leading to high reactivity for Fe$^+$($^6$D) at low kinetic energies in these systems. Indeed, ICR and FTICR studies show that larger alkanes do react with Fe$^+$ in efficient exothermic reactions.[3-5]

Finally, how do we reconcile the behavior observed here for the exothermic reactions with the ideas developed for understanding the reactions of transition-metal ions with dihydrogen? The reactivity "rules" originally suggested by Elkind and Armentrout[11,12,17] for $H_2$ reactions are *diabatic* rules. The present observations illustrate that they break down when there is sufficient spin-orbit coupling to allow reactants to follow the adiabatic PESs.

## Summary

We present a detailed study of the reactions of Fe$^+$ with methane, ethane, and propane. The populations of Fe$^+$ electronic states are manipulated by using different ion sources. Analysis of the data yields the state-specific behavior of the $^6$D ground and $^4$F first excited states of Fe$^+$. From the state-resolved behavior of the ions, we can deduce a wealth of information about the reaction thermochemistry and dynamics of these systems.

The threshold behavior of the endothermic channels enables us to determine values for Fe-H, Fe$^+$-H, Fe$^+$-$CH_3$, and Fe$^+$-$C_2H_5$ bond strengths. The bond strengths reported here for the cationic species differ by about 10 kcal/mol from previous determinations.[7] The differences lie primarily in our ability to determine the state-specific reactivity. In all cases, we find that it is the first excited state of the ion that dominates the observed reactivity at the observed threshold.

The ground state is much less reactive than the first excited state in all endothermic reactions studied here despite being only 0.25 eV lower in energy. In this respect, the behavior of Fe$^+$ with small alkanes is much like its behavior with hydrogen. The enhanced reactivity of the first excited state is easily rationalized by simple molecular orbital arguments. These arguments predict, and the data confirm, that the ground state ion will react via an inefficient impulsive process. For reaction with $CH_4$, as with $H_2$, the first excited state appears to react via a direct mechanism. For the larger alkanes, insertive intermediates appear to be thermodynamically allowed. The products observed are most easily explained via such a mechanism at low energy, although it appears that more direct mechanisms may be involved at higher kinetic energies. Overall, *the electronic considerations for C-H and C-C bond activation appear to be directly analogous with those discussed previously for H-H activation.*[12]

For exothermic reactions of Fe$^+$ with ethane and propane, it is the ground state that is more reactive at low energies. At higher energies, the first excited state is once again more reactive. This difference in behavior is attributed to a crossing of quartet and sextet surfaces which is avoided due to spin-orbit mixing at low kinetic energy but permitted at higher energy. Simple theories such as the Landau-Zener formalism are unable to quantitatively account for the behavior of the system. Finally, the branching ratio between the two exothermic reactions of Fe$^+$ and propane is independent of electronic and kinetic energy. This shows that the branching point occurs after the surface crossing.

The type of surface crossing evident in the present study should be a common feature of ionic and neutral transition-metal systems, due to the large number of electronic states that are generally involved. Indeed, such surface interactions have been postulated in a number of other systems.[6,10,13,22,52] The present results provide hope that quantitative information concerning these spin-orbit interactions can be obtained.

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# Neutral Square Planar Cobalt(III) Complexes

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**Abstract:** The monoanionic square planar cobalt(III) complex, [$PPh_4$][Co($\eta^4$-HMPA-DMP)] (**4**) ($H_4$HMPA-DMP = 2,4-bis(2-hydroxy-2-methylpropanamido)-2,4-dimethyl-3-oxopentane), has been prepared and characterized by $^1$H NMR, solid state and solution magnetic properties, X-ray crystallography, and IR spectroscopy. Compound **4**, and related anionic square planar cobalt(III) complexes, can be alkylated at an amido-*N* oxygen atom to afford the first examples of neutral square planar cobalt(III) complexes. These species have been characterized by $^1$H NMR, solid-state magnetic properties, mass spectroscopy and elemental analysis, a solution molecular weight determination, and IR spectroscopy. All of the compounds exhibit well-resolved paramagnetically shifted $^1$H NMR spectra. Depending upon the donor properties, certain PAC ligands afford stable octahedral cobalt(III) complexes whereas others produce the coordinatively unsaturated square planar complexes. This is of potential significance in the search for new inorganic reagents for atom-transfer and inner-sphere oxidations.

The incompatibility of the majority of the ligands of homogeneous inorganic chemistry with strongly oxidizing media is a limitation confronting the development of selective oxidizing agents. In the past several years our attention has been focused on the design of oxidation resistant ligands. We have shown that it is possible to prepare strongly oxidizing, solution stable complexes by identifying building blocks for polyanionic chelating (PAC) ligands that are compatible with strongly oxidizing media.[2] In the course of this work we have discovered ligand complements that convey unusual chemical and physical properties to metal complexes such as the formation of nonplanar amido-*N* ligands and have identified causative structural and bonding features.[3]

One significant property-determining feature of a ligand complement is the donor capacity, i.e., the ability of a ligand complement to transfer electron density to a metal center in a given oxidation state relative to all other ligand complements of the same topology. An important effect of changing ligand donor capacities can be illustrated by an unusual feature of the coordination chemistry of cobalt(III). The vast majority of cobalt(III) complexes are octahedral. However, when the ligand complement consists of four strongly $\sigma$-donating anions the axial Lewis acidity

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**Table I.** $^1$H NMR (400 MHz) Data for Square Planar Cobalt(III) Complexes and PAC Ligands[i]

| compound | O–C$H_3$ | O–C$H_2$– | $CH_2$–C$H_3$ | OC(C$H_3$) | –NC(C$H_3$) | N$H$ | O$H$ | $H_{Ph}$ | | | | $[PPh_4]^+$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $H_4$HMPA–DMP[a] | | | | 1.4<br>12 H | 1.6<br>12 H | 7.5<br>2 H | 3.0[g]<br>2 H | | | | | |
| $H_4$HMPA-B[a] | | | | 1.4<br>12 H | | 9.3[g]<br>2 H | 4.9[g]<br>2 H | 7.6, 7.2[h]<br>2 × 2 H | | | | |
| Na[Co($\eta^4$-HMPA-DMP)], **3**[b] | | | | 8.5<br>12 H | 5.3<br>12 H | | | | | | | |
| *c* | | | | 12.3<br>12 H | 1.2<br>12 H | | | | | | | |
| [PPh$_4$][Co($\eta^4$-HMPA-DMP)], **4**[b] | | | | 10.9<br>12 H | 4.1<br>12 H | | | | | | | 7.8–7.6<br>20 H |
| *d* | | | | 10.9<br>12 H | 3.4<br>12 H | | | | | | | 6.9–7.0<br>20 H |
| [PPh$_4$][Co($\eta^4$-HMPA-B)], **5**[e] | | | | 10.0<br>12 H | | | | 2.1, [g] −16.8[g]<br>2 × 2 H | | | | 6.9–6.9<br>20 H |
| Co($\eta^4$(Me)HMPA-DMP), **6**[d] | 45.2<br>3 H | | | 21.1, 6.7, 1.8, −0.3<br>4 × 6 H | | | | | | | | |
| Co($\eta^4$-(Me)HMPA-B), **7**[e] | 79.1<br>3 H | | | −7.5, 16.0<br>2 × 6 H | | | | 18.6[g]<br>1 H | −17.1[g]<br>1 H | −39.2[g]<br>1 H | −58.6[g]<br>1 H | |
| Co($\eta^4$-(Et)HMPA-DMP), **8**[f] | | 16.8<br>2 H | −8.3<br>3 H | 20.1, 7.4, 3.7, 0.1<br>4 × 6 H | | | | | | | | |
| Co($\eta^4$-(Et)HMPA-B), **9**[e] | | 50.9<br>2 H | 3.0<br>3 H | 16.4, −6.16<br>2 × 6 H | | | | 18.5[g]<br>1 H | −17.2[g]<br>1 H | −38.1[g]<br>1 H | −57.4[g]<br>1 H | |

[a] Reference 7. [b] Measured in $(CD_3)_2CO$. [c] Measured in $D_2O$. [d] Measured in $CDCl_3$. [e] Measured in $CD_2Cl_2$. [f] Measured in $C_6D_6$. [g] Broad. [h] AA′BB′ pattern. [i] All shifts are slightly concentration dependent (±0.2 ppm).

can be reduced to the point that the rare square planar geometry becomes accessible.[4,5] Square planar cobalt(III)[4f] complexes were first reported in 1966,[4b] and, to our knowledge, the small number of reported examples are all monoanionic. Here we describe the use of strongly donating polyanionic chelating ligands to afford the first examples of neutral square planar cobalt(III) complexes.

An additional point is implicit in this study. Ligand design can be used to produce vacant coordination sites on later transition-metal centers that are usually coordinately saturated. This is of potential value in the search for new homogeneous catalysts for inner-sphere and atom-transfer oxidations. Strong binding of chemically nonactive ligands to give closed shell complexes might be expected to inhibit such reactions.

## Experimental Section

**Materials.** Cyclohexane (practical grade, Matheson, Coleman, and Bell), acetone (EM Science), hexanes (ACS reagent grade, Aldrich), diethyl ether (Baker), ethanol (USI), and pentane (EM Science) were used as received. Benzene (Aldrich, thiophene free) and tetrahydrofuran (EM Science) were distilled from sodium benzophenone ketyl before use. Dichloromethane (EM Science) was distilled from calcium hydride before use. Trimethyloxonium tetrafluoroborate (Alfa), anhydrous cobalt acetate (Alfa), triethyloxonium tetrafluoroborate (Aldrich, 1.0 M solution in $CH_2Cl_2$), silver tetrafluoroborate (Aldrich), tetraphenylphosphonium chloride (Aldrich, 98%), and sodium hydroxide were used as received. Ethyl iodide was purified according to standard procedures before use.[6] Analytical thin-layer chromatography plates were 250 μm silica gel GF (Analtech).

**Physical Measurements.** $^1$H NMR spectra were recorded at 400 MHz on a JEOL GX-40 spectrometer. $^1$H chemical shifts are reported in ppm ($\delta$) vs Me$_4$Si with the solvent ($CDCl_3$ $\delta$ 7.24 ppm, $CD_2Cl_2$ $\delta$ 5.32 ppm, $(CD_3)_2CO$ $\delta$ 2.04 ppm, $C_6D_6$ $\delta$ 7.15 ppm) as internal standard. Infrared spectra were recorded on a Beckman IR 4240 spectrophotometer as Nujol mulls or on a Mattson Sirius 100 FTIR spectrophotometer as $CH_2Cl_2$ solutions in KBr cells of 0.1-mm path length. Mass spectra and elemental analysis data were obtained at the Caltech analytical facility. Magnetic susceptibility measurements were conducted on solid samples at room temperature on a Cahn Faraday magnetic susceptibility balance equipped with a permanent magnet. The apparatus was calibrated with Hg[Co(SCN)$_4$]. Susceptibilities were corrected for diamagnetism by making measurements on the free base ligands and [PPh$_4$]Cl and correcting with use of Pascal's constants where appropriate. A solution molecular weight was determined by osmometry with use of a Signer molecular weight apparatus.[7]

**Syntheses.** The syntheses of the ligands H$_4$HMPA-DMP (2,4-bis(2-hydroxy-2-methylpropanamido)-2,4-dimethyl-3-oxopentane)[8] and H$_4$HMPA-B[8] (2,4-bis(2-hydroxy-2-methylpropanamido)benzene), and the complex [PPh$_4$][Co($\eta^4$-HMPA-B)][5] have been described elsewhere.

**Na[Co($\eta^4$-HMPA-DMP)], 3.** Anhydrous cobalt acetate (1.25 g, 7.06 mmol) was combined with H$_4$HMPA-DMP (2.03 g, 6.42 mmol) in anhydrous ethanol (100 mL) under air, and sodium hydroxide (1.01 g, 25.3 mmol) was added to the purple slurry which was then stirred (5 h). The dark red-brown solution was evaporated to dryness on a rotary evaporator, and acetone (250 mL) was added. The resulting mixture was stirred vigorously and was filtered through a Celite pad to give a bright orange filtrate which was reduced in volume (to 5 mL) on a rotary evaporator. Dichloromethane was added as required to induce crystallization, and the crude material was recrystallized from acetone/dichloromethane to yield orange crystals: yield after drying in vacuo (6 h, 60 °C) 2.01 g (79%): $^1$H NMR see Table I; IR see Table II; UV-vis (95% ethanol, nm) $\lambda_{max}$ ($\epsilon$) 300 (4800), 338 (4600), 384 (4300), 458 (4300); $\mu_{eff}$ (294 K) = 2.9 $\mu_B$. Anal. Calcd for $C_{15}H_{24}CoN_2O_5Na$: C, 45.69; H, 6.14; N, 7.11. Found: C, 45.57; H, 6.21; N, 6.71.

**[PPh$_4$][Co($\eta^4$-HMPA-DMP)]·H$_2$O, 4·H$_2$O.** Na[Co($\eta^4$-HMPA-DMP)] (0.151 g, 383 μmol) and [PPh$_4$]Cl (0.194 g, 517 μmol) were dissolved separately in minimum volumes of water, and the [PPh$_4$]Cl solution was added dropwise to the stirred Na[Co($\eta^4$-HMPA-DMP)] solution. Precipitation of orange crystals began upon mixing. The product was collected and washed with ether: yield 204 mg (84%). Recrystallization from a minimum volume of water yielded orange crystals of **4** as a monohydrate. Anhydrous material was obtained by recrystallization from $CH_2Cl_2$/cyclohexane followed by drying in vacuo: $^1$H NMR see Table I; IR see Table II; UV-vis (95% ethanol, nm) $\lambda_{max}$ ($\epsilon$) 296 (5400), 340 (5100), 383 (4800), 458 (4800); $\mu_{eff}$ (294 K) = 3.0 $\mu_B$. Anal. Calcd for $C_{39}H_{44}CoN_2O_5P\cdot H_2O$: C, 64.28; H, 6.36; N, 3.84. Found: C, 64.39; H, 6.24; N, 3.91.

**Co($\eta^4$-(Me)HMPA-DMP), 6.** A 100-mL three-necked, round-bottomed flask was heated under a stream of nitrogen. After having been cooled under nitrogen dry [PPh$_4$][Co($\eta^4$-HMPA-DMP)] (722 mg, 1.09 mmol) was added and dissolved in freshly distilled dichloromethane (30 mL). [Me$_3$O][BF$_4$] (137 mg, 0.93 mmol) was added under a blanket of nitrogen, and the mixture was stirred (15 min). Additional [Me$_3$O][BF$_4$]

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**Table II.** IR Data for Square Planar Cobalt(III) Complexes ($cm^{-1}$)

| compound | $\nu_{CO}$ (amide) | $\nu_{C=N}$ (iminoester) | $\nu_{CO}$ (ketone) |
|---|---|---|---|
| $H_4$HMPA-DMP[a,b] | 1640 | | 1715 |
| $H_4$HMPA-B[a,b] | 1660 | | |
| Na[Co($\eta^4$-HMPA-DMP)], **3**[a] | 1610 | | 1709 |
| [$PPh_4$][Co($\eta^4$-HMPA-DMP)], **4**[c] | 1611 | | 1699 |
| [$PPh_4$][Co($\eta^4$-HMPA-B)], **5**[c] | 1636 | | |
| Co($\eta^4$-(Me)HMPA-DMP), **6**[c] | 1638 | 1672 | 1711 |
| Co($\eta^4$-(Me)HMPA-B), **7**[c] | 1653 | 1675[d] | |
| Co($\eta^4$-(Et)HMPA-DMP), **8**[c] | 1638 | 1669 | 1711 |
| Co($\eta^4$-(Et)HMPA-B), **9**[c] | 1653 | 1671[d] | |

[a] Nujol mull. [b] Reference 7. [c] Measured in dichloromethane. [d] Shoulder.

(34 mg, 0.23 mmol) was added, and the mixture was further stirred (20 min) and then taken to dryness under vacuum. The residue was dissolved in freshly distilled warm benzene (CAUTION—CANCER SUSPECT AGENT) (60 mL), and the deep red solution was filtered under nitrogen through a Celite pad to remove the byproduct. The filtrate was taken to dryness under vacuum, redissolved in dichloromethane, and again taken to dryness under vacuum. The dissolution in dichloromethane and solvent removal was repeated to yield a dark green powder; yield 373 mg (89%); $^1$H NMR see Table I; IR see Table II; UV–vis ($CH_2Cl_2$, nm) $\lambda_{max}$ ($\epsilon$) 337 (3100), 414 (3500), 463 (3000) sh; MS (parent ion) 386, $C_{16}H_{27}CoN_2O_5$ requires 386.12; $\mu_{eff}$ (294 K) = 3.2 $\mu_B$. Anal. Calcd for $C_{16}H_{27}CoN_2O_5$: C, 49.74; H, 7.04; N, 7.25. Found: C, 48.66; H, 6.88; N, 7.28. This material was difficult to analyse satisfactorily.

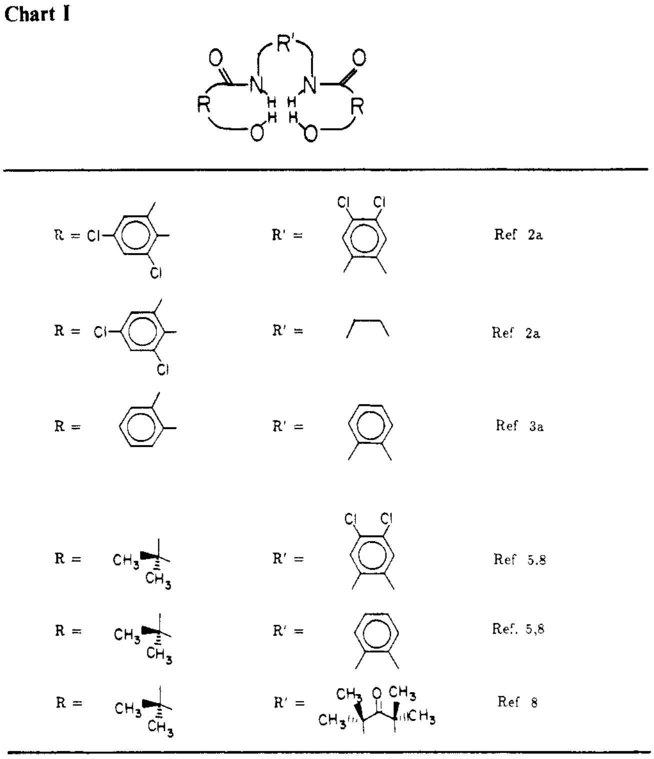
**Co($\eta^5$-(Me)HMPA-B), 7.** This complex was prepared in an analogous manner to the above. Recrystallization was achieved from dichloromethane/hexane: yield 272 mg (86%); $^1$H NMR see Table I; IR see Table II; $\mu_{eff}$ (294 K) = 3.2 $\mu_B$; an analytical sample was obtained by sublimation; MS (parent ion) 350, $C_{15}H_{19}CoN_2O_4$ requires 350.07; solution molecular weight calcd 350.26, found 361; UV–vis ($CH_2Cl_2$, nm) $\lambda_{max}$ ($\epsilon$) 257 (13 000), 372 (2100), 494 (2600), 458 (3000). Anal. Calcd for $C_{15}H_{19}CoN_2O_4$: C, 51.44; H, 5.47; N, 8.00. Found: C, 51.30; H, 5.43; N, 7.92.

**Co($\eta^4$-(Et)HMPA-DMP), 8.** A 100-mL, three-necked, round-bottomed flask was heated under a stream of nitrogen. After having been cooled under nitrogen dry [$PPh_4$][Co($\eta^4$-HMPA-DMP)] (606 mg, 0.85 mmol) was added and dissolved in freshly distilled dichloromethane (15 mL). Ethyl iodide (1.8 mL, ≈3.51 g, 22 mmol) was added. Silver tetrafluoroborate (181 mg, 0.95 mmol) was introduced, the reaction vessel was covered with foil, and the mixture was stirred (8 h). An additional portion of $AgBF_4$ (40 mg, 0.21 mmol) was added, and the mixture was stirred (24 h). The solvent was removed under vacuum, the residue was dissolved in freshly distilled warm benzene (CAUTION—CANCER SUSPECT AGENT) (45 mL), and the deep red solution was filtered under nitrogen through a Celite pad to remove the salts, [$PPh_4$][$BF_4$] and AgI. The filtrate was taken to dryness under vacuum, redissolved in dichloromethane, and again taken to dryness under vacuum. The dissolution in dichloromethane and solvent removal was repeated to yield a green powder: yield 96 mg (28%); $^1$H NMR see Table I; IR see Table II; $\mu_{eff}$ (294 K) = 3.6 $\mu_B$; UV–vis ($CH_2Cl_2$, nm) $\lambda_{max}$ ($\epsilon$) 322 (3300), 406 (3400), 470 (3400); MS (parent ion) 400, $C_{17}H_{29}CoN_2O_5$ requires 400.14; analytical sample purified by sublimation. Anal. Calcd for $C_{17}H_{29}CoN_2O_5$: C, 51.00; H, 7.30; N, 7.00. Found: C, 49.38; H, 7.28; N, 6.73. This material was difficult to analyze satisfactorily. Alkylation with triethyloxonium tetrafluoroborate was also effective in the synthesis of this material.

**Co($\eta^4$-(Et)HMPA-B), 9.** This complex was prepared in an analogous manner to the above. Recrystallization was achieved from dichloromethane/hexane: yield 170 mg (52%); $^1$H NMR see Table I; IR see Table II; MS (parent ion) 364, $C_{16}H_{21}CoN_2O_4$ requires 364.08. $\mu_{eff}$ (294 K) = 3.5 $\mu_B$; UV–vis ($CH_2Cl_2$, nm) $\lambda_{max}$ ($\epsilon$) 254 (11 700), 356 (2000), 496 (2000), 738 (800). Anal. Calcd for $C_{16}H_{21}CoN_2O_4$: C, 52.75; H, 5.81; N, 7.69. Found: C, 53.07; H, 6.12; N, 7.55. Alkylation with triethyloxonium tetrafluoroborate was also effective in the synthesis of this material.

**X-ray Crystal Structure Determination of [$PPh_4$][Co($\eta^4$-HMPA-DMP)]·($H_2O$), 4·($H_2O$).** A single crystal was used for the photographic workup and data collection. Data collection was performed on an Enraf-Nonius CAD4 diffractometer with graphite monochromator. The three check reflections showed no unusual decrease in intensity over the 160 h of data collection. The data were reduced to $F_o^2$ and averaged over $\bar{1}$ symmetry yielding 10 613 reflections. The cobalt and phosphorus atoms were derived from the Patterson map, and the remaining structure was revealed by electron density maps. Hydrogen atoms were located on difference Fourier maps and were not refined. The $B$'s of the hydrogen atoms on the methyl groups are approximately equal to the $B_{eq}$ of the methyl carbon atom, and the hydrogen atoms on the phenyl groups were all assigned the same value, $B = 4.0$. Full-matrix least-squares refinement of the scale factor, atom coordinates, and anisotropic Gaussian parameters resulted in a goodness-of-fit $S$ 2.03 ($n$ = 10 613 reflections, $\upsilon$ = 422 parameters); $R_F$ = 0.055 (9948 reflections, $I > 0$), and $R'_F$ = 0.041 (7685 reflections, $I > 3\sigma$); the form factors for cobalt were corrected for anomalous dispersion. Each shift/error was less than 0.01 in the final cycle, and the final difference map showed no peaks larger than ≈0.5 e/Å$^3$. The details of data collection and refinement are summarized in Table III.

**Chart I**



## Results and Discussion

We have recently produced novel PAC ligands[2,3,5,8] that contain two organic amido-$N$ donors in combination with two phenolato or two alkoxido donors. Within the context of all known ligands these species are very strong donors and are able to stabilize highly oxidized complexes of the middle and later transition metals. A wide range of donor capacities is available from the two types; the alkoxido-containing ligands are the strongest donors as is evident from the considerable stabilization afforded to copper(III) centers (formal potentials for copper(III/II) couples as low as −600 mV vs SCE).[8] While the donor atoms are electronegative nitrogen and oxygen centers, the high p$K_a$ values found for tertiary alcohols and for mono-N-substituted organic amides[9] suggest that their anions are relatively polarizable entities; metal–ligand $\sigma$-bonding might be expected to have significant covalent character. Phenols are considerably more acidic than tertiary alcohols;[9] the phenolato-containing PAC ligands are significantly weaker donors than the alkoxido-containing PAC ligands.[8] The large variation in donor capacities appears to be a principal factor responsible for different chemical behavior for cobalt(III) centers coordinated to the phenolato or alkoxido ligands. The former afford stable octahedral cobalt(III) complexes,[10] whereas the latter produce stable square planar cobalt(III) species with weak axial Lewis acidity.[5] This difference can be rationalized as follows. If, for the sake of simplification, the unligated axis in the square planar complexes is labelled $z$, then two of the axial $\sigma$ metal orbitals (s, $d_{z^2}$) are of $\sigma$* character with respect to the metal–ligand $\sigma$ bonds. It is expected that the stronger these bonds are, the more desta-

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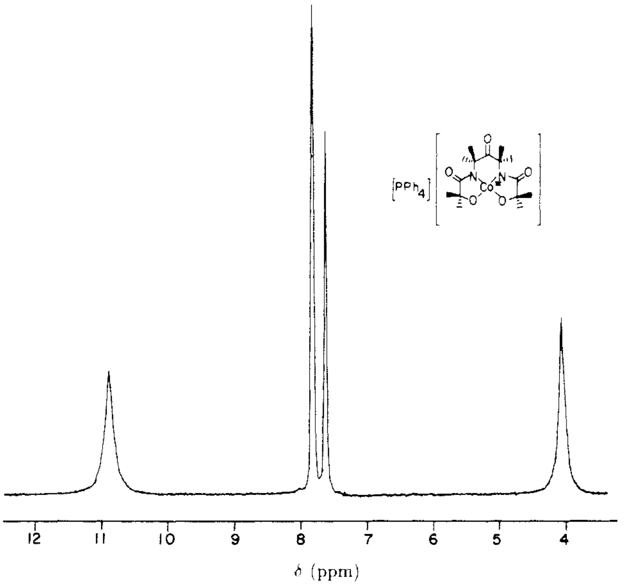


**Figure 1.** $^1H$ NMR (400-MHz) spectrum in $(CD_3)_2CO$ (21 °C) of $[PPh_4][Co(\eta^4\text{-HMPA-DMP})]$, **4**.

**Table III.** Experimental Data for Structure Determination of $[PPh_4][Co(\eta^4\text{-HMPA-DMP})]\cdot(H_2O)$, **4**$\cdot(H_2O)$

| | |
|---|---|
| formula | $CoC_{36}H_{36}N_2O_4P\cdot H_2O$ |
| formula weight | 668.61 |
| unit cell constants | $a$ = 11.300 (3) Å, $b$ = 13.564 (3) Å<br>$c$ = 13.898 (3) Å, $\alpha$ = 114.736 (10)°<br>$\beta$ = 95.862 (12)°, $\gamma$ = 104.293 (11)°<br>$V$ = 1849.1 (8) Å$^3$ |
| $D_{calcd}$ ($Z$ = 2) | 1.201 g cm$^{-3}$ |
| space group | $P\bar{1}$ |
| $\mu$ (Mo K$\alpha$) | 5.279 cm$^{-1}$ |
| scan type and speed | $\theta$–2$\theta$, ≈2° ($\theta$)/min |
| scan range | $\theta$ = 1–30° |
| backgrnd cnting | $t_b/t_s$ = 0.5<br>time at each end of scan |
| collctn range | $-h,\pm k,\pm l$ |
| no. of reflcns measd | 11269 |
| total no. of data, $n$ | 10613 |
| no. of data with $I > 0$ | 9948 |
| no. of data with $I > 3\sigma(I)$ | 7685 |
| no. of params refined, $v$ | 442 |
| $R^a$ (for $I > 0$) | 0.055 |
| $R^a$ (for $I > 3\sigma(I)$) | 0.041 |
| goodness of fit$^b$ | 2.03 |

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] Goodness of fit $= \sum w[F_o^2 - (F_c/k)^2]^2/(n - v)^{1/2}$.

bilized the axial $\sigma^*$ orbitals will be, the weaker the axial Lewis acidity will be.

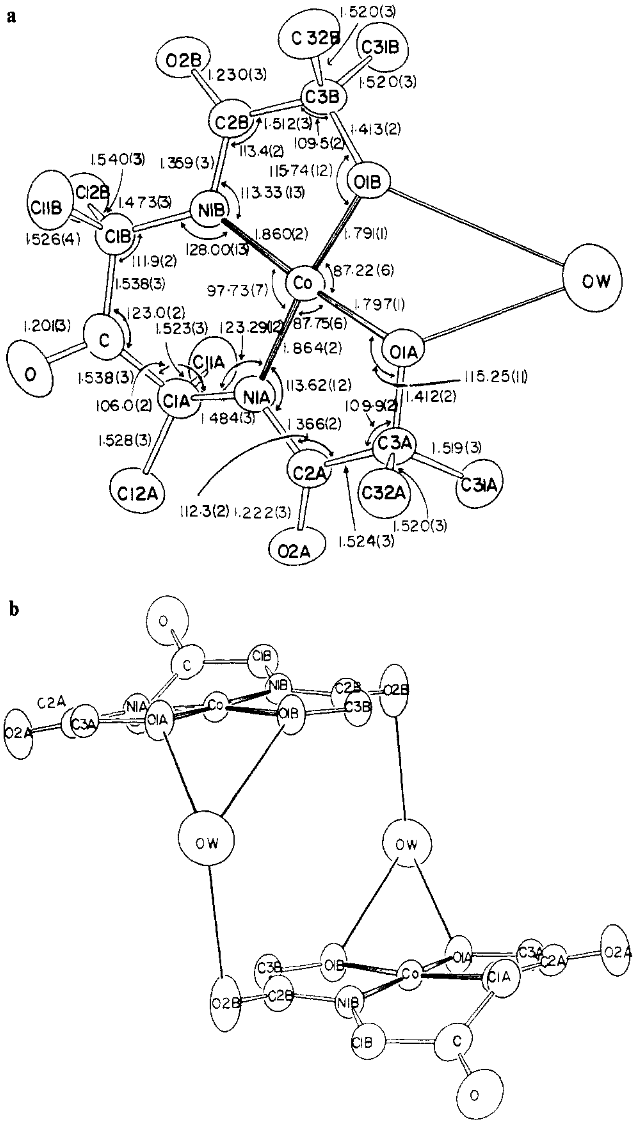


**Figure 2.** (a) Molecular structure of $[Co(\eta^4\text{-HMPA-DMP})]\cdot(H_2O)$ anion and $[PPh_4]^+$ cation. (b) Structure showing two anions bridged by the water solvate molecules.

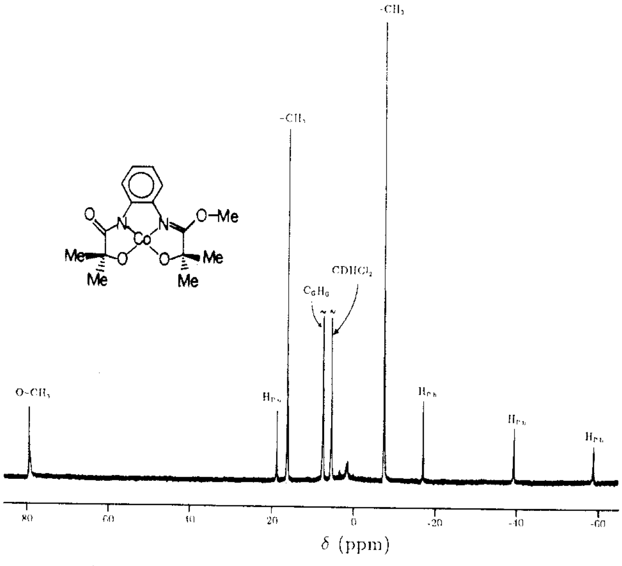


**Figure 3.** $^1H$ NMR (400-MHz) spectrum in $CD_2Cl_2$ (21 °C) of $[Co(\eta^4\text{-(Me)HMPA-B})]$, **7**.

The free base ligand $H_4$HMPA-DMP (2,4-bis(2-hydroxy-2-methylpropanamido)-2,4-dimethyl-3-oxopentane) is readily coordinated to cobalt(III) to afford the monosodium salt $Na[Co(\eta^4\text{-HMPA-DMP})]$, **3**, which undergoes metathesis with tetraphenylphosphonium chloride to give $[PPh_4][Co(\eta^4\text{-HMPA-DMP})]$, **4**. The $^1H$ NMR spectrum of this paramagnetic species in $(CD_3)_2CO$ is shown in Figure 1. Tentative assignment of the methyl signals has been made on the basis of a comparison with the NMR spectra of compounds which have aromatic groups linking the two amide nitrogen atoms, e.g., $[PPh_4][Co(\eta^4\text{-HMPA-B})]$, **5**, ($H_4$-HMPA-B = 2,4-bis(2-hydroxy-2-methylpropanamido)benzene) where the methyl resonance is found at 9.71 ppm in $CD_2Cl_2$ at 298 K. The results of an X-ray crystal structure determination for $[PPh_4][Co(\eta^4\text{-HMPA-DMP})]\cdot(H_2O)$, **4**, are depicted in Figure 2 (Tables III and IV). Note that the tetradentate tetraanion $[\eta^4\text{-HMPA-DMP}]^{4-}$ contains no aromatic groups and can be considered an innocent ligand for the purposes of formal oxidation state assignments. The square planar cobalt(III) complex exhibits short Co–O and Co–N bond lengths for cobalt complexes of PAC ligands.[5,10] The Co–O bond lengths are shorter than the Co–N bond lengths; the tertiary alkoxido groups are probably as important as the amido-*N* groups in

**Table IV.** Important Bond Distances and Angles for $[Co(\eta^4\text{-HMPA-DMP})]^-$

| atom | atom | distance | atom | atom | distance |
|---|---|---|---|---|---|
| Co | N1A | 1.864 (2) | Co | N1B | 1.860 (2) |
| Co | O1B | 1.791 (1) | Co | O1A | 1.797 (1) |
| N1A | C1A | 1.484 (3) | N1B | C1B | 1.473 (3) |
| N1A | C2A | 1.366 (2) | N1B | C2B | 1.359 (3) |
| O1A | C3A | 1.412 (2) | O1B | C3B | 1.413 (2) |
| C2A | O2A | 1.222 (3) | C2B | O2B | 1.230 (3) |
| C2A | C3A | 1.524 (3) | C2B | C3B | 1.512 (3) |
| C1A | C | 1.538 (3) | C1B | C | 1.538 (3) |
| C1A | C11A | 1.523 (3) | C1B | C11B | 1.526 (4) |
| C1A | C12A | 1.528 (3) | C1B | C12B | 1.540 (3) |
| C3A | C31A | 1.519 (3) | C3B | C31B | 1.520 (3) |
| C3A | C32A | 1.520 (3) | C3B | C32B | 1.520 (3) |
| C | O | 1.201 (3) | | | |

| atom | atom | atom | angle | atom | atom | atom | angle |
|---|---|---|---|---|---|---|---|
| O1A | Co | N1A | 87.75 (6) | O1B | Co | N1A | 172.51 (7) |
| N1A | Co | N1B | 97.73 (7) | O1A | Co | O1B | 87.22 (6) |
| N1B | Co | O1A | 173.80 (7) | N1B | Co | O1B | 87.59 (6) |
| C1B | N1B | Co | 128.00 (13) | C1A | N1A | Co | 123.29 (12) |
| C2A | N1A | Co | 113.62 (12) | C2B | N1B | Co | 113.33 (13) |
| C3A | O1A | Co | 115.25 (11) | C3B | O1B | Co | 115.74 (12) |
| C1A | N1A | C2A | 121.2 (2) | C1B | N1B | C2B | 118.0 (2) |
| O2A | C2A | N1A | 127.1 (2) | O2B | C2B | N1B | 126.1 (2) |
| C3A | C2A | N1A | 112.3 (2) | C3B | C2B | N1B | 113.4 (2) |
| C3A | C2A | O2A | 120.6 (2) | C3B | C2B | O2B | 120.4 (2) |
| C2A | C3A | O1A | 109.9 (2) | C2B | C3B | O1B | 109.5 (2) |
| C31A | C3A | O1A | 109.3 (2) | C31B | C3B | O1B | 109.2 (2) |
| C32A | C3A | O1A | 109.3 (2) | C32B | C3B | O1B | 108.9 (2) |
| C31A | C3A | C2A | 108.4 (2) | C31B | C3B | C2B | 110.3 (2) |
| C32A | C3A | C2A | 109.6 (2) | C32B | C3B | C2B | 108.2 (2) |
| C32A | C3A | C31A | 110.4 (2) | C32B | C3B | C31B | 110.6 (2) |
| C11A | C1A | N1A | 108.5 (2) | C11B | C1B | N1B | 108.3 (2) |
| C12A | C1A | N1A | 116.0 (2) | C12B | C1B | N1B | 114.1 (2) |
| C | C1A | N1A | 106.0 (2) | C | C1B | N1B | 111.9 (2) |
| C | C1A | C11A | 111.2 (2) | C | C1B | C11B | 107.3 (2) |
| C | C1A | C12A | 106.4 (2) | C | C1B | C12B | 105.5 (2) |
| C12A | C1A | C11A | 108.7 (2) | C12B | C1B | C11B | 109.5 (2) |
| C1B | C | C1A | 123.0 (2) | | | | |
| O | C | C1A | 119.2 (2) | O | C | C1B | 117.7 (2) |

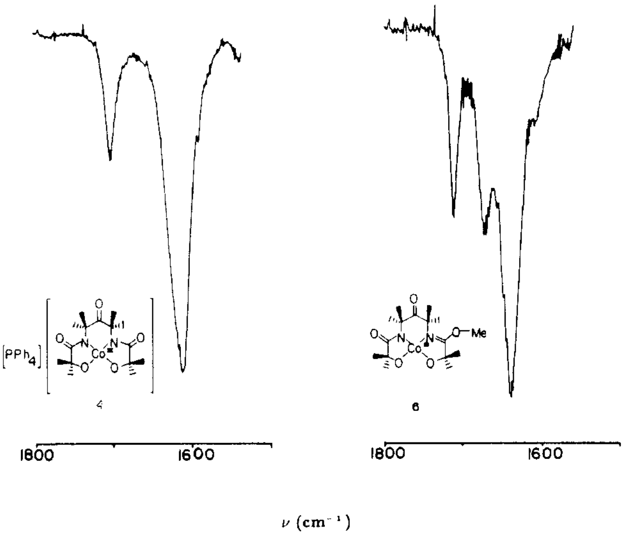
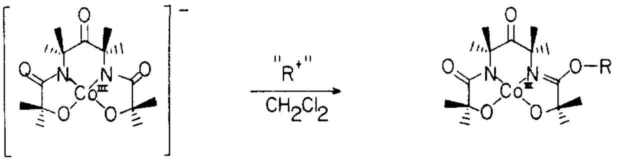


**Figure 4.** IR spectra in $\nu_{CO}$ (amide) and $\nu_{CN}$ (imine) region of **4** and **6** in dichloromethane (0.1-mm cell path length, KBr plates).

contributing to the strong donor capacity of the PAC ligand. With phenoxo-containing ligands, octahedral bis(pyridine) complexes are stable entities.[10] Molecular graphics studies reveal that axial pyridine ligands would suffer some steric clash with the methyl substituents of $[Co(\eta^4\text{-HMPA-DMP})]^-$.[11] It is likely that steric effects also contribute to the reduced axial Lewis acidity of the square planar cobalt(III) alkoxido complexes toward larger ligands.

It is well known that the oxygen atom of amides can be alkylated by oxonium cations to give salts of iminoesters.[13] Alkylation of the square planar cobalt(III) complexes proceeds cleanly with a variety of alkylating agents to give the first neutral square planar cobalt(III) complexes as shown in eq 1 for the starting anion $[Co(\eta^4\text{-HMPA-DMP})]^-$. These species are also the first square planar cobalt(III) complexes of the neutral imino ester-*N* ligand. Attempts to grow crystals suitable for X-ray diffraction were conducted in a wide range of solvents for each of the neutral complexes. Clusters of unsuitable needles resulted. The formulations are based on the following evidence. There are, in fact, several reasonable sites for alkylation of the PAC ligands: an amido-*N* oxygen atom, the cobalt center, an alkoxido oxygen atom, or an amido-*N* nitrogen atom. The alkylation reaction is reversible; in the presence of good nucleophiles the starting anion can be regenerated. This chemical property, in combination with the spectroscopic evidence presented below, forms a strong case for *O*-amide alkylation. $^1$H NMR evidence cannot distinguish between the first three possibilities for **6**. However, alkylation of $[PPh_4][Co(\eta^4\text{-HMPA-B})]$ produces a neutral complex **7** in which four separate signals are found for the phenylene protons (Figure 3) and two separate signals are found for the alkoxide methyl groups; metal alkylation to give a five coordinate complex with an apical methyl group is therefore inconsistent with this data as only two aromatic signals would be expected for this alternative. For the last of the four alkylation sites, amido-*N* alkylation, consistency with the NMR data would appear to require isomerization to O-coordination of the alkylated ligand, a process introducing considerable strain. Furthermore, dealkylation would not be expected in this case.



"$R^+$" = $[Me_3O][BF_4]$, EtI/Ag$[BF_4]$

**6**, R = Me, **8**, R = Et

Evidence consistent with O-alkylation of the amido-*N* oxygen atom is found in the amide/imine stretching region of the IR

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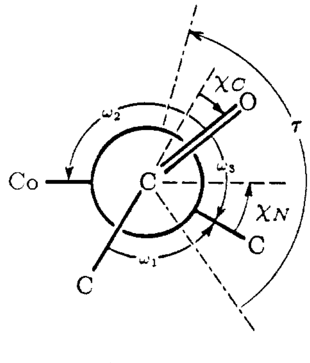
[11] A study of the angular parameters of all organic amido-*N* and related ligands was recently conducted, and nonplanar amido-*N* groups with a large twist angle about the C–N bond were shown to exist in a variety of PAC ligand complexes for three separate reasons (ref 2b,m). In the current structural study the amide nonplanarity parameters are not exceptional: (amido-*N* ligand 1) $\omega_1$= (C3AC2AN1AC1A) = 173.31, $\omega_2$ = (O2AC2AN1ACo) = −171.94, $\omega_3$ = (O2AC2AN1AC1A) = −7.02, $\bar{\tau}$ = 0, $\chi_N$ = 15, $\chi_c$ = 0; (amido-*N* ligand **2**) $\omega_1$ = (C3BC2BN1BC1B) = 165.31, $\omega_2$ = (O2BC2BN1BCo) = 175.31, $\omega_3$ = (O2BC2BN1BC1B) = −13.01, $\bar{\tau}$ = −10, $\chi_N$ = 8.32, $\chi_C$ = −1.68. The small but not insignificant distortion from planarity in $\bar{\tau}$ for amido-*N* ligand **2** and in $\chi_N$ for amido-*N* ligand **1** might be the expression of some ring strain in the overall anion.



$$\tau = ((\omega_1 + \omega_2)/2) \bmod \pi$$

$$\chi_N = (\omega_2 - \omega_3 + \pi) \bmod 2\pi$$

$$\chi_C = (\omega_1 - \omega_3 + \pi) \bmod 2\pi$$

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[13] Kantlehner, *Adv. Org. Chem.* **1979**, *9 pt. 2*, 181–277.

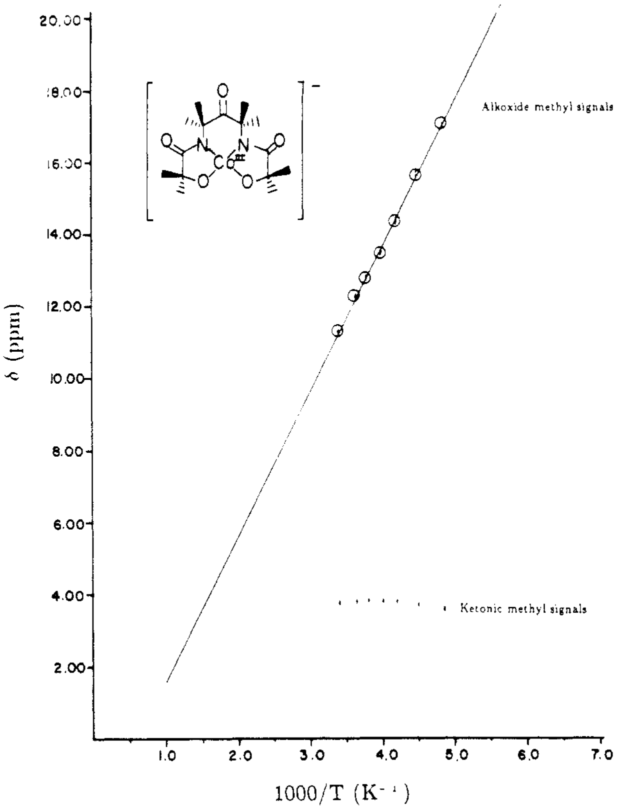

**Figure 5.** Plot of chemical shift data in $CD_2Cl_2$ versus 1000 × $1/T$ for $[PPh_4][Co(\eta^4$-HMPA-DMP)], **4** (least-squares correlation factor for line, $r = 0.999$).

spectrum. The solution IR spectra of **4** and **6** are compared in Figure 4. Whereas two bands are found for **4** ($\nu_{CO}$ (ketone), 1699 $cm^{-1}$ (m), $\nu_{CO}$ (amide), 1611 $cm^{-1}$ (s)), an additional band at 1672 $cm^{-1}$ (m) is found in the spectrum of **6** which we tentatively assign to the $\nu_{C=N}$ vibration of an *N*-imino ester ligand. The IR data for all the complexes are summarized in Table II. Complex **7** was determined to be monomeric in solution by osmometry; solubility limitations prohibited solution molecular weight determinations for the other neutral compounds. O-protonation of amido-*N* ligands has been reported previously.[14] All the proposed neutral cobalt(III) complexes show the expected parent peaks in the mass spectra.

The solid-state magnetic moments (294 K) are listed in the Experimental Section and are consistent in each case with a spin triplet ground state. The results of a chemical shift temperature dependence study for the $^1H$ NMR signals of $[PPh_4][Co(\eta^4$-HMPA-DMP)] are shown in Figure 5. The signal that we have tentatively assigned to the alkoxide methyl resonances shows a considerable dependence upon $1/T$ that is linear over the temperature range examined (184–293 K in $CD_2Cl_2$) indicating that the triplet state is retained over this temperature range. In contrast, the chemical shift of the ketonic methyl signal is almost temperature independent, and the plot is slightly curved. Unfortunately, it has not been possible to obtain such plots for the neutral compounds because of solubility limitations.

## Conclusion

The alkoxide-containing PAC ligands are exceptional donors to transition metals and afford stable square planar cobalt(III) centers that exhibit weak axial Lewis acidity. The tertiary alkoxido donors are probably as important as the amido-*N* donors in contributing to the strong donor capacity. Amido-*N* donors are known to be remarkably strong donor ligands to later transition-metal ions.[15] In comparison, related phenoxido-containing PAC ligands have smaller donor capacity, and the cobalt(III) complexes exhibit a greater axial Lewis acidity—the common octahedral coordination geometry is stable.[8] The axial Lewis acidity of complexes of the alkoxido-containing PAC ligands toward ligands such as pyridine is probably also attenuated by steric factors. Alkylation of one amido-*N* oxygen atom of the monoanionic square planar cobalt(III) complexes proceeds with a variety of reagents to give neutral materials which all available evidence suggests remain square planar in solution. The profile of a ligand complement that will give stable square planar cobalt(III) complexes has been clear for some time based on the distinctive pattern that has emerged for the rare reported cases; four strongly σ-donating anions are required.[4] To our knowledge the O-alkylated species reported here are the first neutral square planar cobalt(III) complexes. The accumulated evidence on cobalt(III) complexes of PAC ligands suggests that increasing the donor capacity in a series of related PAC ligands can attenuate the axial Lewis acidity to the point that the square planar geometry is strongly stabilized. This is of potential value in the design of new ligand complements for inner-sphere and atom-transfer oxidations with later transition metals where strong binding of nonactive Lewis bases ligands is expected to be inhibitory. It is pertinent to note that olefin epoxidation by iodosobenzene proceeds readily in the presence of a series of the square planar cobalt(III) PAC ligand complexes but not in the presence of the related cobalt(III) octahedral complexes of phenoxide-containing ligands.[16]

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**Registry No.** **3**, 111004-54-7; **4**·$H_2O$, 111004-57-0; **5**, 100909-71-5; **6**, 111004-58-1; **7**, 111004-59-2; **8**, 111004-60-5; **9**, 111004-61-6; $H_4$HMPA-DMP, 107680-77-3; $H_4$HMPA-B, 107680-76-2; $[Me_3O][BF_4]$, 420-37-1; EtI, 75-03-6; $[Et_3O][BF_4]$, 368-39-8.

**Supplementary Material Available:** Listings of atomic coordinates and $U_{eq}$'s, hydrogen atom coordinates and *B*'s, all bond angles and distances, anisotropic Gaussian parameters, and important torsion angles (7 pages); listings of structure factor amplitudes (41 pages). Ordering information is given on any current masthead page.

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[15] See, for example: (a) Bossu, F. P.; Chellappa, K. L.; Margerum, D. W. *J. Am. Chem. Soc.* **1977**, *99*, 2195–2203. (b) Margerum, D. W. *Pure Appl. Chem.* **1983**, *55*, 23–34. (c) Margerum, D. W.; Owens, G. D. *Met. Ions. Biol. Syst.* **1981**, *12*, 75–132.

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