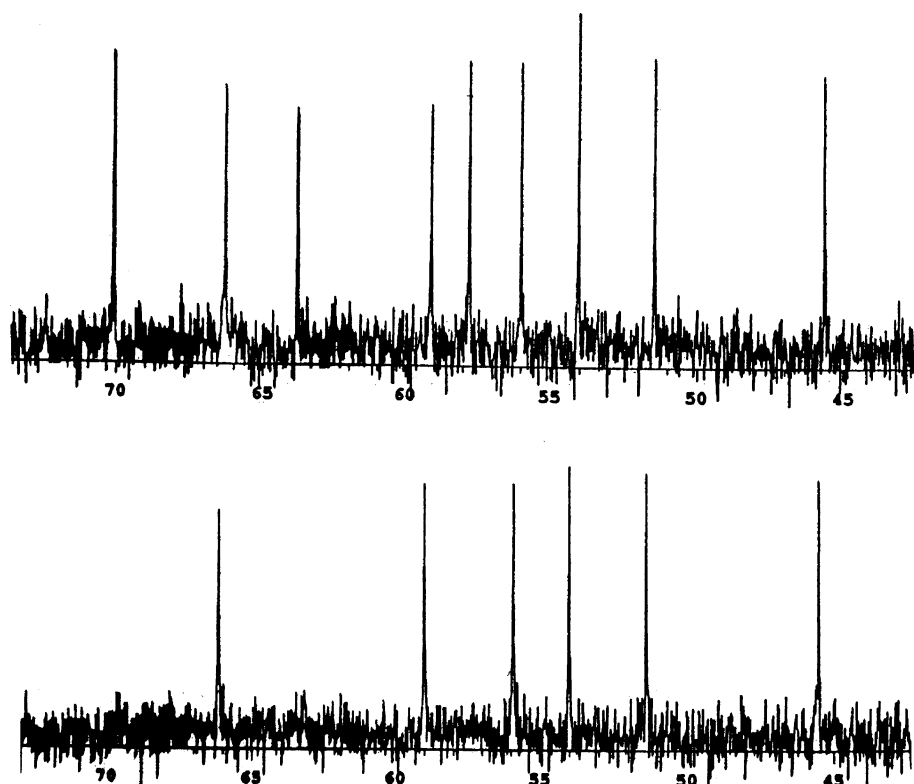


Figure 9. ^{13}C NMR spectra for h_6 - $[\text{Co}(\text{tmptacn-H-C})]^{2+}$ (upper) and d_6 - $[\text{Co}(\text{tmptacn-H-C})]^{2+}$ in $\text{Me}_2\text{SO-}d_6$ in the CH_2 region; the horizontal scale is ca. 40–70 ppm.

The DEPT spectrum of the $[\text{Co}(\text{tmptacn-H-C})]^{2+}$ complex (Figure 11) revealed that one of the tacn CH_2 groups had become a methine, and this fact, coupled with the elemental analysis and chromatographic behavior which indicated a 2+ cation, suggested that the $[\text{Co}(\text{tmptacn})]^{3+}$ complex had undergone some kind of unprecedented rearrangement in which a tacn CH_2 group had become deprotonated and bonded to the metal ion and for the reaction in OD^- one which escaped deuteration in the process. The $\text{Co-}^{13}\text{C}$ signal is a sharp singlet, despite the presence of quadrupolar Co ($I = 7/2$), but this is not always the case for Co(III) -bound carbon.²² The 2D NMR data are complex because of the C_1

symmetry and are presented (uninterpreted) in the Supporting Information (Figures 8S–12S).

The product derived from reaction of the tmptacn complex in OH^- , **6**, was spectroscopically identical to that obtained from $\text{D}_2\text{O}/\text{OD}^-$, **8**, save for the complete exchange of the α -pyridyl CH_2 protons, i.e., the bound $-\text{CH}^-$ contained no D (Figure 8). This interesting result established that, once the tacn $-\text{CH}_2-$ α to the tertiary N was deprotonated, the N- to C-bonded rearrangement ensued much faster than reprotonation. This is not the normal course of events for donor atom rearrangements^{22,23} leading to carbanionic products.

(22) Kofod, P.; Larsen, E.; Larsen, S.; Petersen, C. H.; Springborg, J.; Wang, D. N. *Acta Chem. Scand.* **1992**, *46*, 841–53.

(23) Springborg, J.; Kjellerup, S.; Kofod, P.; Larsen, E.; Nielsen, B. *Acta Chem. Scand.* **1996**, *50*, 531–536.

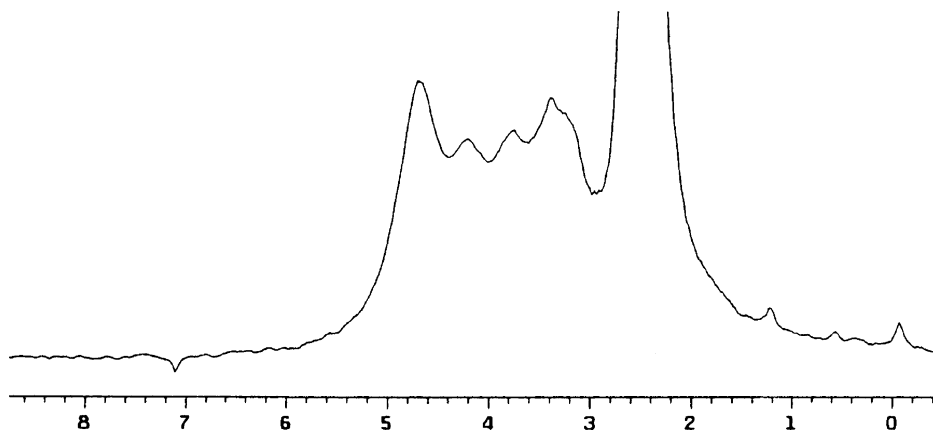


Figure 10. ^1H NMR spectrum of d_6 -[Co(tmptacn-H-C)] $^{2+}$ in $\text{Me}_2\text{SO}-d_6$ at natural abundance. The larger 4.75 ppm signal likely corresponds to two ^2H , the others ^1H . The large (chopped) signal at 2.5 ppm is solvent.

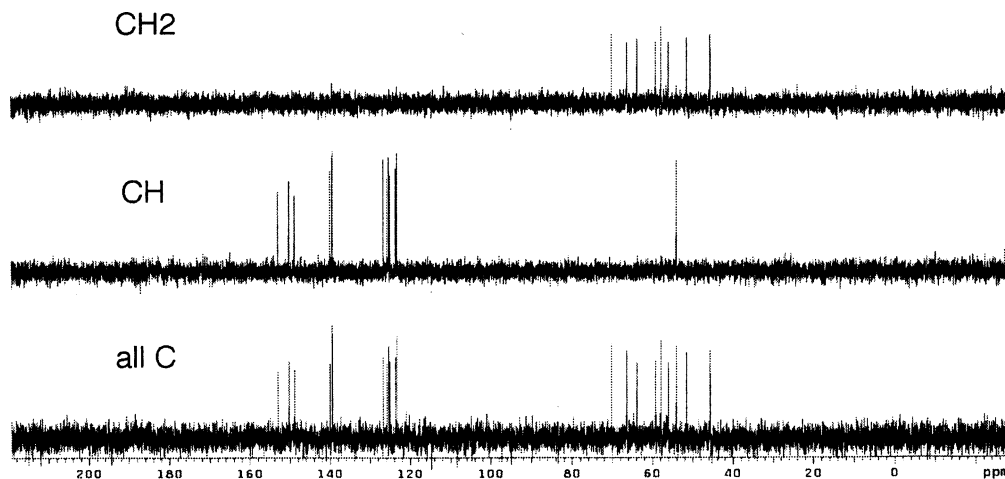


Figure 11. ^{13}C - ^1H DEPT spectrum for [Co(tmptacn-H-C)] $^{2+}$ in $\text{Me}_2\text{SO}-d_6$, showing which one of the original CH_2 in the tmptacn complex has become a CH. It also shows which of the original low-field ^{13}C signals were C(tert) (compare Figure 8).

The ^1H NMR (Figure 13S) and UV-visible spectra (see Experimental Section) of the red-brown rearrangement product **5** changed on addition of strong acid (>1 M), and reversibly. This yellow product **6** we believe is the protonated salt (*exo*-amine, Figure 1). Further, the red-brown and yellow complexes eluted together with the [Co(tmptacn)] $^{3+}$ starting material on Dowex using 2–3 M HCl as eluant. However, on Sephadex under neutral conditions (NaCl as eluant), the red-brown product eluted well in front of the 3+ hexamine. This behavior is consistent with the presence of a weakly basic *uncoordinated* amine center in **5**.

The overall data suggested that a tacn amine had been displaced by a carbanion derived from a CH_2 center within the tacn component of the hexadentate ligand, and this reaction led to a single product. This unique structure was confirmed by a single-crystal X-ray analysis (below). The reaction involves cleavage of a Co–N(tert) bond, and formation of a Co–C(carbanion) bond. While tertiary amines are not good donor atoms to Co(III) (monodentate complexes are unknown), they are observed to bind when part of a multidentate ligand system, but base-catalyzed Co–N cleavage is not unknown in cobalt(III) chemistry, even for the more strongly bound primary amines.^{24,25}

X-ray Structural Analysis of the Red-Brown 6. The product is a racemate, and the Λ configuration is shown

arbitrarily in the ORTEP diagram for the molecular cation, Figure 12. The structure reveals that a Co–N(tert) bond in the macrocyclic tacn residue has been cleaved and replaced by a Co–C bond of an adjacent $-\text{CH}_2-$, which has now been deprotonated. In principle, the bound $-\text{CH}^-$ arises from one of two different carbons (C7 or C8) and one of four different protons (H^g , H^h , H^i , or H^j), but the reaction is both regioselective (100% C8 bonded) and stereoselective (100% H^h removed).

Principal bond lengths and angles are given in Tables 2 and 3, respectively. Two adjacent five-membered rings in the tacn have been replaced by a four-membered ring involving the carbanion and a six-membered ring involving the free amine. The sum of angles for the four-membered ring (Table 3) is 359.7° and this ring is flat, while the latter adopts the favored chair conformation. The ring size for the pyridylmethylene arm attached to this free amine has also been increased from five to six.

The Co–C(17) bond is 1.945(7) Å, a little shorter than similar bonds in related compounds.^{26,27} Cobalt–nitrogen

(24) Buckingham, D. A.; Clark, C. R.; Lewis, T. W. *Inorg. Chem.* **1979**, *18*, 2041–3.

(25) Clarkson, A. J.; Buckingham, D. A.; Rogers, A. J.; Blackman, A. G.; Clark, C. R. *Inorg. Chem.* **2000**, *39*, 4769–4775.

(26) Zhou, X.; Day, A. I.; Edwards, A. J.; Willis, A. C.; Jackson, W. G. *Inorg. Chem.* **2005**, *44*, 452–460.

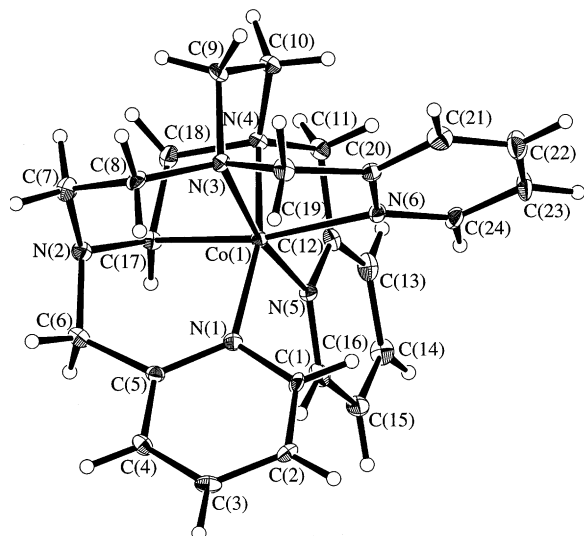


Figure 12. ORTEP diagram for the molecular cation $[\text{Co}(\text{tmptacn-H-C})]^{2+}$ (**6**) with displacement ellipsoids showing 20% probability levels.

Table 2. Selected Bond Lengths (Å) for $[\text{Co}(\text{tmptacn-H-C})(\text{ClO}_4)_2 \cdot 6$

Co(1)	N(1)	1.975(6)	Co(1)	N(3)	2.020(6)
Co(1)	N(4)	1.928(6)	Co(1)	N(5)	1.933(6)
Co(1)	N(6)	2.107(6)	Co(1)	C(17)	1.945(7)
N(1)	C(1)	1.359(9)	N(1)	C(5)	1.351(8)
N(2)	C(6)	1.449(9)	N(2)	C(7)	1.465(9)
N(2)	C(17)	1.415(9)	N(3)	C(8)	1.491(8)
N(3)	C(9)	1.534(9)	N(3)	C(19)	1.487(9)
N(4)	C(10)	1.476(9)	N(4)	C(11)	1.478(8)
N(4)	C(18)	1.515(9)	N(5)	C(12)	1.348(8)
N(5)	C(16)	1.344(9)	N(6)	C(20)	1.352(8)
N(6)	C(24)	1.352(8)			

Table 3. Selected Bond Angles (deg) for $[\text{Co}(\text{tmptacn-H-C})(\text{ClO}_4)_2$

N(1)	Co(1)	N(3)	93.3(2)	N(1)	Co(1)	N(4)	167.0(2)
N(1)	Co(1)	N(5)	97.8(2)	N(1)	Co(1)	N(6)	98.9(2)
N(1)	Co(1)	C(17)	92.5(3)	N(3)	Co(1)	N(4)	86.0(2)
N(3)	Co(1)	N(5)	168.2(2)	N(3)	Co(1)	N(6)	82.1(2)
N(3)	Co(1)	C(17)	94.6(3)	N(4)	Co(1)	N(5)	84.1(3)
N(4)	Co(1)	N(6)	93.9(2)	N(4)	Co(1)	C(17)	74.7(3)
N(5)	Co(1)	N(6)	92.0(2)	N(5)	Co(1)	C(17)	89.1(3)
N(6)	Co(1)	C(17)	168.3(3)	Co(1)	N(1)	C(1)	118.2(5)
Co(1)	N(1)	C(5)	125.1(5)	C(1)	N(1)	C(5)	116.8(6)
C(6)	N(2)	C(7)	113.9(6)	C(6)	N(2)	C(17)	110.1(6)
C(7)	N(2)	C(17)	118.8(6)	Co(1)	N(3)	C(8)	116.4(4)
Co(1)	N(3)	C(9)	108.7(4)	Co(1)	N(3)	C(19)	106.6(4)
C(8)	N(3)	C(9)	106.9(5)	C(8)	N(3)	C(19)	108.6(6)
C(9)	N(3)	C(19)	109.6(6)	Co(1)	N(4)	C(10)	110.8(5)
Co(1)	N(4)	C(11)	110.8(5)	Co(1)	N(4)	C(18)	92.0(4)
C(10)	N(4)	C(11)	113.1(6)	C(10)	N(4)	C(18)	114.9(6)
C(11)	N(4)	C(18)	113.4(6)	Co(1)	N(5)	C(12)	114.8(5)
Co(1)	N(5)	C(16)	127.4(5)	C(12)	N(5)	C(16)	117.8(6)
Co(1)	N(6)	C(20)	112.1(4)	Co(1)	N(6)	C(24)	130.3(5)
C(20)	N(6)	C(24)	116.6(6)				

bond lengths range from 1.928(6) to 2.107(6) Å. The last is lengthened by being trans to the bound carbanion, and this is usual.²⁶ The Co–N3(amine) and Co–N6(imine) bonds are 2.020(6) and 2.107(6) Å, respectively, longer than the average ‘normal’ Co–N bond, and such anomalies have been noted previously^{1,2} in pyridine–amine complexes of this kind.

Bond angles (NCoN and CCoN) about the cobalt vary according to whether they are part of a five- or six-membered

(27) Zhou, X.; Day, A. I.; Willis, A. C.; Jackson, W. G. *J. Chem. Soc., Chem. Commun.* **2003**, 2386–2387.

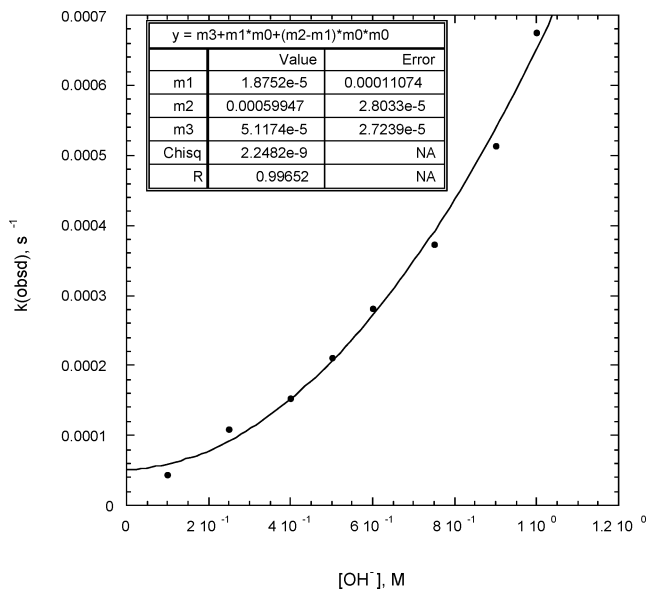


Figure 13. Plot of $k(\text{obsd})$ versus $[\text{OH}^-]$ for the base-catalyzed rearrangement of $[\text{Co}(\text{tmptacn})]^{3+}$ (**3**) at 25 °C. The data are fitted to a model which is first order in $[\text{OH}^-]$ in NaCl and NaOH media but with different specific rates in the two media.

ring or are not part of the same chelate, but none differ dramatically to the octahedral bond angle of 90° except N(3)–Co(1)–C(17), which is 74.7(3)°, part of the four-membered ring. Other angles within this ring are N(4)–C(18)–C(17), 101.6(6)°, C(18)–N(4)–Co(1), 92.0(4)°, and C(18)–C(17)–Co(1), 91.4(4)°. Full structural details are available in the deposited PDF (Supporting Information).

Kinetics for the Base-Catalyzed N- to C-Bonded Rearrangement of 3. This unusual N- to C-bonded linkage isomerization process provides an example of rate-limiting deprotonation, rare²⁸ in Co(III) substitution chemistry. Other examples have been recently discovered,^{1,2,29} curiously with tacn–pyridyl ligand systems very similar to the present, but there the rate-limiting deprotonation involved proton abstraction from pyridyl CH₂ centers, rather than at the tacn backbone. This analogy resulted in a scrutiny of the possible involvement of the pyridyl methylene in the tacn CH₂ deprotonation process.

The changes in the UV–visible absorption spectra for $[\text{Co}(\text{tmptacn})]^{3+}$ reacting in 1 M NaOH, which are shown in Figure 14S, reveal two sharp isosbestic points (436 and 505 nm), characteristic of a single-phase reaction, or one which leads to two or more products in constant proportions. The NMR data established a single product. The kinetics were accurately pseudo-first-order at each $[\text{OH}^-]$; rate data are in the Supporting Information (Table 1S). The plot of $k(\text{obsd})$ vs $[\text{OH}^-]$ is shown in Figure 13, and it indicates an approximate linear dependence on $[\text{OH}^-]$. No special significance is attached to the slight concave curvature evident. It is likely a medium effect arising from the substitution of NaCl by NaOH as $[\text{OH}^-]$ is raised and is usual.³⁰ The base-

(28) Tobe, M. L. *Inorg. Bioinorg. Mech.* **1983**, 2, 1.

(29) Jackson, W. G. *Inorg. React. Mech.* **2002**, 4, 1–30.

(30) Jackson, W. G.; Dickie, A. J.; McKeon, J. A.; Spiccia, L.; Brudenell, S. J.; Hockless, D. C.; Willis, A. C. *Inorg. Chem.* **2005**, 44, 401–409.

catalyzed hydrolysis of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ shows a similar (concave) trend, although less marked for this 2+ reactant.³¹ The data show a half-life for the rearrangement of ca. 17.5 min at 25 °C in 1 M NaOH.

The very much faster base-catalyzed exchange of the α -CH₂ pyridyl protons, and the base-catalyzed rearrangement are quite independent processes, and indeed so is the base-catalyzed racemization reaction, discussed below.

The convex rate plot is the inverse of what would be expected if some net deprotonation of the reactant was occurring at high $[\text{OH}^-]$. If this occurs, it is only to a small extent and clearly obscured by the medium effect. We attempted to measure the deprotonation process independently (see Supporting Information), but there was no evidence of any deprotonation (<2%) at the highest $[\text{OH}^-]$ examined, 1 M. A pK_a of >16 is estimated.

Kinetic Isotope Effect for the N- to C-Bonded Rearrangement of 3. For rate-limiting deprotonation of a C–H center, a pronounced primary kinetic isotope effect is expected, $k_H/k_D \approx 5$.^{1,2} We discovered a method for deuterating the tacn CH₂ centers in question to test this proposition (vide infra) but only to the extent of 1D per 4H³² in one –CH₂–CH₂– arm of the tacn. Here there is stereoselectively (100%) incorporated into each of the two inequivalent –CH₂– centers, C7 and C8 (Figure 3). Thus, if it is assumed that rate-limiting deprotonation occurs with comparable probability from each of these methylene sites and from the same positions occupied by the D (0.5D per position), then the calculated specific rate for the monodeuterated complex **4** is

$$k_D(\text{obsd}) = (1/6k_D + 5/6k_H)/6 = (1/6(k_H/5) + 5/6k_H) = 26/30k_H.$$

The same result is obtained if deprotonation occurs selectively from just one of the four inequivalent sites, and therefore, the observed isotope effect does not comment on this issue. Thus, $k_H/k_D(\text{obsd}) = 1.15$ is predicted. We determined, for 0.50 M NaOH, $k(\text{obsd}) = 3.78 \times 10^{-4} \text{ s}^{-1}$ (**4**) and for the monodeuterated complex, $k(\text{obsd}) = 3.19 \times 10^{-4} \text{ s}^{-1}$ (**4**). Thus, $k_H/k_D(\text{obsd}) = 1.19$, in reasonable agreement with prediction for rate-limiting deprotonation. The effect is relatively small (15%), and given the likely error in the rate constants ($\pm 3\%$), the argument for a primary kinetic isotope effect is not compelling, albeit it is certain that tacn CH₂ deprotonation is rate limiting. The regio- and stereoselective D incorporation into specific sites in the synthesis of the monodeuterated complex **4** (vide supra) is offset by the fact that the C₁-symmetry starting material regenerates a complex of C₃ symmetry and two active sites for the forward N- to C-bonded rearrangement (1D/4H) are necessarily diluted by 8H from the two other arms of the tacn component of the ligand.

Proton Exchange in 3. The methylene protons in **3** were observed to exchange in base and are therefore acidic, albeit

their pK_a 's are not below 14. The complex ion *asym*-[Co-(dmpmetacn)Cl]²⁺ deprotonates in NaOD at one of the four inequivalent α -CH₂ sites, but HD exchange is not observed because the Cl[–] leaves faster than the conjugate base reprotonates; HD exchange is observed, however, for the hydrolysis product, *asym*-[Co(dmpmetacn)OH]²⁺.² The increased positive charge for the [Co(tmptacn)]³⁺ ion should render it more acidic, and thus, given that the terminal methylenepyridine arm is a poor leaving group, ready HD exchange was expected. Indeed, all six α -CH₂ protons are replaced by deuterium in dilute NaOD before any rearrangement of **3** is observed. No (C–)H exchange occurs for **3** in D₂O alone, and qualitatively, the rate was observed to be first order in $[\text{OH}^-]$. The reaction was followed by ¹H and ¹³C NMR spectroscopy. The two α -CH₂ protons are inequivalent and in principle exchange at different rates. However, in the ¹H NMR spectra, the AB quartet (Figure 5, upper) collapses to two singlets of similar intensity corresponding to –C^AH^BD– and –C^AD^BH–. Thereafter, both sets of signals disappear at comparable rates.

Cobalt(III) complexes containing tacn and carrying a 3+ formal charge are known to deprotonate in the pH 12–14 region.²² Although there are no tacn NH protons in [Co(tmptacn)]³⁺ (all nitrogens are tertiary or pyridines), it is noted that deprotonation could arise nonetheless from two sources, from a tacn CH₂ or from a α -pyridyl CH₂, since this work has uncovered base-catalyzed reaction at both sites. However, no exchange was observed at any of the tacn –CH₂– centers, even on prolonged reaction in 1 M NaOD. Further, in an attempt to directly measure a pK_a , we observed no change in the absorption spectrum of [Co(tmptacn)]³⁺ in the range 0–1.0 M NaOH ($I = 1 \text{ M}$, NaCl), and it is estimated that the pK_a 's of either the pyridyl or tacn CH₂ exceed 16.

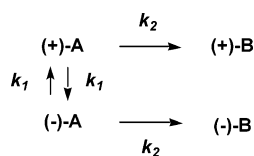
Kinetics of Racemization of 3. The reaction of the tmptacn complex in 1.015 M NaOH was followed polarimetrically and spectrophotometrically at 25 °C using in situ methods. Rate data were treated by nonlinear least-squares fitting to equations of the form $p = p_0 \exp(-k(\text{obsd})t) + p_\infty$, where p is the measured system property (absorbance or optical rotation). Note that p_∞ is small but nonzero for the polarimetric data and does not change further with time, which indicates that reactant racemization is faster, but not a lot faster, than the N- to C-bonded rearrangement, and also that the product does not racemise on the time scale of the kinetics followed. In addition, an isorotatory point was observed at 546 nm (coincidentally one of the polarimeter's Hg lines), consistent with no subsequent product racemization. Good first-order behavior was observed, and rate constants from triplicate runs agreed to $\pm 5\%$.

The rate constant obtained spectrophotometrically is k_2 (Scheme 1) since the instrument cannot distinguish enantiomers, while the polarimetric rate constant obtained is $2k_1 + k_2$. Scheme 1 assumes that the direct A-to-B conversion is retentive (this cannot be deduced from the kinetics alone); A is **3**, B is **6** (Figure 1). The validity of this simplified scheme was checked by using the values of k_1 and k_2 to compute final (+)-B/(–)-B which we have noted is not 1:1.

(31) Jackson, W. G.; Angel, R.; Marty, W., unpublished results.

(32) A more highly ²H-enriched tmptacn sample could be got by cycling in OH^-/D^+ , but each cycle introduces slightly less than one D per cycle.

Scheme 1



The equations describing these two quantities are

$$\begin{aligned}
 [(+)\text{-B}] &= A_0 / (2(2k_1 + k_2)) \{ 2k_1 + 2k_2 - \\
 &\quad (2k_1 + k_2) \exp(-k_2 t) - k_2 \exp(-(2k_1 + k_2)t) \}
 \end{aligned}$$

$$\begin{aligned}
 [(-)\text{-B}] &= A_0 / (2(2k_1 + k_2)) \{ 2k_1 - \\
 &\quad (2k_1 + k_2) \exp(-k_2 t) + k_2 \exp(-(2k_1 + k_2)t) \}
 \end{aligned}$$

The limit $[(+)\text{-B}]/[(-)\text{-B}]$ at complete reaction ($t = \infty$) is $(k_1 + k_2)/k_1$. We have not obtained the product optically pure and so could not determine the optical purity by direct polarimetric measurements. However, the product can be converted back to reactant quantitatively. Thus, the enantiomeric purity of reactant recovered from B in this way directly reflects the relative amounts of $(+)\text{-B}$ and $(-)\text{-B}$. From the values for k_1 ($1.29 \times 10^{-3} \text{ s}^{-1}$) and k_2 ($7.5 \times 10^{-4} \text{ s}^{-1}$), the ratio $(+)\text{-B}/(-)\text{-B}$ translates to a value for the activity, $10^2 k_2 / (2k_1 + k_2)$, which computes as 29% and which compares closely with the experimental value of 30%. This substantiates the essential reactions shown in Scheme 1, whereby racemization of $(+)\text{-}[\text{Co}(\text{tmptacn})]^{3+}$ is a quite separate process to the N-to-C rearrangement which proceeds forward in basic solution with complete retention of activity, as does the reverse process in acid. We note also that the racemization of $(+)\text{-}[\text{Co}(\text{tmptacn})]^{3+}$ is completely quenched in acid.

Racemization of hexaaminecobalt(III) complexes in aqueous solution is normally extremely slow, even in basic solution. Two notable exceptions are the $(+)\text{-}[\text{Co}(\text{tmen})_3]^{3+}$ ion (Figure 1), which is sterically strained and which undergoes very rapid base-catalyzed racemization ($k_{\text{OH}} = 273 \text{ M}^{-1} \text{ s}^{-1}$, $25 \text{ }^\circ\text{C}$, $I = 1.0 \text{ M}$, NaClO_4) via deprotonation at one of the two inequivalent terminal NH_2 centers.^{33,34} The other is $(+)\text{-}[\text{Co}(\text{stn})]^{3+}$ (Figure 1), which apparently is also strained and which racemizes at a modest rate in basic solution ($k_{\text{OH}} = 2.5 \text{ M}^{-1} \text{ s}^{-1}$, $25 \text{ }^\circ\text{C}$).³⁵ The stn complex has sec-NH and terminal prim- NH_2 centers available for deprotonation in basic solution.

The present $(+)\text{-}[\text{Co}(\text{tmptacn})]^{3+}$ is devoid of any NH centers, and since we know that the N-to-C rearrangement which occurs via rate-limiting deprotonation at a tacn $-\text{CH}_2-$ is a completely independent process, the base catalysis for the racemization must arise via deprotonation at one of the two inequivalent pyridyl $\alpha\text{-CH}_2-$ protons. Certainly, these protons completely exchange in basic solution, but faster than the racemization process. This is now an established mechanism for base-catalyzed substitution

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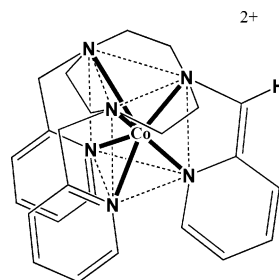
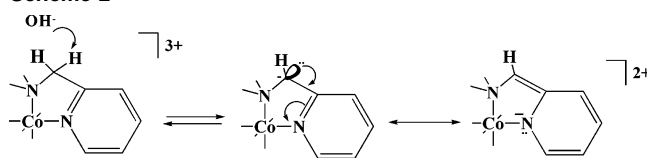
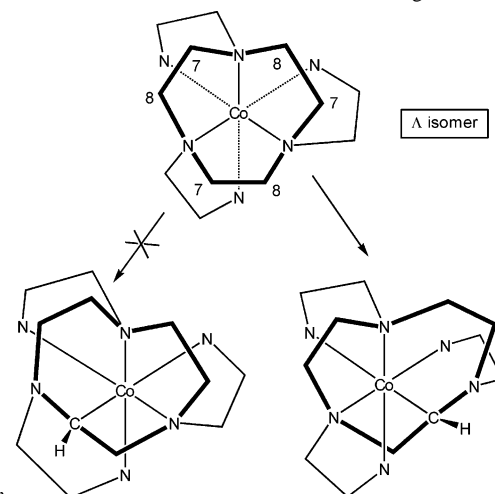


Figure 14. Proposed trigonal prismatic achiral intermediate for the base-catalyzed racemization of $(+)\text{-}[\text{Co}(\text{tmptacn})]^{3+}$.

Scheme 2



Scheme 3. Two Possible Modes of N- to C-Bonded Rearrangement^a



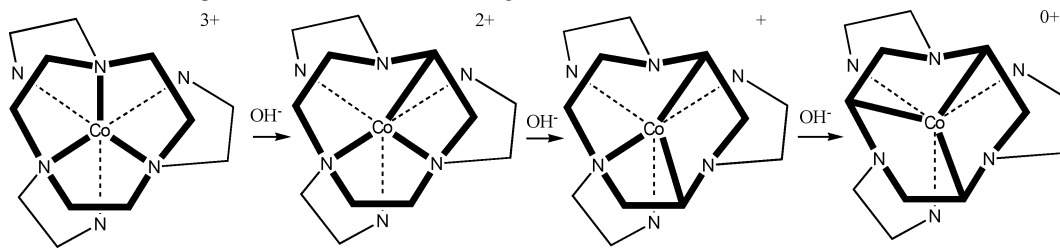
the direction shown.

^a The Alternative Products Are Diastereomers.

for pyridylcobalt(III) complexes,^{1,2,30} but the present example for a racemization is a first—the other examples have involved substitution with geometric and optical retention. We imagine a trigonal twist via a trigonal prismatic geometry (Figure 14), promoted by the deprotonated $\alpha\text{-pyridyl}-\text{CH}_2-$ which we have argued² generates an activating amidate center bound to $\text{Co}(\text{III})$ (Scheme 2).

This process may even be assisted by a ground-state distortion toward the trigonal prismatic geometry, as observed for several other metal complexes of the tmptacn ligand (also known as tptcn).^{8,9}

N- to C-Bonded Rearrangement Mechanism. The N-bonded tmptacn complex **3** converts irreversibly in strong base to one of four stereochemically possible C-bonded isomers of **6**. The complete retention of the chirality about the cobalt is the first fact. Second, the reactant chooses one of two carbons to react with, and furthermore it chooses one of two hydrogens on this carbon, although the latter is dictated by the need to have the carbanion have its lone pair directed toward the metal ion. Scheme 3 depicts the reactant viewed down the C_3 axis and showing C7 positioned over a chelate arm of the Λ reactant; C8 is a distinct alternate site

Scheme 4. Possible 'Windmill' Sequence of N- to C-Bonded Rearrangements

for reaction evident from the fact that it is not positioned over the chelate arm. The facts are that the reaction proceeds exclusively in the direction shown.

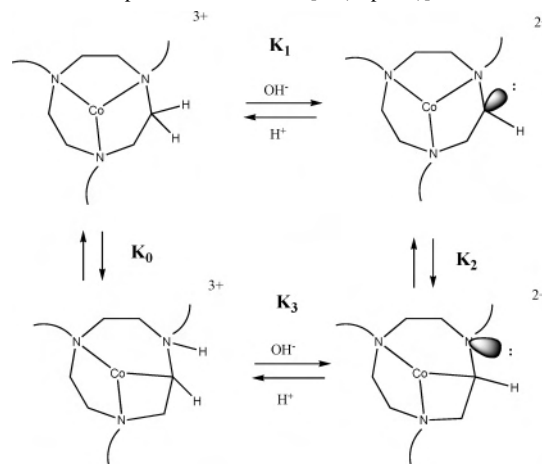
The reason for the choice of exclusive deprotonation at C7 is not obvious from Scheme 3. Dreiding stereomodels show that, for the preferred isomeric product, the C-bonded tacn portion of the hexadentate ligand is strained due mainly to the four-membered ring, but the six-membered-ring portion of the tacn is in a relatively unstrained chair conformation. Further, for the portion of the molecule containing the free amine and a pyridylmethylene 'arm', the six-membered ring is mostly flat and in a relatively unstrained envelope conformation. If one compares the diastereomer derived from a bonded C8 rather than C7 carbon, the latter six-membered ring is impossible to construct without severely distorting bond angles about cobalt, and the ring itself is severely distorted; further, the six-membered ring in the tacn portion of the molecule is in a boat rather than chair conformation.

The reaction sequence as depicted accommodates the experimental observations for the forward reaction, but more detail is required to explain the remarkable observation that in the reverse process the D is distributed equally between C7 and C8 in the regenerated tmptacn complex, as discussed below.

The $[\text{Co}(\text{tmptacn-H-C})]^{2+}$ complex **6** is stable in strong OH^- solution. Anticipated were further N- to C-bonded rearrangements, as shown (Scheme 4). While this windmill effect would be anticipated to alleviate the strained four-membered ring problem, there is a reduction in the charge of the complex as the sequence proceeds, and this clearly is the limiting factor—the much reduced acidity of the methylene centers becomes the issue, and the N-to-C rearrangement sequence stops abruptly at the very first stage.

Although the $[\text{Co}(\text{tmptacn-H-C})]^{2+}$ complex exchanges its pyridyl $-\text{CH}_2-$ protons, like the parent $[\text{Co}(\text{tmptacn})]^{3+}$ complex, these are very much slower processes. All six such protons are inequivalent, and the exchange processes are both sequential and complex, as studied by both proton and carbon NMR (Supporting Information).^{20,36}

Reverse Reaction—Rearrangement of C-bonded **6 to N-bonded **3** in Aqueous Acid.** There is clear evidence that the C-bonded complex $[\text{Co}(\text{tmptacn-H-C})]^{2+}$ protonates in strong acid ($\text{p}K_{\text{a}}$ ca. 0); indeed, a protonated form could be crystallized (see Experimental Section). The established structure of the precursor complex reveals the free amine site that is the only one available for protonation, that α to

Scheme 5. Schematic Representation of the Acid–Base and N- versus C-bonded Species Derived from $[\text{Co}(\text{tmptacn})]^{3+}$ **3** in Water

the coordinated carbanion. This protonated amine transfers its proton to the carbanion on recoordination of the nitrogen. We have not examined the acid dependence of the rate for the reverse reaction but suspect that the role of the proton is simply to trap the carbanion after it is (very slowly) dissociated. Reflux temperatures under acid conditions were required to reverse the reaction, which occurs on the minute time scale. The reverse reaction occurs also at neutral pH, but very slowly (hours to days); there is a competitive oxidation process which interfered with quantitative measurements on the equilibrium distribution in the pH region where both N- and C-bonded forms coexisted (*vide infra*). Experiments conducted on this equilibrium showed that the C-bonded species prevails exclusively (>99%) in the $[\text{OH}^-]$ range 0.1–1.0 M, but at pH 7 and below, the N-bonded form predominates (>99%).

The species involved in the equilibria are shown schematically in Scheme 5.

Knowing estimates for K_1 ($<10^{-4}$, based on a $\text{p}K_{\text{a}}$ of >18 for $[\text{Co}(\text{tmptacn})]^{3+}$) and estimates for the equilibrium distributions between $[\text{Co}(\text{tmptacn})]^{3+}$ and $[\text{Co}(\text{tmptacn-H-C})]^{2+}$ at pH 14 ($>100:1$ 2+ C-bonded complex) and pH 7 ($>100:1$ N-bonded 3+ species), K_2 can be estimated as $>10^6$. Similarly, having an estimate for the $\text{p}K_{\text{a}}$ of the protonated C-bonded complex (ca. 0; this work) leads to a value for K_3 of 10^{14} (based on $\text{p}K_{\text{w}}$ 14). The relationship $K_0 = K_1 K_2 / K_3$ holds for this system of cyclic equilibria as the K 's are defined ('product' is defined by the arrow adjacent to the K value), and hence, K_0 is estimated as 10^{-12} . This analysis shows that, while the N-bonded linkage isomer is intrinsically much more stable than the C-bonded form (K_0), the reverse is true of the deprotonated forms (K_2). Clearly, a C-bonded

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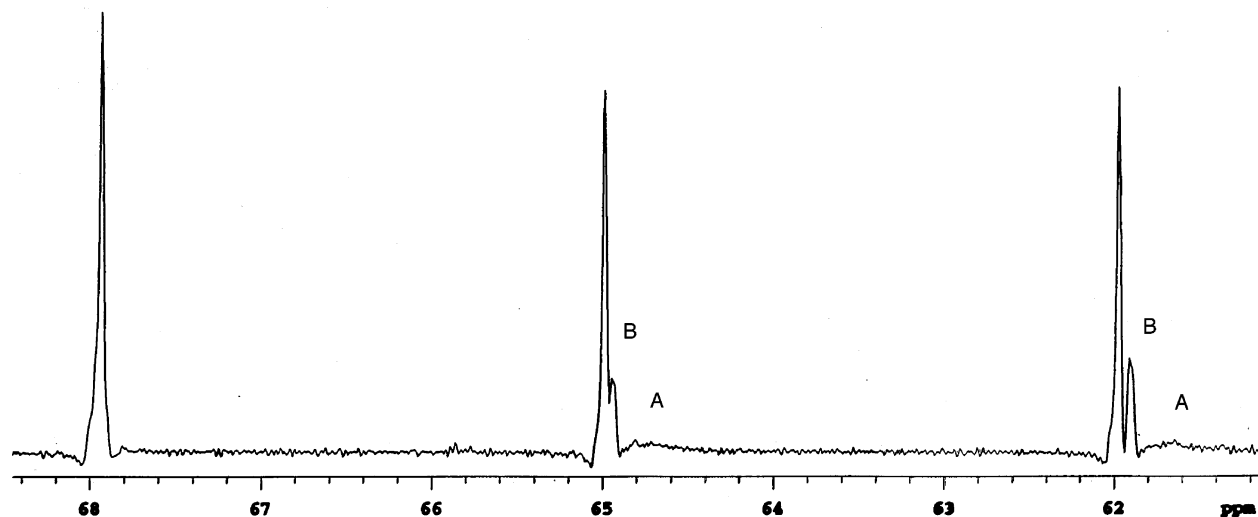


Figure 15. High-resolution ^{13}C NMR spectrum ($\text{Me}_2\text{SO}-d_6$) for d_1 - $[\text{Co}(\text{tmptacn})](\text{ClO}_4)_3$ (**4**) reformed from $[\text{Co}(\text{tmptacn-H-C})]^{2+}$ (**6**) in $\text{D}_2\text{O}/\text{D}^+$. The 'A's' represent the satellite α -C-D signals, broadened to near nonrecognition, while the 'B's' are the β -isotopically shifted $-\text{CH}_2-\text{CHD}-$ satellites.

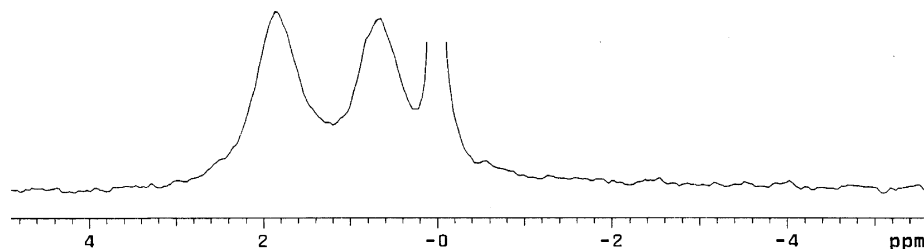


Figure 16. ^2H NMR spectrum of d_1 - $[\text{Co}(\text{tmptacn})](\text{ClO}_4)_3$ recovered from $[\text{Co}(\text{tmptacn-H-C})]^{2+}$ reacted in $\text{D}_2\text{O}/\text{D}^+$ in $\text{Me}_2\text{SO}-h_6$ at natural abundance. The spectrum is referenced to solvent (2.50 ppm) shown at 0 ppm. The two complex ^2H signals are thus at 4.4 and 3.2 ppm.

carbanion binds more strongly than an amine, and this driving force wins in the energy race against a strained four-membered plus unstrained six-membered rings versus the more favorable two five-membered rings in the reactant amine complex.

The carbanion complex **6** in $\text{D}_2\text{O}/\text{D}_2\text{SO}_4$ resulted in partial conversion to **7**. After 5 min reaction at 90°C , reactant **6** and product **4** were separated on Sephadex and isolated; the recovered reactant showed zero D incorporation. For the same reaction conducted on a longer time scale (30 min), the $[\text{Co}(\text{tmptacn})]^{3+}$ was isolated and examined for deuterium content. The stoichiometry of the reaction requires the incorporation of one D, but more could be incorporated by pre or subsequent H-D exchange. The former is eliminated by the control experiment just described, and the latter is also eliminated by the observation of no change in the tmptacn complex when boiled in $\text{D}_2\text{O}/\text{D}_2\text{SO}_4$ for 30 min.

The ^1H NMR spectrum (Figure 5, lower) of the reformed C-tacn monodeuterated d_1 - $[\text{Co}(\text{tmptacn})](\text{ClO}_4)_3$ complex **4** gives little indication of the site(s) of deuteration; the difficulty with identifying the site or sites of deuteration from this spectrum alone lies in the fact that one D is diluted not by one set of the four inequivalent tacn CH_2 's but rather by three, since the reverse C- to N-bonded rearrangement regenerates the C_3 symmetry. The proton integrations are 3:3:3:3 initially and 2.5:3:2.5:3 on selective D-incorporation.

The high-resolution^{20,36} ^{13}C NMR spectrum (Figure 15) resolved the issue. The C-D group under conditions of broadband proton decoupling normally gives rise to a broad,

partly resolved triplet of reduced intensity, and this is isotopically shifted upfield. However, for the C attached to the CD group, the signal is sharp and also isotopically shifted upfield. This β shift is small (ca. 10 Hz at 100 MHz for ^{13}C), but clearly resolved. The ^{13}C NMR spectrum for **4** reveals two β C-CDH- satellites, each at an intensity of 1/3 relative to the larger signal; the third carbon signal at ca. 68 ppm corresponds to the (undeuterated) pyridyl methylene. Thus, for any single molecule of the tris complex, there are two $-\text{CH}_2-\text{CH}_2-$ tacn residues and one $-\text{CHD}-\text{CH}_2-$; half the molecules have one D at one carbon (C7, Figure 3) and the other half have one D at C8.

The protonation (deuteronation) reaction of the specific carbanion carbon thus leads to scrambling across the two inequivalent carbons in that 'arm'. It does not, however, become scrambled across all four inequivalent proton sites but is confined to two and is thus oriented stereoselectively (100%) at each carbon. The ^2H NMR spectrum also shows this clearly, despite the intrinsic poorer resolution; the sites that acquire the D are so designated (Figure 16). The distinction between half a D on each of the two inequivalent methylenes, as against one D on one particular carbon, is important mechanistically.

The 1:1 distribution across two inequivalent sites initially suggested an intermediate in which the two carbons, but not the attached proton(s), became equivalent. A candidate, discussed again ahead, is a trigonal prismatic structure derived from the octahedron through a trigonal twist. A consequence of this suggestion is that **6** would completely

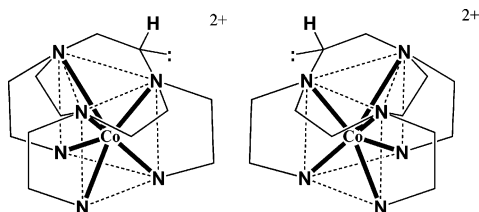


Figure 17. Trigonal prismatic intermediates deprotonated at C7 (left) and C8 (right) and showing that they are enantiomeric.

racemize en route back to **3** in hot aqueous acid. We carried out this experiment on partly resolved **6** generated in situ from **3** in NaOD, and the recovered tmptacn complex after heating in acid had the expected activity, as described earlier (zero racemization in the reformation step). The trigonal prismatic structure is therefore excluded as an intermediate in the reverse C- to N-bonded process.

There appear to be no other examples of acid-reversed N- to C- or S- to C-bonded rearrangements. However, there has been a report of an attempt to achieve this. Wagenknecht et al. report an unsuccessful attempt with one of their C-bonded multidentate ligand complexes in triflic acid.³⁷ Systems best suited to observing this very slow dealkylation process in acid are those where there are no protonatable donor atoms, since acid, especially neat triflic acid, will strip off any ligands bearing lone pairs of electrons, such as the carboxylate donors in the Legg systems^{38,39} and some of the complexes of Wagenknecht et al.³⁷

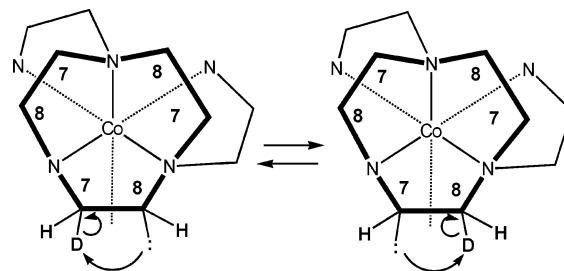
Mechanism for the Reverse C- to N-bonded Rearrangement—Conversion 6 to 3 in Aqueous Acid. The principle, from microscopic reversibility, is that the reverse reaction must follow the same path as the forward reaction, or reactions, if there are more than one.

There was an initial scenario, already alluded to, which warranted closer scrutiny. Deprotonation at C7 or C8 concurrent with rearrangement to a trigonal prismatic structure leads to intermediates which at first sight seem to be the same and which might accommodate the 1:1 D-scrambling at C7 and C8 for the reverse process. However, these intermediates are in fact chiral and enantiomeric (Figure 17). If either is formed, other than exclusively, the C-bonded product in the forward direction would be partly racemized, yet they would have to be formed 1:1 to accommodate the D incorporation pattern for the reverse process. This mechanism is therefore inconsistent with the experimental facts.

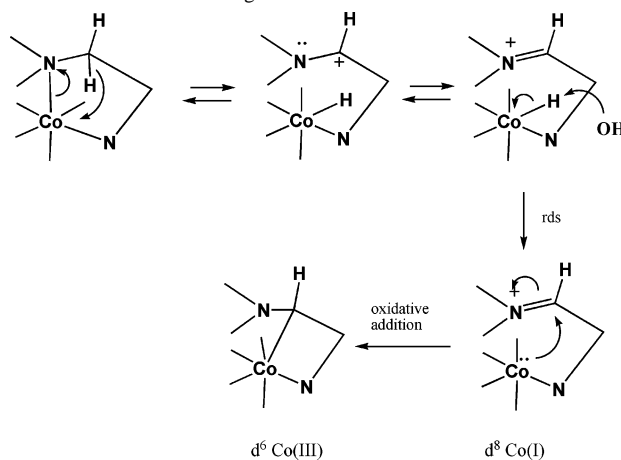
A first proposal consistent with the facts is an intramolecular 1,2-proton shift, shown in Scheme 6. How such a shift could come about is not obvious from Scheme 3, which would seem to require H⁺/D⁺ transfer across nitrogen, but the C7 and C8 alternatives are, because of the C₃ symmetry, also within the same chelate.

This possibility means that initial deprotonation of the tris complex could occur at either C7 or C8, with a switch in

Scheme 6. Proposed 1,2-Proton/Deuteron Shift for the Reaction of [Co(tmptacn-H-C)]²⁺ in D₂O/D⁺



Scheme 7. Intramolecular Hydride Shift Mechanism to Accommodate the N- to C-bonded Rearrangement



the carbanion site to that ultimately preferred for the subsequent N- to C-bonded rearrangement.

A second mechanistic suggestion is equally radical (Scheme 7). In this process, a hydride ion is transferred (reversibly) to the metal ion. Hydride is removed from Co(III) as H⁺ in basic solution, as the rate-determining step to generate nucleophilic Co(I) which then attacks the imine carbon to generate the Co–C bond as shown. Imine formation from either C7 or C8 accommodates D incorporation into either carbon in the reverse process. There is no direct evidence to support such a series of steps, but a stable hydridocobalt(III) amine complex is known,⁴⁰ and it is known also that Co(III)–H can be made to react as Co(III) + H⁺, or as Co(I) + H⁺ (in basic solution).^{40,41}

Spontaneous Oxidation of 5. In an attempt to directly optically resolve this complex, we employed chromatography on Sephadex using Na₂(+)-tart as the eluant. Over a period of a few days, no separation had been achieved and the initially red-brown reactant had become yellow. We recovered the entire material and recrystallized it to purity. A sample was also synthesized by refluxing the tris complex in 1 M NaOAc/D₂O for 1 h. This proved to be a mixture of the tris complex and its oxidation product, which we could separate on Sephadex; all the α-pyridyl methylenes in both product and recovered reactant were deuterated, but none of the tacn CH₂ protons were. The new material had almost

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the same ^1H (Figure 15S) and ^{13}C NMR spectra (Figure 16S) as the $[\text{Co}(\text{tmptacn})]^{3+}$ species; except for a few, all resonances were trebled. It was a single species, however, and we assigned the structure $[\text{Co}(\text{tmptacn-OH})]^{3+}$, shown in Figure 1, on the basis of the C_1 symmetry and the chemical shift (ca. 90 ppm) for the $-\text{CH}(\text{OH})-$ group α to the amine. This presumably was the original carbanion carbon. The rest of the spectrum (Figure 16S) has a very close similarity to that for $[\text{Co}(\text{tmptacn})]^{3+}$ (Figure 5).

In the ^1H NMR spectrum (Figure 15S, upper), a signal could not be immediately assigned to the OH proton in the expected region (ca. 7–10 ppm), but the integration (4:3:3:3) was indicative of an extra proton under the lowest-field pyridyl multiplet. We tried to shift this out by varying the counterion, often a successful strategy for resolving overlaps,⁴² only to shift it upfield under the next-highest-field pyridyl multiplet (integration 3:4:3:3). However, the sharp doublet, part of this multiplet, disappeared in $\text{Me}_2\text{SO}-d_6$ containing a drop of D_2O (Figure 17S) and was therefore clearly assigned to the OH proton, split into a doublet by the attached CH.

In summary, there is a regio- and stereoselective incorporation of a hydroxy substituent and clearly the carbanion has oxidized en route back to the tmptacn complex. At this time, the location and orientation of the hydroxy substituent and the oxidation mechanism are unknown. Oxidations akin to this are turning up with increasing frequency and are especially associated with Co(III)–carbanion linkages.⁴³ Recently, we discovered a similar oxidation reaction of a carbanion complex where $-\text{CH}_2-\text{Co}(\text{III})$ became $-\text{C}(\text{H})-\text{OH}-\text{Co}(\text{III})$, and this was characterized by a single-crystal X-ray structure.²⁶ Spiccia et al. had previously reported¹⁵ the unanticipated $-\text{OH}$ substitution of $-\text{H}$ in a C atom α to a bound amine in a Co(III)–imine complex, thereby generating an amide.

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Conclusions

The $[\text{Co}(\text{tmptacn})]^{3+}$ complex rearranges smoothly in aqueous OH^- to a complex involving C-bonded tacn, despite the four-membered chelate ring that this required. The corresponding taetacn complex, which entails the same reactant geometry save for aminoethyl ($\text{NH}_2\text{CH}_2\text{CH}_2-$) rather than pyridylmethylene (2-pyridyl- CH_2-) arms, is demonstrably unreactive. This initially suggested a role for the pyridine in the N- to C-rearrangement. However, the $[\text{Co}(\text{tmptacn})]^{3+}$ species, which differs from the taetacn complex only in having ‘arms’ which are one carbon longer (1-aminopropyl, $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$), does show clear evidence of a N- to C-bonded rearrangement, but the reaction is very much slower. The factors controlling the *relative* rates of these interesting rearrangement processes remain unclear at present.

This work led to the idea that ligands such as dmpdacn or tmpdacn (Figure 1) might bind through the central carbon on deprotonation, given that the structures are otherwise very similar and the fact that such binding would result in three five-membered rings for the macrocyclic component of the penta- or hexadentate ligand. Indeed, this idea has been brought to fruition²⁶ for dmpdacn, and the even more surprising component of the complexation reaction is that no added base is required to drive it—the C–H bond cleaves spontaneously under remarkably mild conditions.

Acknowledgment. Financial support from the Australian Research Council is gratefully acknowledged. We thank Dr. Ben Freasier for constructive input into the data analysis and Dr. Barry Gray for assistance with the 2D NMR experiments.

Supporting Information Available: Some experimental details; Table 1S, kinetic data; Figures 1S–17S, 1D and 2D NMR data; a crystallographic file in PDF format for $[\text{Co}(\text{tmptacn-H-C})](\text{ClO}_4)_2$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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