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Facile C–H Bond Activation: Synthesis of the N_4C Donor Set Pentadentate Ligand 1,4-Bis(2-pyridylmethyl)-1,4-diazacyclononane (dmpdacn) and a Structural Study of Its Alkyl–Cobalt(III) Complex $[Co(dmpdacn\text{-}C)(OH_2)](ClO_4)_2 \cdot H_2O$ and Its Hydroxylated Derivative $[Co(dmpdacnOH\text{-}O)Cl](ClO_4)_2 \cdot C_3H_6O$

Xiangting Zhou,[†] Anthony I. Day,[†] Alison J. Edwards,[‡] Anthony C. Willis,[‡] and W. Gregory Jackson*,[†]

School of Physical, Environmental and Mathematical Sciences, University College, The University of New South Wales, Australian Defence Force Academy, Canberra ACT 2600, Australia, and Research School of Chemistry, Australian National University, Canberra ACT 0200, Australia

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The 1,4-bis(2-pyridylmethyl)-1,4-diazacyclononane (dmpdacn) ligand with a N_4C donor set deprotonates at a CH_2 γ to an amine under extraordinarily mild conditions (pH 7) and binds as a pentadentate ligand to Co(III) as the $[Co(dmpdacn\text{-}C)(OH_2)]^{2+}$ complex. This complex was characterized by 1D and 2D NMR techniques, and a single-crystal X-ray structure is reported. In an alternative synthesis from Co(II), dmpdacn, and air, the same C-bonded complex is obtained along with a novel hydroxylated Co(III) complex $[Co(dmpdacnOH\text{-}O)Cl]^{2+}$ which has been similarly characterized. Here the carbanion has been oxidized, a C- to O-bonded rearrangement has taken place, and the bound aqua group is replaced by Cl^-. The base hydrolysis kinetics of the hydroxylated Co(III) complex are reported, and mechanisms for this and the unusually facile C–H cleavage and CH_2 oxidation reactions are discussed.

Introduction

Metal-ion mediated activation of carbon−hydrogen bonds of organic molecules is a fundamentally important chemical process. Since the discovery of the stable natural product coenzyme B_{12}, a cobalt(III) complex containing a σ-bonded alkyl ligand,[1] there has been a vast amount of interest in synthetic complexes, and the elucidation of the conditions that stabilize alkyl−cobalt(III) moieties has been a significant issue. Many alkylcobalt(III) compounds are oxygen or moisture sensitive, the latter preventing tractable aqueous chemistry. The cobalt(III)−carbon σ-bond has, however, in a number of cases proven to be quite robust. For example, the simple pentaamminemethylcobalt(III) cation is sufficiently robust in aqueous ammonia to allow for spectroscopic characterization,[2] yet it defied synthesis for many years. A closely related methyl−cobalt(III) compound of the saturated macrocyclic ligand 1,4,8,11-tetraazacyclotetradecane can be recrystallized from water without decomposition.[3,4] Alkyl−cobalt(III) compounds with other saturated macrocyclic ligands have now been prepared by employing various synthetic strategies, and several of the complexes have been structurally characterized.[3−7]

Alkylcobalt(III) complexes have also been prepared by base-induced transformations of coordination complexes. For example, an intermolecular reaction of the cobalt(III) complex of dacoda(1,5-diazacyclooctane-*N*,*N*′-diacetate dianion) in base involves deprotonation of a methylene group and subsequent coordination of the carbanion.[8,9] Additional cobalt(III) compounds with a Co−C σ-bond have been prepared by the reaction of thioether donor ligand compounds

* To whom correspondence should be addressed. E-mail: wgj@adfa.edu.au. Phone: +61 2 62688078. Fax: +61 2 62688090.
[†] The University of New South Wales.
[‡] Australian National University.

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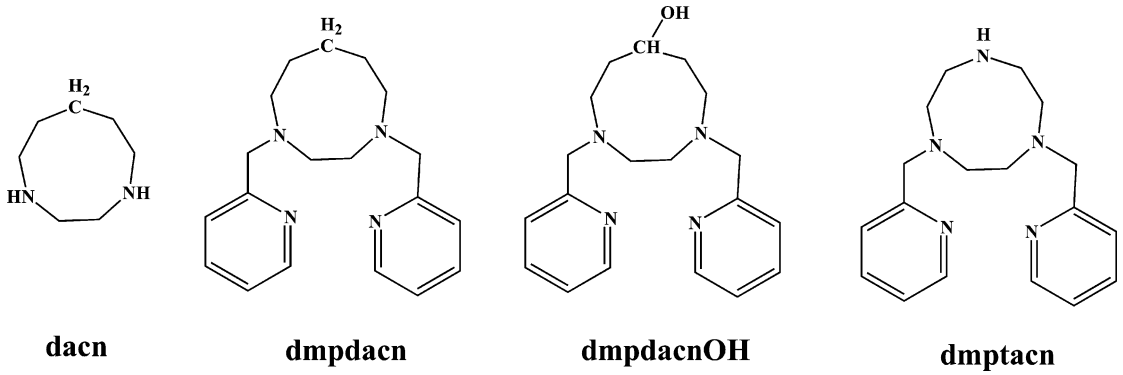
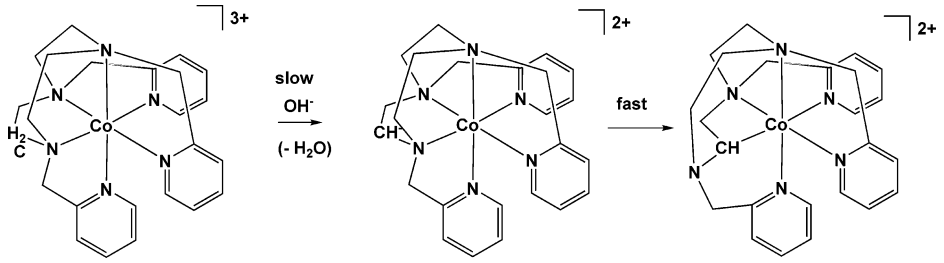


Figure 1. Ligand abbreviations.

Scheme 1. N- to C-Bonded Rearrangement of $[Co(tmptacn)]^{3+}$



in basic solution for which the α-CH_2 on deprotonation displaces the thioether.[10−15]

The tacn derived hexadentate cobalt(III) complex $[Co(tmptacn)]^{3+}$ rearranges stereoselectively in base[16] to form a stable carbanion complex as shown in Scheme 1. The reaction occurs by deprotonation at a CH_2 center adjacent to the tacn *sec*-amine, which is unprecedented. The reaction proceeds readily and completely ($t_{1/2}$ ca. 15 min in 1 M NaOH, 25 °C), as displayed in Scheme 1, despite the formation of a strained four-membered ring.

This suggested that a similar ligand to dmptacn, bearing a CH_2 in place of a NH group in the tacn component of the ligand, dmpdacn (Figure 1), might well coordinate with Co(III) under basic conditions. In this case the preferred five-membered rings would be retained, and perhaps, *strong* base would not be required to drive the reaction. This has been realized, with C−H activation occurring under extremely mild conditions as described herein. Under certain conditions, facile oxidation at carbon and donor atom rearrangement are observed as well, and these reactions are also reported.

Experimental Section

NMR spectra were recorded on a Varian Unity Plus 400 MHz Spectrometer for 1D ^1H and ^{13}C spectra (20 °C), and 2D spectra (25 °C, DQCOSY and NOESY). For solutions in $CDCl_3$, the residual solvent peaks (δ_H 7.24, δ_C 77.0, central peak) were used as internal standards. For D_2O, dioxane was the internal reference (δ_H 3.75 and δ_C 69.26, relative to DSS). For Me_2SO-d_6 as solvent, the central peak of the CD_3 quintet or septet was convenient as the reference (δ_H 2.50 and δ_C 39.37, relative to $SiMe_4$).

All other materials were acquired from commercial sources, were reagent grade or better, and were used without further purification unless otherwise indicated. Solvents were predried over activated molecular sieves, then refluxed over an appropriate drying agent under an atmosphere of nitrogen, and finally fractionated by distillation and stored under dry nitrogen. The cation exchange medium was Dowex 50W-X2 (H^+ form, 200−400 mesh; BioRad). *N*,*N*′-Bis(*p*-tosyl)ethylenediamine and its disodium salt were freshly prepared according to reported methods.[17] Carbon dioxide free Milli-Q water was used routinely for all physical measurements.

Elemental C, H, N, and Cl analyses were performed by the Microanalytical Unit, Research School of Chemistry, Australian National University.

Kinetic Studies. UV−vis absorption spectra (300−700 nm) and absorbance versus time traces were recorded with use of a Hewlett-Packard 8453 diode-array spectrophotometer thermostated to 25.00 ± 0.1 °C by water circulation from a Lauda bath. Specfit global analysis software was used to analyze the kinetic data.

A 1.00 mL (Pipetman) portion of the aqueous complex solution was placed in one compartment of a 1 cm quartz bifurcated cell, and 1.00 mL of the appropriate buffer or NaOH (I = 2.0 M, NaCl) was placed in the other. The cell was placed in the spectrophotometer housing and allowed to equilibrate (25.0 ± 0.1 °C) for 10 min. The cell was shaken to mix the two solutions and initiate reaction and returned to the cell housing and the spectral scans commenced. The kinetics of acid hydrolysis were measured independently using dilute $HClO_4$ solutions (0.001−0.1 M).

The spectrophotometric data were routinely checked to ensure absorbances in the wavelength range chosen for analysis did not exceed 1.5, and that the data covered at least $2t_{1/2}$ of reaction (more

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usually $3-4t_{1/2}$). All kinetic runs were performed in triplicate, using [Co] in the range 0.001−0.02 M to achieve the desired absorbance change.

1,5-Bis(*p*-tolylsulfonato)pentane, pndt.[18,19] A sample of 1,5-pentanediol (26 g, 0.25 mol) was dissolved in pyridine (50 mL) and cooled in an ice bath. *p*-Toluenesulfonyl chloride (94.1 g 0.53 mol) in pyridine (150 mL) was added dropwise over 1 h, during which time a white precipitate formed. The solution was stirred for 5 h at 0 °C. Upon the slow addition of H_2O (1 L), the white product precipitated, and it was isolated by filtration and washed with cold water (1 L). The crude product was recrystallized by dissolving in hot methanol (450 mL) and cooling. Yield 86.6 g, 84%. ^{1}H NMR ($CDCl_3$): δ 1.32 (2H, quintet, $OCH_2CH_2CH_2CH_2$-CH_2O), 1.57 (4H, $OCH_2CH_2CH_2$), 2.42 (6H, s, CH_3Ar), 3.94 (4H, t, OCH_2CH_2), 7.31(4H, d, aromatic), 7.74 ppm (4H, d, aromatic). ^{13}C NMR ($CDCl_3$): δ 21.45, 21.60, 28.11, 69.94, 127.8, 129.85, 132.85, 144.82 ppm. Anal. Calcd for $C_{19}H_{24}O_6S_2$: C, 55.32, H, 5.86. Found: C, 54.87, H, 5.65%.

1,4-Ditosyl-1,4-diazacyclononane, dacndt. The following is a better alternative to previously described methods.[20,21] Freshly prepared[17] and dried *N*,*N*′-bis(*p*-tosyl)ethylenediamine-*N*,*N*′-disodium salt (0.05 mol) in dry DMF (50 mL) was slowly heated to 100−120° under N_2. A clear solution resulted after dropwise addition of 1,5-bis(*p*-tolylsulfonato)pentane (0.05 mol)[18,19] in DMF over 1 h. After further heating overnight, the volume was reduced substantially by vacuum distillation, and ice-cold water (200 mL) was added. With cooling, the crude product precipitated as a white solid. It was filtered, washed with cold water, dried, and finally recrystallized from 1:1 chloroform/ethanol. Yield: 50%. Anal. Calcd for $C_{21}H_{28}N_2O_4S_2$: C, 57.77, H, 6.46, N, 6.42. Found: C, 57.50, H, 6.34, N, 6.20%. ^{1}H NMR ($CDCl_3$): δ 1.89 (2H, quintet, $NCH_2CH_2CH_2CH_2CH_2N$), 2.03 (4H, m, $NCH_2CH_2CH_2CH_2$), 2.41 (6H, s, CH_3Ar), 3.27 (4H, t, NCH_2CH_2N), 7.28 (4H, d, aromatic), 7.63 ppm (4H, d, aromatic). ^{13}C NMR ($CDCl_3$): δ 21.48, 25.23, 27.10, 51.49, 126.96, 129.74, 135.28, 143.38 ppm.

1,4-Diazacyclononane, dacn. A solution of recrystallized dacndt (3.48 g, 7.98 mmol) in HBr (48%)/acetic acid was heated at 90 °C under a nitrogen atmosphere for 48 h. It was then rotary evaporated to a syrup and cooled in an ice bath, and absolute ethanol (250 mL) was added slowly with stirring, followed by ether (500 mL). The resulting white precipitate of dacn·2HBr was filtered, washed with ether and air-dried, and then dissolved in water (100 mL) and boiled with charcoal. After filtration, the solution was diluted to 1000 mL and loaded onto a Dowex column. The column was washed with water, and then with 0.5 M HCl followed by 1.0 M HCl. Elution of the otherwise colorless amineH_2^{2+} was evident as a change in consistency of the resin as it eluted. Crystalline dacn·2HCl was obtained by evaporating the eluate to a small volume and completing the crystallization with the addition of ethanol. ^{1}H NMR (D_2O): δ 1.66 (2H, q, $NCH_2CH_2CH_2$ CH_2CH_2N), 1.80 (4H, m, $NCH_2CH_2CH_2$), 3.21 (4H, t, $NCH_2CH_2CH_2CH_2CH_2N$), 3.51 (4H, s, $NCH_2CH_2CH_2$), 4.64 ppm (2H, s, N*H*). ^{13}C NMR (D_2O): δ 22.29, 22.85, 42.18, 45.53 ppm. These values compare favorably with literature data.[20,21]

Dacn·2HCl was dissolved in water, cooled in an ice bath, and basified to pH ca. 14 by the cautious addition of 10 M NaOH. The solution was extracted with $CHCl_3$ or CH_2Cl_2 (3 × 250 mL), and the resulting organic layers were combined and dried over $MgSO_4$. After removal of solvent, dacn was obtained as a solid. Yield: 0.95 g, 93%. ^{1}H NMR ($CDCl_3$): δ 1.46 (4H, m, $NCH_2CH_2CH_2$), 1.55 (2H, m, $NCH_2CH_2CH_2$), 2.62 (4H, s, NCH_2CH_2N), 2.67 (4H, t, $NCH_2CH_2CH_2CH_2CH_2N$), 3.34 ppm (2H, br, N*H*). ^{13}C NMR: δ ($CDCl_3$) 24.47, 25.64, 45.52, 45.82 ppm.

1,4-Bis(2-pyridylmethyl)-1,4-diazacyclononane, dmpdacn. To an aqueous solution (25 mL) of 1,4-diazacyclononane hydrochloride **(**dacn·2HCl*;* 2.00 g, 10.0 mmol) was added 2-picolyl chloride hydrochloride (3.28 g, 20 mmol). To this slurry was added 2 M sodium hydroxide at room temperature in small amounts with stirring until a clear, alkaline (pH ∼ 11) solution was obtained. The aqueous solution was extracted with $CHCl_3$ (3 × 50 mL), and the organic component was dried over $MgSO_4$. A yellow oil was obtained after removal of solvent on a rotary evaporator in vacuo; it crystallized upon storing at 5°C overnight. The compound was used without further purification in the preparation of its metal complexes. Yield: 1.4 g, 45%. ^{1}H NMR ($CDCl_3$): δ 1.61 (2H, m, $NCH_2CH_2CH_2CH_2CH_2N$), 1.74 (4H, m, $NCH_2CH_2CH_2CH_2$), 2.48 (4H, s, NCH_2CH_2N), 2.70 (4H, t, $NCH_2CH_2CH_2CH_2$), 3.73 (4H, s, NCH_2py), 7.05 (2H, t, pyH), 7.46 ppm (2H, d, pyH), 7.57 (2H, t, pyH), 8.42 (2H, d, pyH). ^{13}C NMR ($CDCl_3$): δ 28.21, 28.26, 56.90, 58.13, 65.89, 122.75, 124.24, 137.26, 129.72, 161.77 ppm.

[Co(dmpdacn-*C*)(OH$_2$)](ClO$_4$)$_2$·H$_2$O and [Co(dmpdacnOH-*O*)Cl](ClO$_4$)$_2$. *Caution! Perchlorate Salts Are Potentially Explosive.* Method A. *trans*-$[Co(py)_4Cl_2]Cl\cdot 6H_2O$[22] (0.59 g, 1 mmol) was dissolved in methanol (10 mL), and a methanolic solution (2 mL) of dmpdacn (0.31 g, 1 mmol) was added. The mixture was heated to 60 °C for 30 min. After further heating on a steam bath with an equal volume of concentrated HCl for 1 h, the solution was diluted to 1 L with water and adsorbed on a cation-exchange (Dowex) column. The column was thoroughly washed with water and then eluted with 1 M HCl to remove residual Co^{2+}. Elution with 2 M HCl removed an orange band. The solution was concentrated on a rotary evaporator, and $NaClO_4$ was added. On standing, orange $[Co(dmpdacn\text{-}C)(OH_2)](ClO_4)_2\cdot H_2O$ crystallized and was collected and air-dried. (Yield: 0.48 g, 80%.) Anal. Calcd for $C_{19}H_{30}N_4Cl_2O_{10.5}Co$: C, 37.27, H, 4.61, N, 9.15, Cl, 11.58. Found: C, 36.96, H, 4.61, N, 8.69, Cl, 11.37%. ^{13}C NMR (D_2O): δ 40.23, 42.69, 56.18, 62.74, 63.78, 63.87, 64.81, 70.26, 70.91, 125.83, 126.13, 128.07, 128.59, 142.65, 143.11, 152.21, 152.56, 164.26, 165.34 ppm.

Method B. $CoCl_2\cdot 6H_2O$ (1.33 g, 5.6 mmol) was dissolved in cold water (10 mL), and an ethanolic solution (10 mL) of dmpdacn (1.86 g, 6 mmol) was added. Air was bubbled through the mixture, and it had become dark red-brown after 8 h. It was then heated on a steam bath with an equal volume of concentrated HCl for 1 h, diluted to 800 mL with water, and then adsorbed on a Dowex column. The column was thoroughly washed with water and with 1 M HCl to remove residual Co^{2+}. The red and orange bands were removed successively by elution with 2 M HCl. These solutions were concentrated in vacuo, and $NaClO_4$ and ethanol were added. On standing, the red and orange compounds crystallized. Each was collected and washed with ethanol and ether, and air-dried. Yields: 1.70 g, 45% (red); 1.86 g, 55% (orange). The orange compound proved to be the same as that obtained by method A, while the red compound was a new material, $[Co(dmpdacnOH\text{-}O)Cl](ClO_4)_2.C_2H_5OH\cdot 0.5H_2O$. Anal. Calcd for $C_{21}H_{33}N_4Cl_3O_{10.5}$-Co: C, 37.37, H, 5.08, N, 8.30, Cl, 15.76. Found: C, 37.02, H, 4.62, N, 8.37, Cl, 15.71%. ^{1}H NMR (Me_2SO-d_6): δ CH_2, 2.24 (4H, m), 2.40−3.81 (10H, m); NCH_2CH_2CH(OH), 4.50 (1H, m); NCH_2-

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Table 1. Crystallographic Data for [Co(dmpdacn-*C*)(OH_2)]$(ClO_4)_2$·H_2O and Co(dmpdacnOH-*O*)Cl]$(ClO_4)_2$·acetone

	[Co(dmpdacn-*C*)-(OH_2)]$(ClO_4)_2$·H_2O	[Co(dmpdacnOH-*O*)-Cl]$(ClO_4)_2$·C_3H_6O
formula	$C_{19}H_{29}Cl_2CoN_4O_{10}$	$C_{22}H_{32}Cl_3CoN_4O_9$
M	603.3	677.84
cryst syst	monoclinic	monoclinic
space group	*Cc* (No. 9)	$P2_1/a$
a/Å	9.1169(2)	12.78330(10)
b/Å	25.5635(6)	11.63720(10)
c/Å	11.4461(2)	18.5013(2)
β/deg	108.463(1)	102.8308(4)
V/Å^3	2530.32(9)	2683.56(4)
Z	4	4
T/K	295	200
λ(Mo Kα)/Å	0.71073	0.71073
D_c/Mg m^{-3}	1.584	1.678
μ/mm^{-1}	0.949	1
abs correction	Sortav[26]	Gaussian[27]
no. observed/unique data	5598/4592, $I > 3\sigma(I)$	7860/3948, $I > 3\sigma(I)$
no. refined params	349	326
R	0.323	0.0413
R_w	0.386	0.0475
S	1.0378	1.0678

py, 4.31 (2H, m), 4.76, 5.03 (2H, m); py*H*, 6.90 (1H, d), 7.41(1H, t), 7.76 (1H, d), 7.98 (2H, m), 8.11 (1H, t), 8.43 (1H, t), 9.27 (1H, d); CH−O*H*, 9.62 ppm (1H, br). ^{13}C NMR (Me_2SO-d_6): δ 30.70, 31.22, 54.81, 55.22, 55.77, 59.79, 64.84, 67.69, 72.88, 123.20, 125.81, 126.64, 126.93, 141.07, 142.10, 150.49, 155.11, 162.35, 163.63 ppm.

X-ray Structural Analyses. Diffraction images were measured on a Nonius Kappa CCD diffractometer. Intensity data were extracted using standard methods.[23] The structures were solved by direct methods[24,25] and refined by full-matrix least-squares procedures based on *F*.[26] The non-H atoms were refined anisotropically, and H atoms attached to C atoms were included in the models at calculated positions. H atoms of the solvating water molecule of [Co(dmpdacn-*C*)(OH_2)]$(ClO_4)_2$·H_2O were located in innerdata difference electron density maps and refined with restraints imposed on the O−H distance. These H atom locations are consistent with a sensible hydrogen-bonding network. The solvating acetone of [Co-(dmpdacnOH-*O*)Cl]$(ClO_4)_2$·C_3H_6O was observed to be highly disordered, and for the contribution of this region of the structure (169 Å^3 per unit cell), the data were modified by means of the SQUEEZE routine of PLATON.[27] The crystal data and refinement parameters are summarized in Table 1.

Results and Discussion

Preparation of dmpdacn and Its Complexes. 1,4-Diazacyclononane (dacn**)** was prepared using the methods developed by Richman and Atkins for 1,4,7-triazacyclononane.[17,28] The disodium salt of ditosyl-ethylenediamine

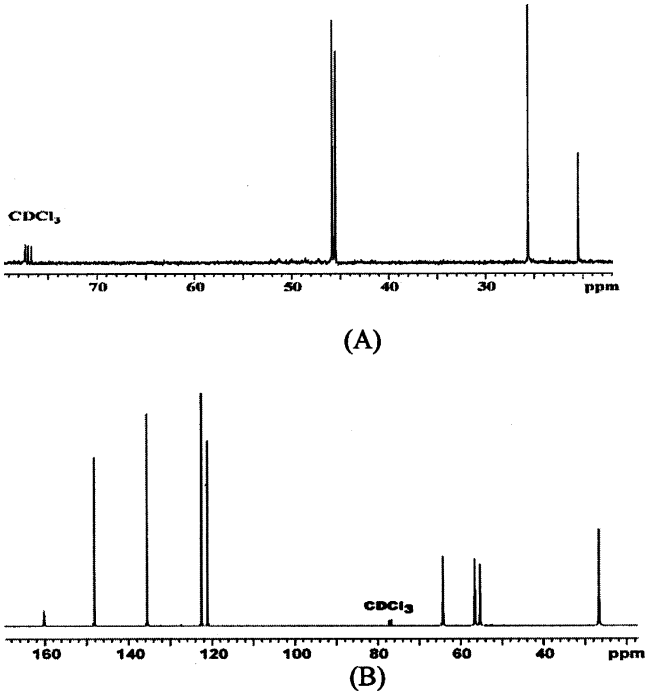

Figure 2. ^{13}C NMR spectra of dacn (A) and dmpdacn (B) in $CDCl_3$.

was condensed with 1,5-bis(*p*-tolylsulfonato)pentane (pndt) to obtain *N*,*N*′-ditosyl-1,4-diazacyclononone (dacndt) which was then deprotected by refluxing in 30% hydrobromic acid/acetic acid. ^{13}C and ^{1}H NMR data for the isolated product were consistent with the reported data.[21] There was evidence for the presence of some cyclic 1,4,10,13-tetraaza-cyclooctadecane (taon) in some batches. A cation-exchange isolation procedure was developed to remove this side product; $dacnH_2^{2+}$ elutes first followed by and well separated from $taonH_4^{4+}$.

The synthetic routes to the macrocyclic ligand dmpdacn and its complexes are summarized in Scheme 2. These followed the procedures for the syntheses of the analogous ligands 1,4-bis(2-pyridylmethyl)-1,4,7-triazacyclononane (dmptacn)[29] and 4,7-bis(2-pyridylmethyl)-4,7-diaza-1-oxa-cyclononane (dmpdocn).[30]

The ^{13}C NMR spectra for the free bases are shown in Figure 2. They show 4 and 10 signals, respectively. The central carbon γ to nitrogen on the dacn ring has half intensity and has the highest field chemical shift since it is furthest from the nitrogen. The highest field peak in Figure 2B comprises two accidentally anisochronous peaks: the carbons β and γ to the amine nitrogen in the dacn ring.

The cobalt(III) complexes were prepared either by aerial oxidation of $CoCl_2$·$6H_2O$ in the presence of free ligand or by direct reaction of *trans*-[Co(py)$_4$Cl$_2$]Cl·$6H_2O$ with the free amine in warm methanol. Orange [Co(dmpdacn-*C*)(OH_2)]-$(ClO_4)_2$·H_2O was the sole product from the second method, but an additional (red) material was isolated in the oxidation synthesis. Both complexes were purified by ion-exchange

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(29) Spiccia, L.; Fallon, G. D.; Grannas, M. J.; Nichols, P. J.; Tiekink, E. R. T. *Inorg. Chim. Acta* **1998**, *279* (2), 192.
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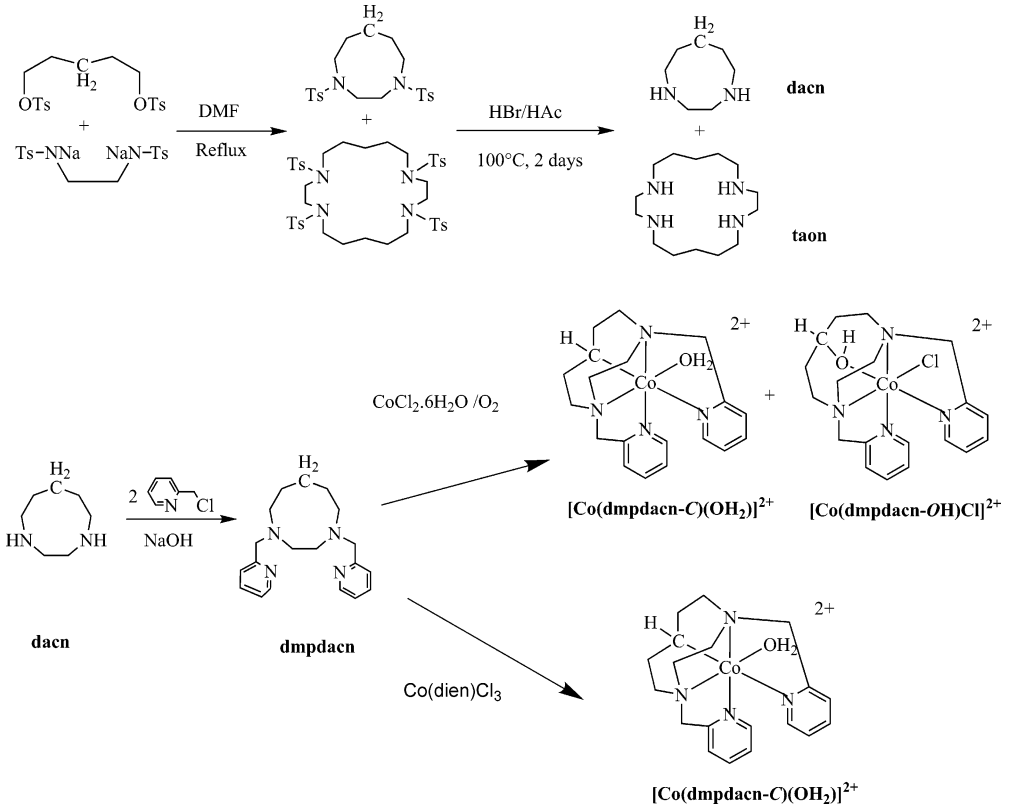
Scheme 2. Synthetic Routes to Dmpdacn and the Co(III) Complexes of Dmpdacn and DmpdacnOH



chromatography, and crystallized as perchlorate salts. The orange and red compounds had the same number of signals in their ^{13}C NMR spectra. Microanalyses and NMR data supported the empirical formula [Co(dmpdacn-*C*)(OH_2)](ClO_4)$_2$·H_2O for the orange complex.[31] The red compound proved to be [Co(dmpdacnOH-*O*)Cl](ClO_4)$_2$;[32] the −CH$^-$− in the orange compound had become −CH(OH)−, and the new ligand is oxygen rather than carbon bound, consistent with our earlier analogous observation for the daedacn ligand bound to cobalt.[33,34]

Characterization of [Co(dmpdacn-*C*)(OH_2)](ClO_4)$_2$·H_2O. Nineteen distinct signals are observed in the ^{13}C NMR spectrum of [Co(dmpdacn-*C*)(OH_2)](ClO_4)$_2$·H_2O (Figure 3A), 7 resonances between δ 40.23 and 64.81 ppm (6 for the methylene carbons and 1 methine on the dacn backbone), 2 resonances at δ 70.26 and 70.91 ppm for the methylene carbons on the pyridyl arms, and 10 resonances between δ 120 and 170 ppm for the pyridyl carbons. The cation is asymmetric. In contrast, the ^{13}C spectrum of uncoordinated dmpdacn shows only 10 resonances. This symmetry is lost in the Co(III) complex indicating that the water coordinates *cis* to the bonded γ-carbon on the dacn ring, as depicted for isomer A (*asym*) shown in Figure 4. Isomer B (*sym*) that has σ symmetry is the only other possible isomer; the NMR data eliminate this possibility.

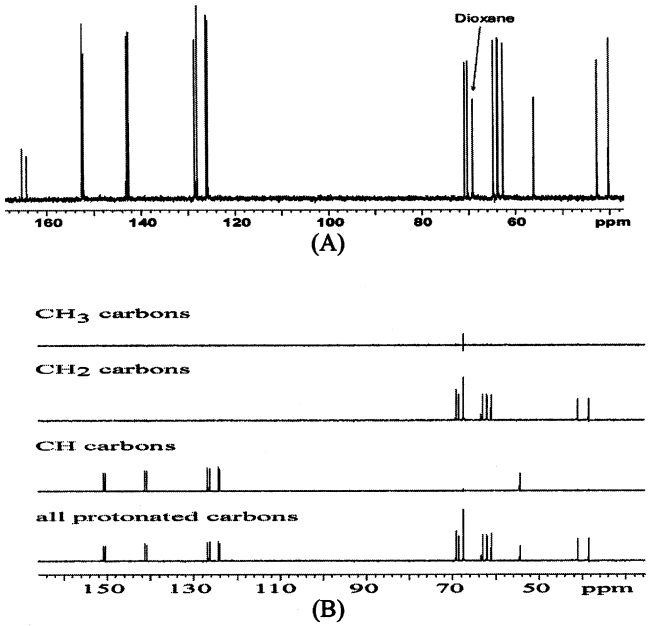


Figure 3. ^{13}C (A) and ^{13}C DEPT (B) NMR spectra of *asym*-[Co(dmpdacn-*C*)(OH_2)](ClO_4)$_2$ in D_2O.

From the ^{13}C DEPT NMR spectrum of [Co(dmpdacn-*C*)(OH_2)]$^{2+}$ (Figure 3B), the resonance at δ 56.20 ppm can be assigned to the cobalt-bound carbon atom, as this is the only aliphatic CH group, and its existence is direct evidence that the alkyl group is deprotonated. The structure has been

(31) The X-ray structure established 1 lattice water per Co whereas the elemental analyses better fitted 1.5H_2O. Possibly there are both mono- and dihydrates in the bulk crystal sample.
(32) The X-ray structure was carried out on a sample derived from aqueous acetone and shows 1 acetone per Co. The elemental analysis was performed on a sample derived from aqueous ethanol, and the lattice contains one ethanol and a half water per Co.
(33) Jackson, W. G.; Zhou, X.; Willis, A. C.; Edwards, A. Results to be published.
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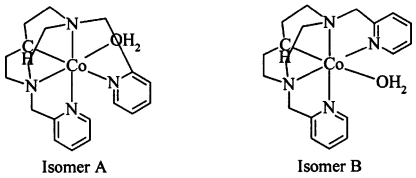

Figure 4. The two possible isomers for $[Co(dmpdacn\text{-}C)(OH_2)]^{2+}$.

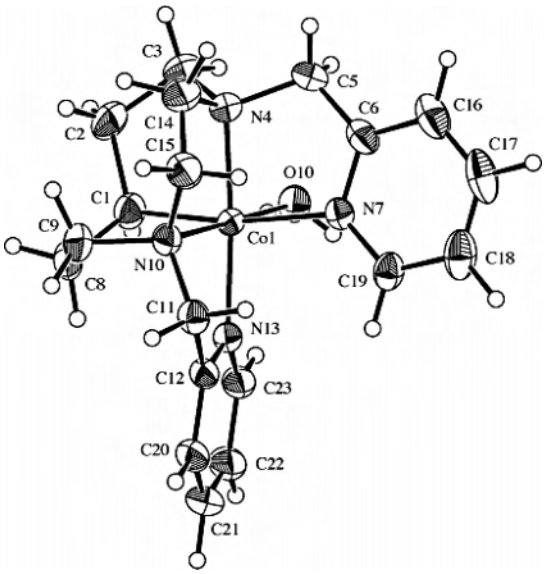

Figure 5. Structure of the *asym*-$[Co(dmpdacn\text{-}C)(OH_2)]^{2+}$ cation. Anisotropic displacement parameters are shown at the 30% probability level.

confirmed by the X-ray crystallographic study. On coordination, the ^{13}C resonance frequency of the carbanion donor undergoes a sharp downfield shift, ca. 28 ppm, as observed for another C-bonded macrocyclic complex.[16] The reduced intensity of this signal is consistent with the smaller nOe expected due to the loss of a proton, and direct attachment to quadrupolar Co. ^{13}C resonances for Co-bonded C atoms are usually weak or undetected.[10,35]

The downfield shift for the carbanion carbon is comparable to that observed for a number of related macrocyclic compounds containing Co−C linkages but is in contrast to the marked upfield shift for compounds containing mixed amine−carboxylate donor sets where it is argued[8,9,36] the Co−C linkage is ionic in nature. At this stage, we do not understand the reason for the constrasting behavior.

The structure of the $[Co(dmpdacn\text{-}C)(OH_2)]^{2+}$ cation is shown in Figure 5. The salt crystallizes in the space group *Cc* (monoclinic) with four formula units per unit cell (Figure 6S, Supporting Information). The central γ carbon on the dacn backbone of the ligand is confirmed to bind to the metal ion, analogous to the NH group in the tacn derivative dmptacn. The chelate rings are retained in the preferred five-membered forms with the formation of a Co−C bond at this γ position. The aqua group is *cis* to the coordinated γ carbon (isomer A, Figure 4). Structural parameters are recorded in Tables 2S and 3S (Supporting Information). The Co−O10 bond length (1.963(2) Å) is similar in length to other Co−O bonds, for example, 1.945(6) Å in $[Co(dmptacn)(OH_2)](ClO_4)_2\cdot H_2O$.[37] Also, the Co−N(dacn) and Co−N(py) distances (1.932(3) and 1.949(7)/1.930(3) Å, respectively) compare favorably to the corresponding distances in $[Co(dmptacn)(OH_2)](ClO_4)_2\cdot H_2O$ (1.935(7) and 1.906(7)/1.936(7) Å, respectively). The length of the Co−C1 bond (1.968(3) Å) in $[Co(dmpdacn\text{-}C)(OH_2)](ClO_4)_2\cdot H_2O$ is slightly longer than the Co−C bond (1.945(7) Å) in $[Co(tmptacn\text{-}C)](ClO_4)_2$[33] but still lies within the range 1.94−2.05 Å found in alkyl−cobalt(III) species where the coordinated alkyl carbon is part of a polydentate ligand.[34] The strong *trans* influence of the alkyl group σ-bonded to the metal atom is clear: the Co−N7 bond 2.069(4) Å, *trans* to the Co−C1 bond, is significantly longer than usual pyridine-N−cobalt(III) bonds; the average of the remaining three Co−N distances is 1.937 Å. The length of the Co−N7 bond suggests that it is relatively weak and probably also relatively labile. A similar *trans* influence has been noted for a number of Co(III) complexes containing Co−C σ-bonds including $[Co(tmptacn\text{-}C)](ClO_4)_2$.[16] We note evidence for a possible *cis*-Co−C influence, with the Co−OH_2 bond *cis* to Co−C lengthened. Further, the bonded water is unusually labile and is substituted "instantly" by DMSO in $Me_2SO\text{-}d_6$ (NMR).

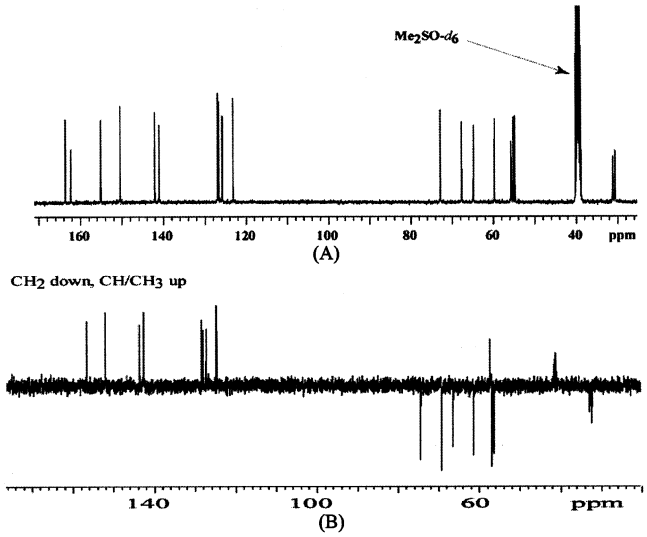

Figure 6. ^{13}C (A) and ^{13}C DEPT (B) NMR spectra of *asym*-$[Co(dmpdacnOH\text{-}O)Cl](ClO_4)_2$ in $Me_2SO\text{-}d_6$.

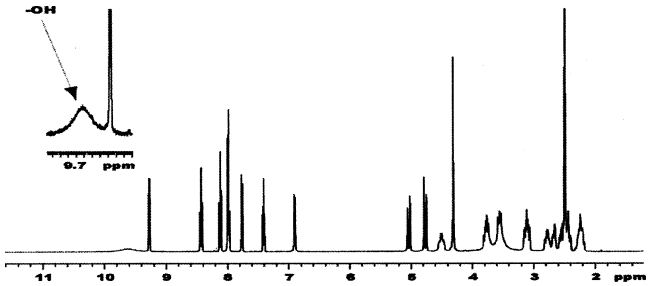

Figure 7. ^1H NMR spectrum of *asym*-$[Co(dmpdacnOH\text{-}O)Cl](ClO_4)_2$ in $Me_2SO\text{-}d_6$.

(35) Zhou, X.; Day, A. I.; Willis, A. C.; Jackson, W. G. *Chem. Commun.* **2003**, 2386.
(36) Hu, C.; Chin, R. M.; Nguyen, T. D.; Wagenknecht, P. S.; Nathan, L. C. *Inorg. Chem.* **2003**, *42*, 7602.
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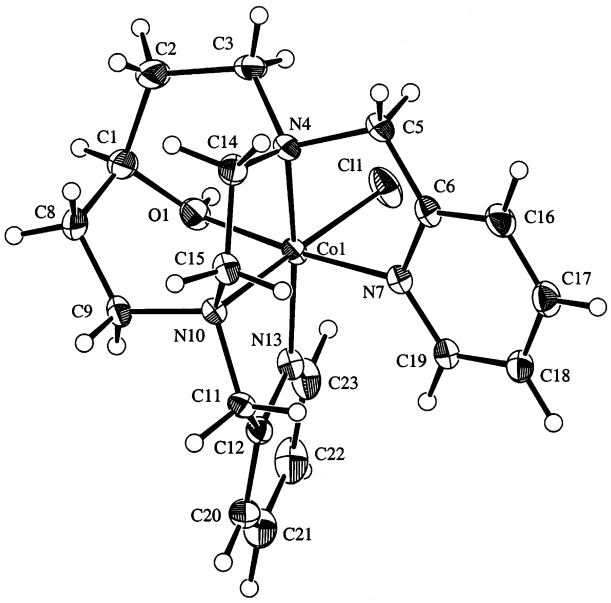


Figure 8. Structure of the cation *asym*-[Co(dmpdacnOH-*O*)Cl]$^{2+}$ with labeling of selected atoms. Anisotropic displacement parameters are at the 30% probability level.

We have also been unable to isolate any Co−Cl complexes for carbon-bonded macrocyclic ligand complexes from aqueous solution, presumably because of the lability of the chloro complex that rapidly hydrolyzes.

Characterization of [Co(dmpdacnOH-*O*)Cl](ClO$_4$)$_2$. The ^{13}C and ^{13}C DEPT NMR spectra for [Co(dmpdacnOH-*O*)Cl](ClO$_4$)$_2$ are shown in Figure 6. The ligand is coordinated to Co(III) in the asymmetric configuration. The DEPT spectrum unambiguously demonstrates that the resonance signal at δ 55.77 ppm is the CH group, Figure 6B. The existence of a CH group rather than $-CH_2-$ shows that the hydrogen abstraction has occurred during the oxygenation process, and this is also reflected in the ^{1}H NMR spectrum, Figure 7. The broad proton resonance at very low field (δ 9.62 ppm) is assigned to the hydroxyl proton; it exchanges upon addition of D_2O. The UV−vis spectrum is typical for a $Co^{III}N_4OCl$ chromophore (Figure 9), and the *X*-ray structural determination verifies that the ligand has been oxidized along with the metal ion during the oxygenation process, with the insertion of a new donor atom.

[Co(dmpdacnOH-*O*)Cl](ClO$_4$)$_2$·acetone crystallizes in the monoclinic space group $P2_1/a$ with four formula units per unit cell (Figure 10S, Supporting Information). The molecular cation is illustrated in Figure 8, and structural parameters are given in Tables 4S and 5S (Supporting Information). Important structural features are the Co−N(dacn) distances Co−N4 (1.975(3) Å) and Co−N10 (1.968(2) Å) which are significantly longer than in the corresponding alkyl−cobalt(III) complex [Co(dmpdacn-*C*)(OH$_2$)](ClO$_4$)$_2$·H$_2$O and other Co(III) complexes of pendant-arm ligands[16,37] derived from tacn. In contrast, the Co−N(C$_5$H$_4$N) distances (Co−N7 1.939(2) Å and Co−N13 1.949(3) Å) are short but still within the normal range 1.94−2.05 Å.[38,39] The Co−O1 bond length (1.922(2) Å) in [Co(dmpdacnOH-*O*)Cl](ClO$_4$)$_2$ is very similar to the Co1−O1 (1.9274(18) Å) bond length in the related complex [Co(daedacnOH-*O*)Cl](ClO$_4$)$_2$ (dae = di-2-aminoethyl).[33]

Base Hydrolysis of *asym*-[Co(dmpdacnO-*O*)Cl]$^+$. The OH proton of [Co(dmpdacnOH-*O*)Cl]$^{2+}$ is acidic (pK_a ca. 6) and is totally removed under the basic conditions employed for the kinetics to form [Co(dmpdacnO-*O*)Cl]$^+$, as shown in Scheme 3. This is evidenced by the UV−vis

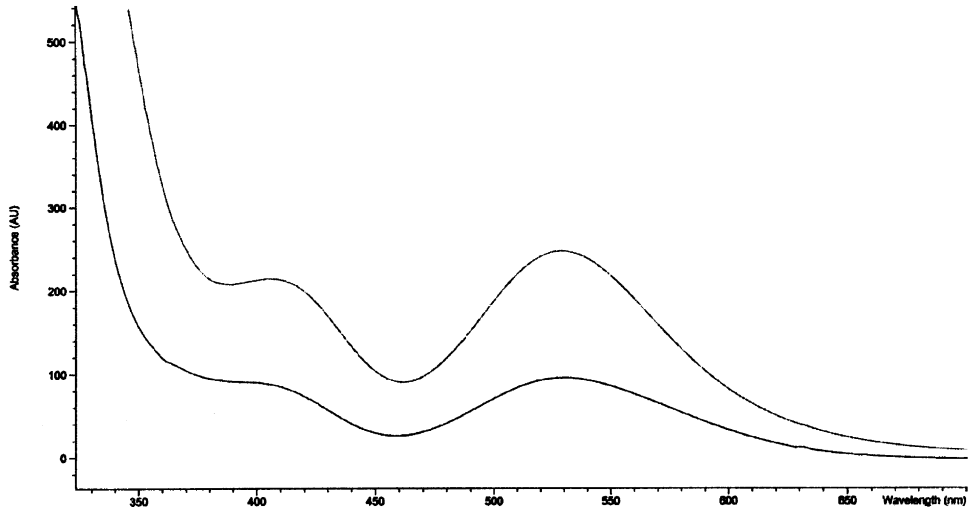
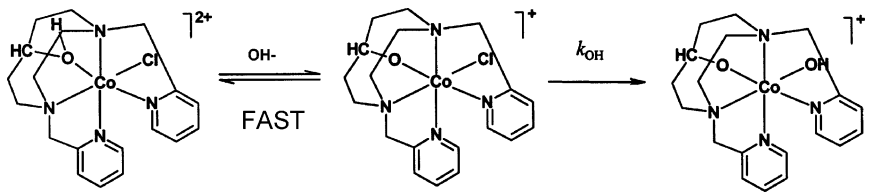


Figure 9. Absorption spectra of *asym*-[Co(dmpdacnOH-*O*)Cl]$^{2+}$ (lower) and *asym*-[Co(dmpdacnO-*O*)Cl]$^+$ (upper) in H_2O.

Scheme 3. Base-Catalyzed Hydrolysis of *asym*-[Co(dmpdacnO-*O*]$^+$



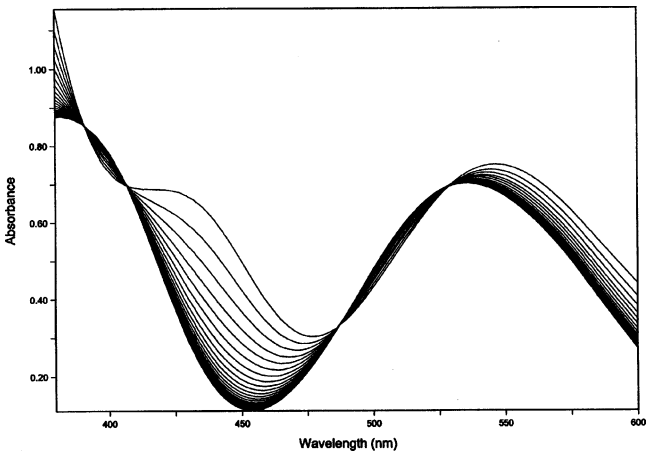


Figure 10. Changes in the absorption spectra with time for the base hydrolysis of $[Co(dmpdacnO\text{-}O)Cl]^+$.

absorption spectra that reflect the reversible equilibrium in acid and base, Figure 9.

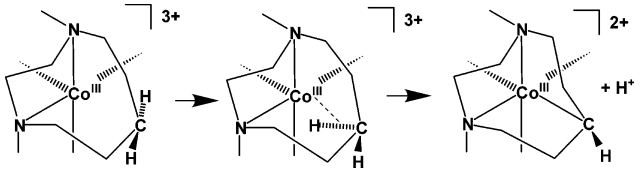
The typical changes in the absorption spectra for *asym*-$[Co(dmpdacnO\text{-}O)Cl]^+$ as it reacts in base are presented in Figure 10; the product is *asym*-$[Co(dmpdacnO\text{-}O)OH]^+$.

The sharp isosbestic points are consistent with a clean reaction through to the corresponding hydroxo complex. The plot of k_{obsd} versus $[OH^-]$ is shown in Figure 13S (Supporting Information), which follows the equation of the form $k_{obsd} = k_s + k_{OH}[OH^-]$.

The intercept represents the rate constant for the spontaneous hydrolysis pathway, while the slope gives k_{OH} for the base-catalyzed hydrolysis route. The low value for the latter (ca. 8×10^{-3} M^{-1} s^{-1}), compared to a typical 2+ chloropentaaminecobalt(III) complex, is consistent with the low charge (1+), hence low acidity, and it also reflects the lack of any acidic NH proton. Indeed, the compound must hydrolyze by α-pyridyl deprotonation[40] because there is no NH center. For *asym*-$[Co(dmpdacnOH\text{-}O)Cl]^{2+}$ undergoing acid hydrolysis, the measured value of k_s is 1.08×10^{-3} s^{-1}, which is smaller than the value derived from the intercept in Figure 13S, 1.48×10^{-3} s^{-1}; however, the latter corresponds to aquation of the different O-deprotonated species *asym*-$[Co(dmpdacnO\text{-}O)Cl]^+$. It is apparent that the *cis*-alkoxy group (vs *cis*-alcohol) does not provide much labilization for the acid hydrolysis reaction.

Mechanism of Alkyl−Cobalt(III) Bond Formation. There was an expectation that the free dmpdacn ligand, which has a conventional N_4 donor set, could become pentadentate. The ligand has a $-CH_2-$ stereochemically positioned such that deprotonation, with subsequent carbanion coordination, could lead to an N_4C donor set and a metal complex structure with all five-membered rings. Indeed it does, and no added base is required (unlike the case for tmptacn[16]): it occurs under neutral conditions, despite the enormously low acidity constant for the γ-CH_2- center involved ($pK_a > 16$). This

Scheme 4. Free Alkane to Agostically Bonded Metal-Carbanion Transformation



particular CH is several C−C bonds remote from the electron withdrawing NH center, and clearly the activation is not driven by the electron withdrawing capacity of the NH center, as might have been adjudged from the tmptacn chemistry[16] where the α-CH_2 center was involved.

The result suggests that some initial activation is involved to overcome the low acidity problem, perhaps via the alkane−metal "agostic" interaction, Scheme 4. Prototype metal ion−alkane complexes have been spectroscopically characterized in the solid phase, but recently, their existence (and high reactivity) has been established by NMR studies in solution.[41] The oxidation state at which the M−C bond forms is unknown.

The reaction shown in Scheme 1 can be quantitatively reversed in acid by heating (Scheme 5).[16] We believe the strain in the four-membered ring contributes to this instability in acid solution. By contrast, the present alkyl complex $[Co(dmpdacn\text{-}C)(OH_2)]^{2+}$ is remarkably stable toward ring opening in acid. This species involves all five-membered rings, and the coordinated carbanion is within a macrocycle, which we believe renders it kinetically stable to ring opening in acid.

Mechanism of Ligand Oxidation. Reaction of the free macrocyclic ligand dmpdacn with *trans*-$[Co^{III}(py)_4Cl_2]Cl$ forms the alkyl−cobalt(III) complex *asym*-$[Co(dmpdacn\text{-}C)(OH_2)]^{2+}$ exclusively. When acidic or basic solutions of the alkyl−cobalt complex $[Co(dmpdacn\text{-}C)(OH_2)]^{2+}$ are vigorously purged with oxygen, nothing changes over a 24 h period. However, aerial oxidation of cobalt(II) solutions containing dmpdacn yields not only $[Co(dmpdacn\text{-}C)(OH_2)]^{2+}$ but also $[Co(dmpdacnOH\text{-}O)Cl]^+$. Here the bound carbon has undergone a $2e^-$ oxidation to an alcohol, the oxygen of which becomes the bonded atom. The carbon is also required to invert for this to happen. The alcohol oxygen is likely derived from the oxygen also used to raise Co(II) to Co(III), and not from solvent water. This is consistent with the result reported by Irisa et al.,[42] that the hydroxy oxygen α to an amine of an amino acid originates from the molecular oxygen. The insertion of oxygen into M−C σ bonds in a palladium system has also been documented,[43−45] but observation of such a reaction for C−Co(III) is only the second example (the analogue of dmpdacn which has $-CH_2-CH_2-$ linked "arms" being the first[33,34]).

(38) Data extracted from the many structural references given in D. A. House's article (ref 39).
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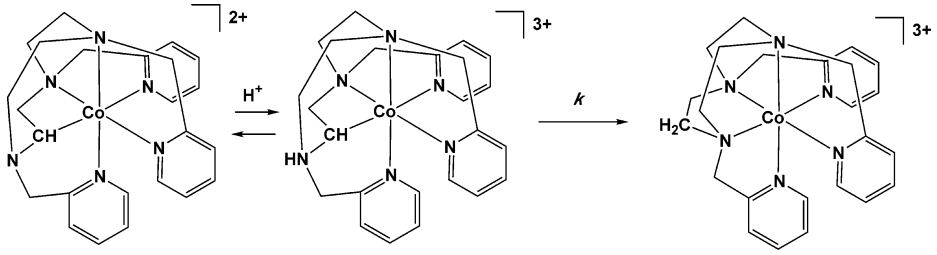
Scheme 5. C- to N-Bonded Reverse Rearrangement in Aqueous Acid



Dioxygen complexes of Co(III) form readily in aqueous solutions of Co(II) salts and amine ligands in the presence of O_2 and are usually binuclear with a μ-peroxo bridge.[46,47] Superoxo bridged dinuclear ions can also form under such conditions. Less common but nonetheless well-known cobalt(III)−peroxide structures involve sideways bonded peroxo (O_2^{2-}) complexes formed from Co(I) + ligand + O_2, or Co(III) + O_2^{2-},[48] and a peroxo cobalt(III) complex involving simultaneous bridging and sideways bonding.[49] The early dioxygen chemistry has been reviewed by Martell[46] and Williams.[50] Three types of reactions were described by which cobalt dioxygen complexes become converted irreversibly to mononuclear cobalt(III) complexes. Of these, one involves oxidative dehydrogenation of the coordinated ligand by coordinated dioxygen, and another, oxygen insertion into the coordinated ligand. The factors that control the tendencies of cobalt(III) peroxo complexes to undergo such reactions are not well understood, and it is still not possible to predict the course of reaction. Considerably more is known about such reactions and the related chemistry of imines formed from bound amines, for the ruthenium (and osmium) metal ion systems where M(IV) is implicated as the active metal ion oxidation state;[51−53] this chemistry has been reviewed.[54]

Since the Co(III)−alkyl complex is known to be resistant to oxidation at carbon, then the oxidation at carbon must occur either prior to or synchronous with the Co(II) to Co(III) process. Further detailed mechanistic speculation is unwarranted until the origin of the hydroxy oxygen is confirmed.

Summary

The ligand 1,4-bis(2-pyridylmethyl)-1,4-diazacyclononane, dmpdacn, forms alkyl−cobalt(III) complexes under extremely mild conditions with an (amine)$_4$(CH$^-$) donor set

Spectroscopic and structural analyses show that the C−H bond activation has occurred on the carbon γ to nitrogen on the dacn portion of the ligand, at the same position of the −NH− of the dmptacn analogue. Indeed, the two complexes *asym*-[Co(dmptacn)(OH$_2$)]$^{3+}$ and *asym*-[Co(dmpdacn-*C*)(OH$_2$)]$^{2+}$ are isoelectronic and have closely related solid-state structures (Figure 5 and ref 34). The alkyl−Co(III) complex has a Co−C bond distance of 1.966(6) Å, which is comparable with the Co−C bond of the dmptacn rearranged product[16] of 1.945(7) Å.

The [Co(dmpdacn-*C*)(OH$_2$)]$^{2+}$ complex is the sole product derived from a cobalt(III) substrate, but when the ligand is aerated in the presence of Co(II) salts, a new hydroxylated ligand complex [Co(dmpdacnOH-*O*)Cl]$^{2+}$ is formed along with the dmpdacn carbanion complex. The bonding has changed from C to O which requires the carbanion to invert, oxidize, and add a proton; accompanying these changes are increases in the associated chelate ring sizes. This appears to be the first report of alkyl−Co(III) and hydroxylated alkyl−Co(III) complexes formed in one process.

The first step in the hydrolysis kinetics of [Co(dmpdacnOH-*O*)Cl]$^{2+}$ is the (rapid and reversible) removal of the proton of the hydroxyl group on addition of base, to form the alkoxy complex [Co(dmpdacnO-*O*)Cl]$^+$, followed by rate determining loss of Cl$^-$. The *asym* stereochemistry is retained in the ligand substitution process. In acid solution, the OH proton is retained, and slow hydrolysis of Cl$^-$ is observed. The value for k_{OH} for the alkoxy complex is finite rather than zero, indicating deprotonation at the $-CH_2$ α to a pyridyl since there are no NH centers. The value is comparable to that for *asym*-[Co(dmpmetacn)Cl]$^{2+}$ (0.70 M^{-1} s^{-1}) which has been established[40] to base hydrolyze by this unique pseudo-aminate mechanism.

Acknowledgment. We thank the microanalytical unit at the Research School of Chemistry, Australian National University. X.Z. is grateful to UNSW@ADFA for a UCPRS scholarship. Financial assistance from the Australian Research Council is also gratefully acknowledged.

Supporting Information Available: Bond lengths (Table 2S), bond angles (Table 3S), unit cell diagram (Figure 6S) for *asym*-[Co(dmpdacn-*C*)(OH$_2$)](ClO$_4$)$_2$·H$_2$O; rate plot (Figure 13S); bond lengths (Table 4S), bond angles (Table 5S), and unit cell diagram (Figure 10S) for *asym*-[Co(dmpdacnOH-*O*)Cl](ClO$_4$)$_2$·acetone. Crystallographic files in CIF format for *asym*-[Co(dmpdacn-*C*)(OH$_2$)](ClO$_4$)$_2$·H$_2$O and *asym*-[Co(dmpdacnOH-*O*)Cl]ClO$_4$.C$_3$H$_6$O. This material is available free of charge via the Internet at http://pubs.acs.org.

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