Contribution from the Department of Chemistry, Emory University, Atlanta, Georgia 30322, and Istituto di Chimica, Universita di Trieste, 34127 Trieste, Italy

Organocobalt B_{12} Models. An Assessment of the Cis Effect Using Bis(glyoximato) as a Sterically Minimal Equatorial Atom Set. Structures of *trans*-Bis(glyoximato)methyl(L)cobalt(III), with L = Triphenylphosphine and Trimethyl Phosphite

PAUL J. TOSCANO, THOMAS F. SWIDER, LUIGI G. MARZILLI,* NEVENKA BRESCIANI-PAHOR, and LUCIO RANDACCIO

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A synthetic scheme leading to bis(glyoximato)alkylcobalt(III) complexes in moderate yields is reported. Single-crystal X-ray diffraction, spectroscopic, and rate studies were undertaken to compare the bis(glyoximato) compounds to their bis(dimethylglyoximato) analogues. The molecular structures of $(C_6H_5)_3PCo(GH)_2CH_3$ (**1**) (where GH = the monoanion of glyoxime) and $(CH_3O)_3PCo(GH)_2CH_3$ (**2**) were determined. **1** crystallizes in space group $P\bar{1}$ with a = 11.197 (7) Å, b = 9.259 (6) Å, c = 11.327 (7) Å, α = 84.0 (1)°, β = 95.2 (1)°, γ = 96.4 (1)°, and Z = 2. **2** crystallizes in space group *Pnma* with a = 17.30 (1) Å, b = 10.730 (8) Å, c = 8.044 (7) Å, and Z = 4. The ^{13}C NMR spectra of several complexes and the reaction of **2** with Br^- were studied, as well as the ligand-exchange rates for representative complexes. Comparisons of the structural, spectroscopic, and rate values of the GH complexes with those of the DH (where DH = the monoanion of dimethylglyoxime) complexes showed that steric effects are of little importance and that differences may be explained as arising from the poorer electron-donating power of the GH ligand as compared to that of DH.

Introduction

For some time now, we have been interested in steric factors that lead to weakening of the Co–C bond in vitamin B_{12} model compounds in order to evaluate whether a conformational change in the B_{12}-coenzyme–enzyme complex is responsible for the Co–C bond cleavage step in catalysis by B_{12}-dependent enzymes. Such a mechanochemical mechanism has recently gained wider acceptance;[1-6] in the coenzyme, steric distortions are proposed as being caused by enzyme side chains.[1-6]

We have previously studied bis(dimethylglyoximato) complexes of cobalt, $LCo(DH)_2R$ (where DH is the monoanion of dimethylglyoxime), in order to assess the steric influence of bulky alkyl groups (R) and neutral ligands (L) on ground-state structural parameters.[7-14] This work has shown that a variety of distortions occur, including lengthening of the Co–L[7,8,10,13] and Co–R[7,8] bonds, angle changes within both L and R,[9,10] bending of the DH units away from bulky groups,[8,10-12,14] and displacement of the Co atom from the 4 N equatorial plane defined by the DH groups.[8,13]

In order to determine if interactions between the methyl groups in the DH units with axial ligands are important factors in causing bond lengths and angle distortions, we have investigated bis(glyoximato)cobalt(III) complexes, $LCo(GH)_2R$ (where GH is the monoanion of glyoxime), which contain only hydrogen atoms as substituents on the dioxime units. These complexes have been little studied previously; consequently we have devised synthetic schemes to obtain reasonable quantities and variety of complexes. The ^{13}C NMR spectra of several complexes, as well as the reaction of $(CH_3O)_3PCo(GH)_2CH_3$ with Br^-, have been studied to assess the electronic effect of the glyoxime. Finally the structures of $(CH_3O)_3PCo(GH)_2CH_3$ and $(C_6H_5)_3PCo(GH)_2CH_3$ were determined by single-crystal X-ray diffraction in order to evaluate the cis influence of the equatorial bis(glyoximato) ligand system. The availability of these new structural data afforded an opportunity for us to compare ligand-exchange rates with those for DH complexes.

Experimental Section

Glyoxime was purchased from K & K Rare and Fine Chemicals. Pyridine was obtained from Aldrich (99+%, Gold Label grade). Cobalt(II) chloride hexahydrate and other ligands were obtained from standard sources and used as received. All solvents were reagent grade and used without further purification. ^1H NMR spectra were obtained at ambient temperature on a Varian EM-390 spectrometer operating at 90 MHz. ^{13}C NMR spectra were obtained on a Varian CFT-20 spectrometer operating at 20 MHz with a deuterium lock. All NMR spectra were referenced to $(CH_3)_4Si$. Elemental analyses were performed by Atlantic Microlabs, Inc. (Atlanta, GA).

Preparations of Complexes. $Co(GH_2)Cl_2$. Glyoxime (2.73 g, 31.0 mmol) was added to a solution of $CoCl_2 \cdot 6H_2O$ (3.75 g, 15.8 mmol) in acetone (150 mL) and warmed and stirred for 30 min. During this time, purple product precipitated. The reaction mixture was cooled at 0–5 °C and the product collected and washed with a little acetone and diethyl ether; yield 0.95 g (27.6%). Anal. Calcd for $C_2H_4Cl_2N_2O_2Co$: C, 11.02; H, 1.85; N, 12.86; Cl, 32.54. Found: C, 11.06; H, 1.92; N, 12.80; Cl, 32.45.

pyCo(GH)$_2$Cl. Glyoxime (8.10 g, 92 mmol) was added to a solution of $CoCl_2 \cdot 6H_2O$ (10.0 g, 42 mmol) in 95% ethanol (200 mL), followed by pyridine (6.88 g, 86 mmol). The mixture was vigorously aerated for 20 min with occasional swirling. Then water (10 mL) was added and the mixture was aerated for another 1.5 h. The product was collected, washed well with water, and air-dried. Yields averaged about 40%. Anal. Calcd for $C_9H_{11}ClN_5O_4Co$: C, 31.10; H, 3.19; N, 20.15. Found: C, 31.19; H, 3.21; N, 20.08. ^1H NMR ($CDCl_3$): δ 8.28 (m, 2 H, py α-H), 7.77 (m, 1 H, py γ-H), 7.65 (s, 4 H, N=CH), 7.32 (m, 2 H py β-H).

4-*t*-BupyCo(GH)$_2$Cl. Glyoxime (2.07 g, 23.5 mmol) was added to a solution of $CoCl_2 \cdot 6H_2O$ (2.5 g, 10.5 mmol) in 95% ethanol (75 mL), followed by 4-*tert*-butylpyridine (2.93 g, 21.7 mmol). The mixture was vigorously aerated for 20 min with occasional swirling.

* To whom correspondence should be addressed at Emory University.

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Then water (10 mL) was added and aeration was continued for 1.5 h. The product was collected, washed well with water, and air-dried; yield 1.55 g (36.6%). Anal. Calcd for $C_{13}H_{19}ClN_5O_4Co$: C, 38.68; H, 4.79; N, 17.31. Found: C, 38.56; H, 4.74; N, 17.35. ^1H NMR ($CDCl_3$): δ 8.10 (m, 2 H, *t*-Bupy α-H), 7.67 (s, 4 H, N=CH), 7.28 (m, 2 H, *t*-Bupy β-H), 1.25 (s, 9 H, *t*-Bupy CH_3). ^{13}C NMR ($CDCl_3$): δ 164.82 (s, *t*-Bupy γ-C), 150.07 (s, *t*-Bupy α-C), 140.64 (s, C=N), 123.51 (s, *t*-Bupy β-C), 35.14 (s, *t*-Bupy quat C), 30.11 (s, *t*-Bupy CH_3).

$(CH_3O)_3PCo(GH)_2Cl$. Trimethyl phosphite (0.44 g, 3.5 mmol) was added dropwise to a solution of 4-*t*-BupyCo$(GH)_2Cl$ (1.3 g, 3.2 mmol) in CH_2Cl_2 (20 mL). The product precipitated immediately and was collected and washed with petroleum ether; yield 1.1 g (87%). Anal. Calcd for $C_7H_{15}ClN_4O_7PCo$: C, 21.42; H, 3.85; N, 14.27. Found: C, 21.57; H, 3.87; N, 14.23. ^1H NMR (Me_2SO-d_6): δ 7.80 (d, ^4J(P–H) = 3.5 Hz, 4 H, N=CH), 3.73 (d, ^3J(P–H) = 10.8 Hz, 9 H, OCH_3).

$Bu_3PCo(GH)_2Cl$. Tri-*n*-butylphosphine (0.29 g, 0.14 mmol) was added to a suspension of pyCo$(GH)_2Cl$ (0.50 g, 0.14 mmol) in CH_2Cl_2 (20 mL), and the mixture was stirred for 20 min. The resulting brown solution was triturated with petroleum ether, causing a sticky oil to precipitate. The organic solvents were allowed to evaporate; the sticky residue was treated with water (10 mL), and acetone was added dropwise until a little solid formed. Scratching with a spatula induced the remainder of the oil to form a powder, which was collected and air-dried; yield 0.36 g (54.7%). Anal. Calcd for $C_{16}H_{33}ClN_4O_4PCo$: C, 40.82; H, 7.06; N, 11.90. Found: C, 40.99; H, 7.09; N, 11.87. ^1H NMR ($CDCl_3$): δ 7.67 (d, ^4J(P–H) = 2.3 Hz, 4 H, N=CH), 0.8–1.8 (m, 27 H, PBu_3).

pyCo$(GH)_2$R (R = CH_3, C_2H_5, *i*-C_3H_7). A solution of NaOH (1.84 g, 46 mmol) in water (10 mL) was added to a suspension of pyCo$(GH)_2Cl$ (4.0 g, 11.5 mmol) in methanol (200 mL), and the mixture was put under a blanket of nitrogen. After 2 min, alkylating agent (69 mmol) was added, followed by a solution of $NaBH_4$ (0.87 g, 23 mmol) in water (10 mL). The reaction mixture was stirred for 1 h (2 h in the case of the isopropyl derivative); then the nitrogen blanket was removed and acetone (15 mL) added. After it was stirred for 10 min, the reaction mixture was filtered through Celite and the filtrate concentrated on a rotary evaporator. Sometimes the product would precipitate when the organic solvents had been removed. In this case, it was collected, washed with a little water, and air-dried. If the product remained in solution, water (50 mL) was added and the aqueous solution was extracted with CH_2Cl_2 (2 × 50 mL). The combined CH_2Cl_2 fractions were dried over Na_2SO_4 and concentrated on a rotary evaporator. The product was then collected and washed with a little petroleum ether.

pyCo$(GH)_2CH_3$ was prepared with use of methyl iodide as alkylating agent. Yields averaged 35%. Anal. Calcd for $C_{10}H_{14}N_5O_4Co$: C, 36.71; H, 4.31; N, 21.41. Found: C, 36.72; H, 4.43; N, 21.36. ^1H NMR ($CDCl_3$): δ 8.67 (m, 2 H, py α-H), 7.83 (m, 1 H, py γ-H), 7.43 (m, 2 H, py β-H), 7.43 (s, 4 H, N=CH), 1.02 (s, 3 H, Co–CH_3).

pyCo$(GH)_2C_2H_5$ was prepared in 25% yield with use of ethyl iodide as alkylating agent. Anal. Calcd for $C_{11}H_{16}N_5O_4Co$: C, 38.72; H, 4.73; N, 20.53. Found: C, 38.85; H, 4.77; N, 20.49. ^1H NMR ($CDCl_3$): δ 8.67 (m, 2 H, py α-H), 7.83 (m, 1 H, py γ-H), 7.48 (s, 4 H, N=CH), 7.42 (m, 2 H, py β-H), 1.90 (q, 2 H, Co–CH_2), 0.53 (t, 3 H, Et CH_3).

pyCo$(GH)_2$-*i*-C_3H_7 was prepared in 7% yield with use of isopropyl bromide as alkylating agent. Anal. Calcd for $C_{12}H_{18}N_5O_4Co$: C, 40.57; H, 5.11; N, 19.71. Found: C, 40.69; H, 5.19; N, 19.59. ^1H NMR ($CDCl_3$): δ 8.66 (m, 2 H, py α-H), 7.80 (m, 1 H, py γ-H), 7.46 (s, 4 H, N=CH), 7.38 (m, 2 H, py β-H), 1.98 (m, 1 H, *i*-Pr-H), 0.62 (d, 6 H, *i*-Pr CH_3).

4-*t*-BupyCo$(GH)_2CH_3$·0.5H_2O. This complex was prepared similarly to pyCo$(GH)_2CH_3$ by alkylating 4-*t*-BupyCo$(GH)_2Cl$ with methyl iodide. Anal. Calcd for $C_{14}N_{22}N_5O_4Co$·0.5H_2O: C, 42.86; H, 5.91; N, 17.85. Found: C, 42.79; H, 5.90; N, 17.84. ^1H NMR ($CDCl_3$): δ 8.50 (m, 2 H, *t*-Bupy α-H), 7.42 (s, 4 H, N=CH), 7.35 (m, 2 H, *t*-Bupy β-H), 1.28 (s, 9 H, *t*-Bupy CH_3), 0.99 (s, 3 H, Co–CH_3). ^{13}C NMR ($CDCl_3$): δ 162.77 (s, *t*-Bupy γ-C), 149.19 (s, *t*-Bupy α-C), 137.81 (s, C=N), 122.79 (s, *t*-Bupy β-C), 34.97 (s, *t*-Bupy quat C), 30.25 (s, *t*-Bupy CH_3).

$H_2OCo(GH)_2CH_3$. Dowex 50W-X8 ion-exchange resin (H^+ form, 50–100 mesh, 2.0 g) was added to a solution of pyCo$(GH)_2CH_3$ (1.32 g, 4.0 mmol) in a mixture of methanol (140 mL) and water (20 mL), and the mixture was warmed and stirred in a beaker covered with a watch glass for 45 min. The solution was filtered hot and the filtrate allowed to concentrate to a small volume at room temperature. The orange product was collected and washed well with acetone and CH_2Cl_2; yield 0.72 g (67%). Anal. Calcd for $C_5H_{11}N_4O_5Co$: C, 22.57; H, 4.17; N, 21.05. Found: C, 22.67; H, 4.21; N, 20.98. ^1H NMR (Me_2SO-d_6): δ 7.70 (s, 4 H, N=CH), 0.38 (br s, 3 H, Co–CH_3).

$(C_6H_5)_3PCo(GH)_2CH_3$. $H_2OCo(GH)_2CH_3$ (0.22 g, 0.83 mmol) and triphenylphosphine (0.22 g, 0.84 mmol) were suspended in a mixture of absolute methanol (50 mL) and CH_2Cl_2 (50 mL) and stirred for 1.5 h. An orange solution resulted, which was filtered and concentrated to near-dryness on a rotary evaporator. The orange product was collected and washed with diethyl ether; yield 0.38 g (89.8%). Anal. Calcd for $C_{23}H_{24}N_4O_4PCo$: C, 54.13; H, 4.74; N, 10.98. Found: C, 53.98; H, 4.79; N, 10.96. ^1H NMR ($CDCl_3$): δ 7.40 (d, 15 H, P(C_6H_5)$_3$), 7.12 (d, ^4J(P–H) = 3.1 Hz, 4 H, N=CH), 1.38 (d, ^3J(P–H) 3.6 Hz, 3 H, Co–CH_3).

$(CH_3O)_3PCo(GH)_2CH_3$. $H_2OCo(GH)_2CH_3$ (0.33 g, 1.24 mmol) and trimethyl phosphite (0.16 g, 1.27 mmol) were suspended in a mixture of absolute methanol (75 mL) and CH_2Cl_2 (75 mL) and stirred for 1.5 h. A yellow solution resulted, which was filtered and concentrated to near-dryness on a rotary evaporator. The yellow product was collected and washed with diethyl ether; yield 0.43 g (93.2%). Anal. Calcd for $C_8H_{18}N_4O_7PCo$: C, 25.82; H, 4.87; N, 15.05. Found: C, 25.93; H, 4.89; N, 15.05. ^1H NMR ($CDCl_3$): δ 7.45 (d, ^4J(P–H) = 4.2 Hz, 4 H, N=CH), 3.67 (d, ^3J(P–H) = 10.2 Hz, 9 H, OCH_3), 1.27 (d, ^3J(P–H) = 6.3 Hz, 3 H, Co–CH_3). ^{13}C NMR ($CDCl_3$): δ 136.87 (d, ^3J(P–C) = 2.0 Hz, C=N), 53.00 (d, ^2J(P–C) = 6.8 Hz, OCH_3).

(c-C_6H_{11})$_3$PCo$(GH)_2CH_3$. $H_2OCo(GH)_2CH_3$ (0.22 g, 0.83 mmol) and tricyclohexylphosphine (0.25 g, 0.90 mmol) were suspended in a mixture of absolute methanol (50 mL) and CH_2Cl_2 (50 mL) and stirred for 1.5 h. An orange-yellow solution resulted, which was filtered and concentrated to near dryness on a rotary evaporator. The yellow-orange product was recrystallized by placing it in CH_2Cl_2 (20 mL) containing tricyclohexylphosphine (0.15 g), filtering the mixture, and concentrating the filtrate to small volume on a rotary evaporator. The final product was collected and washed with a small amount of absolute diethyl ether; yield 0.21 g (48%). Anal. Calcd for $C_{23}H_{42}N_4O_4PCo$: C, 52.27; H, 8.01; N, 10.60. Found: C, 52.08; H, 8.02; N, 10.62. ^1H NMR ($CDCl_3$): δ 7.46 (d, ^4J(P–H) = 2.7 Hz, 4 H, N=CH), 1.16 (d, ^3J(P–H) = 3.3 Hz, 3 H, Co–CH_3), 0.8–2.0 (br, 33 H, P(c-C_6H_{11})$_3$).

$H_2OCo(GH)_2C_2H_5$. This complex was prepared similarly to $H_2OCo(GH)_2CH_3$, with use of pyCo$(GH)_2C_2H_5$ as starting material. Anal. Calcd for $C_6H_{13}N_4O_5Co$: C, 25.73; H, 4.68; N, 20.00. Found: C, 25.82; H, 4.68; N, 19.97. ^1H NMR (Me_2SO-d_6): δ 7.70 (s, 4 H, N=CH), 1.37 (br q, 2 H, Co–CH_2), 0.15 (t, 3 H, Et CH_3).

$(CH_3O)_3PCo(GH)_2C_2H_5$. This complex was prepared similarly to $(CH_3O)_3PCo(GH)_2CH_3$ with use of $H_2OCo(GH)_2C_2H_5$ as starting material. Anal. Calcd for $C_9H_{20}N_4O_7PCo$: C, 27.99; H, 5.22; N, 14.51. Found: C, 28.05; H, 5.18; N, 14.53. ^1H NMR ($CDCl_3$): δ 7.45 (d, ^4J(P–H) = 4.4 Hz, 4 H, N=CH), 3.68 (d, ^3J(P–H) = 10.2 Hz, 9 H, OCH_3), 1.90 (m, 2 H, Co–CH_2), 0.62 (m, 3 H, Et CH_3). ^{13}C NMR ($CDCl_3$): δ 136.76 (d, ^3J(P–C) = 2.1 Hz, C=N), 52.95 (d, ^2J(P–C) = 6.8 Hz, OCH_3), 13.80 (d, ^3J(P–C) = 6.5 Hz, Et CH_3).

$H_2OCo(GH)_2P(O)(OCH_3)_2$. A mixture of $(CH_3O)_3PCo(GH)_2Cl$ (1.1 g, 2.8 mmol) and LiCl (0.71 g, 16.8 mmol) in water (60 mL) was heated at reflux for 2 h and filtered hot. The filtrate was set aside in a fume hood and evaporated to half-volume. The precipitated product was collected and air-dried; yield 0.55 g (55%). Anal. Calcd for $C_6H_{14}N_4O_8PCo$: C, 20.01; H, 3.92; N, 15.56. Found: C, 20.16; H, 3.87; N, 15.55. ^1H NMR (Me_2SO-d_6): δ 7.75 (d, ^4J(P–H) = 2.5 Hz, 4 H, N=CH), 3.37 (d, ^3J(P–H) = 10.8 Hz, 6 H, OCH_3).

$(CH_3O)_3PCo(GH)_2P(O)(OCH_3)_2$. A mixture of $H_2OCo(GH)_2P(O)(OCH_3)_2$ (0.30 g, 0.83 mmol) and trimethyl phosphite (0.20 g, 1.7 mmol) in absolute methanol (50 mL) was stirred for 3 h and filtered. The filtrate was evaporated to dryness on a rotary evaporator, and the residue was treated with CH_2Cl_2 (15 mL) and filtered. Petroleum ether was added to the filtrate to precipitate the product, which was collected and air-dried; yield 0.18 g (46%). Anal. Calcd for $C_9H_{21}N_4O_{10}P_2Co$: C, 23.19; H, 4.54; N, 12.02. Found: C, 23.20; H, 4.50; N, 12.04. ^1H NMR ($CDCl_3$): δ 7.53 (t, ^4J(P–H) = 3.6 Hz, 4 H, N=CH), 3.72 (d, ^3J(P–H) = 10.5 Hz, 9 H, OCH_3), 3.62 (d, ^3J(P–H) = 10.8 Hz, 6 H, OCH_3). ^{13}C NMR ($CDCl_3$): δ 139.41 (s, C=N), 54.04 (d, ^2J(P–C) = 7.7 Hz, phosphite OCH_3), 53.17 (d,

Table I. Crystallographic Data for Compounds 1 and 2

	$CoPN_4O_4C_{23}H_{24}$ (1)	$CoPN_4O_7C_8H_{18}$ (2)
M_r	510.4	372.2
a, Å	11.197 (7)	17.30 (1)
b, Å	9.259 (6)	10.730 (8)
c, Å	11.327 (7)	8.044 (7)
α, deg	84.0 (1)	
β, deg	95.2 (1)	
γ, deg	96.4 (1)	
D_{measd}, g cm^{-3}	1.45	1.64
D_{calcd}, g cm^{-3}	1.47	1.65
Z	2	4
systematic absences	none	$0kl$ ($k + l = 2n$), $hk0$ ($h = 2n$)
space group	$P\bar{1}$	*Pnma*
μ, cm^{-1}	8.8	13.4
λ(Mo Kα), Å	0.7107	0.7107
F(000)	528	768
cryst dimens, cm^3	0.04 × 0.04 × 0.06	0.08 × 0.07 × 0.08
no. of reflcns measd	5889	2109
no. of indep reflcns ($I \geq 3\sigma(I)$)	3447	1330
no. of varied parameters	299	113
max 2θ, deg (Mo K$\bar{\alpha}$)	56	56
R	0.030	0.032
R_w	0.042	0.049

^2J(P–C) = 8.5 Hz, phosphonate OCH_3).

Crystal Data. Crystals of $(C_6H_5)_3PCo(GH)_2CH_3$ (1) were obtained by slow evaporation from acetone/water at 0–5 °C. Crystals of $(CH_3O)_3PCo(GH)_2CH_3$ (2) were obtained similarly from CH_2Cl_2/*n*-heptane. Cell dimensions were determined from Weissenberg and precession photographs and refined on a Siemens AED single-crystal diffractometer. The results are given in Table I. One check reflection intensity was measured every 100 reflections. There was no systematic variation throughout the data collection, which was carried out with use of the θ–2θ scan technique. The intensities for which $I \geq 3\sigma(I)$ were corrected for Lorentz and polarization factors but not for absorption (Table I) and anomalous dispersion. The absorption correction was not applied because of the small size of the crystals and the small absorption coefficient.

Solution and Refinement of the Structures. Both structures were solved by conventional Patterson and Fourier methods and refined by block-diagonal least-squares methods. The final cycles were done by full-matrix least-squares methods including the contributions of hydrogen atoms at calculated positions (held constant at $B = 5$ Å^2) and anisotropic temperature factors for non-hydrogen atoms. The hydrogen atoms attached to C(5) of **2** were not included. The choice of space group *Pnma* for **2** was suggested by statistical tests and by the final refinement. Final R values are given in Table I. The final weighting scheme was $w = 1/(A + |F_o| + B|F_o|^2)$, where $A = 7.6$ and $B = 0.021$ for **1** and $A = 9.1$ and $B = 0.017$ for **2**, were chosen so as to maintain $w(|F_o| - |F_c|)^2$ essentially constant over all ranges of F_o and (sin θ)/λ. Atomic scattering factors were those given in ref 15. All the calculations were done by using the computer programs from XRAY 70.[16] Final positional parameters for non-hydrogen atoms are given in Table II. Anisotropic thermal parameters for non-hydrogen atoms, calculated and observed structure factors, and hydrogen atom fractional coordinates have been deposited as supplementary material.

Rate Studies. The spectral change in the ^{1}H NMR spectrum of the methyl group bound to cobalt in $(CH_3O)_3PCo(GH)_2CH_3$ was used to monitor the analogue of reaction 1 (vide infra). The methods used previously gave correlation coefficients of 0.998 (average of three runs) at 31.5 ± 0.5 °C.[17] Ligand-exchange reactions were monitored spectrophotometrically (Cary 14) at 25 ± 0.01 °C, in CH_2Cl_2 solvent, at λ 500–520 nm.

Results and Discussion

Syntheses of Complexes. A thorough search of the chemical literature revealed that $pyCo(GH)_2CH_3$ was the only Co(III) complex of glyoxime previously isolated. Schrauzer and Windgassen synthesized this complex via the sodium borohydride reduction of a basic aqueous methanol mixture of $CoCl_2 \cdot 6H_2O$, glyoxime, and pyridine in the presence of methyl iodide.[18] The reported yield of complex was only 2.5% based upon starting cobalt salt. We have found that the apparently slight difference in the electronic and perhaps steric properties of the GH ligand compared to those of the DH ligand nevertheless results in considerably greater difficulties in syntheses.

In light of the lack of preparative procedures for bis(glyoximato)cobalt(III) complexes, we initially attempted synthetic techniques that had been successful for the analogous bis(dimethylglyoximato)cobalt(III) complexes. Consequently, we attempted to prepare $Co(GH)(GH_2)Cl_2$, since $Co(DH)(DH_2)Cl_2$ has proved to be an extremely useful entry into the DH series.[19] However, when glyoxime was combined with $CoCl_2 \cdot 6H_2O$ (2:1 ratio) in acetone, the only isolable compound

Table II. Fractional Atomic Coordinates (× 10^4) for Non-Hydrogen Atoms of 1 and 2

	x	y	z
		1	
Co	3578 (0)	2196 (0)	1585 (0)
P	2066 (0)	1375 (1)	2981 (0)
O(1)	5455 (2)	2992 (3)	3357 (2)
O(2)	3093 (2)	−520 (3)	527 (2)
O(3)	1893 (2)	1493 (3)	−363 (2)
O(4)	4285 (2)	5007 (2)	2434 (2)
N(1)	4885 (2)	1921 (3)	2727 (2)
N(2)	3777 (2)	262 (3)	1345 (2)
N(3)	2402 (2)	2534 (3)	323 (2)
N(4)	3522 (2)	4207 (2)	1701 (2)
C(1)	5277 (3)	648 (4)	2821 (3)
C(2)	4623 (3)	−326 (4)	2017 (3)
C(3)	2092 (3)	3851 (4)	155 (2)
C(4)	2759 (3)	4846 (3)	940 (3)
C(5)	4846 (3)	2840 (5)	409 (3)
C(6)	1807 (2)	−618 (2)	3127 (2)
C(7)	2677 (3)	−1387 (3)	3817 (3)
C(8)	2567 (3)	−2915 (3)	3906 (3)
C(9)	1597 (4)	−3665 (3)	3322 (3)
C(10)	732 (3)	−2922 (3)	2656 (4)
C(11)	833 (3)	−1393 (3)	2537 (3)
C(12)	565 (2)	2009 (2)	2629 (2)
C(13)	−33 (2)	1873 (3)	1493 (2)
C(14)	−1176 (2)	2346 (3)	1225 (3)
C(15)	−1720 (2)	2966 (4)	2067 (3)
C(16)	−1138 (3)	3126 (4)	3185 (3)
C(17)	3 (2)	2651 (3)	3476 (2)
C(18)	2409 (2)	1796 (2)	4534 (2)
C(19)	1936 (2)	891 (3)	5491 (2)
C(20)	2143 (3)	1297 (3)	6653 (2)
C(21)	2804 (3)	2602 (4)	6871 (2)
C(22)	3259 (3)	3512 (4)	5936 (3)
C(23)	3078 (3)	3106 (3)	4762 (2)
		2	
Co	1472 (0)	2500	2442 (1)
P	729 (1)	2500	120 (1)
O(1)	927 (1)	96 (2)	3431 (3)
O(2)	2108 (1)	99 (2)	1703 (3)
O(3)	−144 (2)	2500	471 (4)
O(4)	660 (3)	917 (4)	−536 (5)
O(41)	969 (2)	1992 (4)	−1560 (5)
N(1)	821 (1)	1341 (2)	3518 (3)
N(2)	2177 (1)	1348 (2)	1525 (3)
C(1)	265 (2)	1825 (3)	4398 (3)
C(2)	2762 (3)	1821 (3)	730 (4)
C(3)	2139 (3)	2500	4536 (5)
C(4)	−726 (3)	2500	−830 (7)
C(5)	1050 (2)	492 (4)	−1754 (5)

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was a purple solid. Elemental analysis gave an empirical formula of $Co(GH_2)Cl_2$. Whether discrete molecules, dimers, or higher oligomers exist in the solid is not known at present. The compound is water soluble, giving a pink solution. The Co atom is likely in the +2 oxidation state with the ligands tetrahedrally arranged about it. Several complexes of the $M(XH_2)Cl_2$ type (where XH_2 is a general dioxime and M = Cu(II),[20-22] Pd(II),[22,23] or Pt(II)[22,23]) are known. A single-crystal X-ray diffraction study of $Cu(DH_2)Cl_2$ has shown that, in the solid state, chains of dimers exist with square-planar coordination about the Cu atoms.[20] IR spectral evidence has suggested that a similar structure probably obtains for the analogous Pd(II) and Pt(II) complexes, as well as for $M(XH_2)Cl_2$ (M = Cu(II), Pd(II)) with dioximes other than DH_2.[22] However, it is unlikely that $Co(GH_2)Cl_2$ has square-planar geometry. Since this compound failed to provide us with a pathway to organocobalt(III) compounds, it was not investigated further.

Other routes to $Co(GH)(GH_2)Cl_2$ were not successful. Vigorous aeration of acetone solutions still resulted in $Co(GH_2)Cl_2$. Aeration of 95% ethanol solutions of reactants produced a green solution, but no solid products could be isolated. Our lack of success in obtaining $Co(GH)(GH_2)Cl_2$ is likely due to either the preference of glyoxime for the anti-anti-anti conformation[24] or the relatively weaker electron-donating power of glyoxime (compared to that of dimethylglyoxime, vide infra), which does not provide a strong enough ligand field in conjunction with the chloride ligands to promote oxidation of Co(II).

When a stream of air was drawn through an aqueous ethanolic mixture of $CoCl_2 \cdot 6H_2O$ and glyoxime in the presence of pyridine, $pyCo(GH)_2Cl$ was obtained. The reaction worked as well for 4-*tert*-butylpyridine but not for 4-cyanopyridine, a weakly basic pyridine, which suggests that the coordination of electron-donating pyridines aids the oxidation of the cobalt atom. Although $pyCo(GH)_2Cl$ is only slightly soluble in CH_2Cl_2, in this solvent the pyridine ligand could be displaced by the extremely good ligand tri-*n*-butylphosphine. $(CH_3O)_3PCo(GH)_2Cl$ was prepared by treating 4-*t*-Bupy-$Co(GH)_2Cl$ (which is very soluble in CH_2Cl_2) with $P(OCH_3)_3$ and exploiting the near-insolubility of the product complex in this solvent.

Although the 4-R$pyCo(GH)_2Cl$ complexes (where R = H or *t*-Bu) could be alkylated via $NaBH_4$ reduction in the presence of appropriate alkylating agent, yields were considerably lower than for the DH complexes prepared by this method.[19] The lower yields are most likely due to the instability of the reduced species, $LCo(I)(GH)_2$, to their reduced nucleophilicity, or to a combination of both factors. Schrauzer and Deutsch have previously reported the relative instability of $LCo(I)(GH)_2$, where L = py, $S(CH_3)_2$, or H_2O.[25] In addition, these workers found that $Bu_3PCo(I)(GH)_2$ was approximately 600 times less nucleophilic than $Bu_3PCo(I)(DH)_2$ and hypothesized that this result may be due to lower electron donation by the GH ligands relative to that by the DH ligands.[25]

The $pyCo(GH)_2R$ complexs (where R = CH_3, C_2H_5) were converted to $H_2OCo(GH)_2R$ with use of Dowex 50W-X8 ion-exchange resin (H^+ form) similarly to the corresponding DH complexes.[26] The coordinated H_2O ligand could be easily exchanged for other ligands (e.g. $P(OCH_3)_3$, $P(C_6H_5)_3$, and $P(c\text{-}C_6H_{11})_3$) in methanol/CH_2Cl_2.

$H_2OCo(GH)_2P(O)(OCH_3)_2$ was formed by boiling $(CH_3O)_3PCo(GH)_2Cl$ in the presence of excess aqueous LiCl. The conversion of coordinated $P(OCH_3)_3$ to the uninegative dimethyl phosphonate ligand is a well-documented reaction in the DH series.[17,27] Furthermore, the rate of the attack of nucleophile on coordinated $P(OCH_3)_3$ may be quantified and used as a measure of the overall electron donation of the cobalt moiety (vide infra).[17]

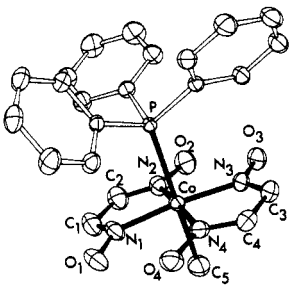

Figure 1. Numbering scheme for the non-hydrogen atoms of **1**.

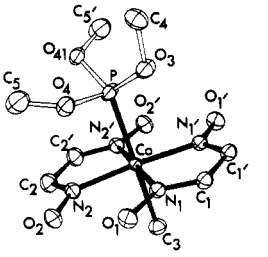

Figure 2. Numbering scheme for the non-hydrogen atoms of **2**. Primed atoms are related to nonprimed atoms by a crystallographic mirror plane bisecting the C(1)–C(1′) and C(2)–C(2′) bonds and containing Co, P, C(3), C(4), and O(3).

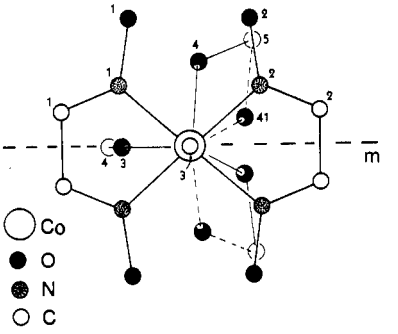

Figure 3. The two orientations of the $P(OCH_3)_3$ ligand with respect to the equatorial plane in **2**.

X-ray Crystallographic Studies. Description of the Structures. ORTEP drawings of crystallographically independent molecules of **1** and **2** with the atom-numbering schemes are depicted in Figures 1 and 2, respectively.

The four N atoms of the $(GH)_2$ unit are coplanar within ±0.003 Å (**1**) and are strictly planar in **2**. The cobalt atoms are displaced 0.11 Å (**1**) and 0.08 Å (**2**) from their mean planes toward phosphine. The deviation from planarity of the $Co(GH)_2$ unit is relatively small in both molecules; the interplanar angles α are 6.1° (**1**) and 4.1° (**2**), respectively, where α is the dihedral angle between the two GH units. Bond lengths and angles of the $Co(GH)_2$ moiety are very similar in both complexes. For example, the mean Co–N bond lengths are 1.883 (2) Å (**1**) and 1.887 (2) Å (**2**). The O···O distances are 2.490 (3) (mean) and 2.472 (3) Å in **1** and **2**, respectively.

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Table III. Structural Comparison between $LCo(DH)_2Me$ and $LCo(GH)_2Me$ Complexes with L = PPh_3 and $P(OMe)_3$[a]

	$Ph_3PCo(DH)_2Me$	$Ph_3PCo(GH)_2Me$	$(MeO)_3PCo(DH)_2Me$	$(MeO)_3PCo(GH)_2Me$
Co–P	2.418 (1)	2.428 (1)	2.256 (4)	2.268 (1)
Co–C	2.026 (6)	2.033 (3)	2.014 (14)	2.041 (4)
Co–N	1.891 (5)	1.883 (2)	1.881 (12)	1.887 (2)
N–O	1.358 (6)	1.353 (3)	1.35 (2)	1.352 (3)
C–N	1.314 (8)	1.296 (4)	1.32 (2)	1.301 (4)
C–C	1.456 (9)	1.445 (5)	1.45 (2)	1.453 (5)
P–Co–C	175.4 (2)	178.8 (1)	177.2 (5)	179.9 (0)
P–Co–N	93.4 (1)	93.3 (1)	92.1 (4)	92.4 (1)
C–Co–N	86.6 (2)	86.7 (1)	87.8 (7)	87.6 (1)
N(1)–Co–N(2)	81.7 (2)	82.0 (1)	81.3 (6)	82.1 (1)
N(2)–Co–N(3)	98.0 (2)	97.7 (1)	98.6 (6)	97.7 (1)
Co–N–O	123.1 (4)	123.7 (2)	122 (1)	123.3 (2)
Co–N–C	116.5 (4)	115.8 (2)	117 (1)	115.7 (2)
C–N–O	120.9 (5)	120.4 (2)	121 (1)	121.0 (2)
N–C–C	112.7 (6)	113.3 (3)	113 (1)	113.3 (3)
α[b]	11	6	10	4
d[c]	0.11	0.11	0.10	0.08

[a] Distances are given in angstroms and angles in degrees. [b] For the $(DH)_2$ derivatives, the α value refers to the angles between the DH units without including the side methyl groups. α values are given in degrees. [c] Displacement of the Co from the equatorial plane, given in angstroms.

In **1**, the $CH_3CoP(C_6H_5)_3$ fragment is characterized by a C–Co–P angle of 178.8 (1)° and Co–C and Co–P bond lengths of 2.033 (3) and 2.428 (1) Å, respectively.

In **2**, the corresponding values for the $CH_3CoP(OCH_3)_3$ fragment are 179.85 (2)°, 2.041 (4) Å, and 2.268 (1) Å. The $P(OCH_3)_3$ ligand was found to be disordered, having two different orientations with respect to the plane of the equatorial ligands (Figure 3).

Structural Comparisons. It is of interest to compare the structures of the bis(glyoximato) complexes in this study with those of analogous bis(dimethylglyoximato) complexes.[13,28] The mean bond lengths and angles are compared in Table III.

The comparison shows that all the geometrical parameters for the four complexes are equal within experimental error except for the Co–P bond lengths, the C–Co–P angles, and the α angles. The C–Co–P and α angles appear to be smaller, while the Co–P bonds are slightly, but significantly, longer in the $(GH)_2$ derivatives. We have already shown that the above structural parameters are related to the steric interaction between the phosphorus ligand and the equatorial ligand system,[13] although some influence of crystal packing cannot be completely ruled out. However, in the present case we believe that the greater planarity of the $(GH)_2$ complexes, as compared with that of the $(DH)_2$ analogues, may be mainly ascribed to the reduced interaction between phosphorus ligand side groups and the $(GH)_2$ ligands, which possess no peripheral methyl groups. This is also in agreement with the values of the C–Co–P angles, which are nearly 180° in the $(GH)_2$ compounds. On the other hand, the slight lengthening of the Co–P bond in the $(GH)_2$ complexes (if significant) might be due to the weaker electronic donation of the GH ligand compared to that of the DH ligand. Ordinarily, one might have expected the opposite trend but studies with relatively weak donor ligand systems such as salen[29] (where salen = bis(salicylaldehyde) ethylenediimine) and saloph[30] (where saloph = bis(salicylaldehyde) phenylenediimine) have indicated longer bonds to axial ligands.

Spectroscopic and Rate Studies. The ^{13}C NMR spectra of $LCo(GH)_2R$ (where L = $P(OCH_3)_3$, R = CH_3, C_2H_5, $P(O)(OCH_3)_2$ and L = 4-*t*-Bupy, R = CH_3, Cl) were determined. From previous studies, we have shown that the ^{13}C chemical shifts of the ester carbons of coordinated $P(OCH_3)_3$ and the γ-carbon of coordinated 4-*t*-Bupy in $LCo(DH)_2R$ complexes correlate well with log k_{obsd} for reaction 1 and are good measures of the electron donor ability of the rest of the cobalt complex (viewed as a substituent) and independent of steric effects.[17,31] The ^{13}C chemical shifts of the ester carbons in $(CH_3O)_3PCo(GH)_2R$ ranged from 0.75 to 0.79 ppm downfield from the shifts in the corresponding $(CH_3O)_3PCo(DH)_2R$ complexes. The ^{13}C shifts for the γ-carbon in 4-*t*-Bupy$Co(GH)_2R$ (R = CH_3, Cl) were 0.93 and 0.97 ppm downfield, respectively, from the shifts in the corresponding DH complexes.

Table IV.[a] Rate Comparisons for Ligand-Exchange Reactions, $LCo(OxH)_2R + L' \rightarrow L'Co(OxH)_2R + L$ (Where OxH = GH or DH)

L, R	k_{obsd}(GH), s^{-1}	k_{obsd}(DH)/k_{obsd}(GH)
$P(OCH_3)_3$, CH_3	$(5.3 \pm 0.1) \times 10^{-5}$	72
$P(C_6H_5)_3$, CH_3	$(4.6 \pm 0.1) \times 10^{-3}$	14
$P(c\text{-}C_6H_{11})_3$, CH_3	$(3.3 \pm 0.1) \times 10^{-3}$	115
py, CH_3	$(8.7 \pm 0.1) \times 10^{-5}$	92
py, C_2H_5	$(3.0 \pm 0.1) \times 10^{-3}$	29
py, $i\text{-}C_3H_7$	$(5.2 \pm 0.8) \times 10^{-2}$	58

[a] Conditions: CH_2Cl_2, 25 °C, [Co] = 0.01 M, [L'] = 0.1 M (pseudo-first-order conditions). L' = $P(n\text{-}C_4H_9)_3$ except for L = $P(OCH_3)_3$, where L' = 1-methylimidazole. Values for the DH compounds are taken from ref 32 except for $pyCo(DH)_2C_2H_5$, which was prepared as described in ref 32. Anal. Calcd for $C_{15}H_{28}N_5O_4Co$: C, 45.32; H, 6.09; N, 17.64. Found: C, 45.09; H, 6.15; N, 17.58.

$$(CH_3O)_3PCo(DH)_2R + Br^- \rightarrow [(CH_3O)_2(O)PCo(DH)_2R]^- + CH_3Br \quad (1)$$

We determined the pseudo-first-order rate constant for $(CH_3O)_3PCo(GH)_2CH_3$ in reaction 1 as $k_{obsd} = (3.11 \pm 0.06) \times 10^{-6}$ s^{-1} (average of three runs). Using a least-squares line for log k_{obsd} vs. $\delta(O^{13}CH_3)$ determined previously for the DH series,[17] we calculate $k_{calcd} = 3.89 \times 10^{-6}$ s^{-1} for this GH complex ($\delta(O^{13}CH_3) = 53.00$), which is in good agreement with the measured value. These results imply that the $Co(GH)_2R$ group is considerably more electron attracting than $Co(DH)_2R$ since our previous studies have demonstrated that downfield shifts for these carbon atoms are associated with electron withdrawal by the cobalt moiety.[17,31] Furthermore,

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one may conclude that the GH ligand is less electron donating that the DH ligand in agreement with the findings of Schrauzer's group (vide supra).

This conclusion gains further support from the ligand exchange rate data in Table IV. The DH compounds undergo ligand exchange of the neutral axial ligand at rates ~14–115 times faster than those for the GH compounds. Steric factors are probably not as important as electronic factors in influencing these decreased relative rates. If steric factors were important, we would have expected that, for the bulky triphenylphosphine leaving ligand, the relative rate would have been greater than for the nonbulky trimethyl phosphite leaving ligand. All the results, therefore, suggest that the differences in spectral properties and reaction rates are a consequence of electronic effects rather than steric effects. Slight differences are observed in comparisons of structures of the DH and GH compounds, but these have no appreciable effects on the relative chemistry of the two ligand systems.

One of the striking features of our studies with the DH model compounds is the relatively similar bond length and bond angles about the Co–C–C moieties in models[7-11,33] and in coenzyme B_{12}.[34,35] Considering the vast difference in steric and electronic properties between the natural corrin equatorial ligand and dioxime ligands, one would not have a priori expected such similarities in the Co–C bond length and Co–C–C bond angle. However, if the primary determinant of these parameters involves nonbonded interactions between the close-in atoms, particularly between the β-C moiety and the inner coordination sphere, then the similarities are more easily understood. Clearly, further work is needed to more precisely define the steric factors which control Co–C bond length and Co–C–C bond angles, particularly as these might pertain to the promotion of Co–C bond homolysis by B_{12}-dependent enzymes.

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Note Added in Proof. While this paper was in press, a preparation of $Co(GH_2)Cl_2$ appeared (Egharevba, G. O.; Megnamisi-Belombe, M. *Transition Met. Chem.* **1982**, *7*, 357) that was analogous to the method reported here. The crystal structures of $H_2OCo(GH)_2Br$ (Megnamisi-Belombe, M.; Endres, H.; Rossato, E. *Acta Crystallogr., Sect. C* **1983**, *C39*, 705) and the complex salt $[Co(H_2O)_6][Co(GH)_2Br_2]_2$ (Egharevba, G. O.; Megnamisi-Belombe, M.; Endres, H.; Rossato, E. *Acta Crystallogr., Sect. B* **1982**, *B38*, 2901) have been determined.

Registry No. **1**, 87155-69-9; **2**, 87155-70-2; $Co(GH_2)Cl_2$, 84724-51-6; $pyCo(GH)_2Cl$, 87155-61-1; 4-*t*-$BupyCo(GH)_2Cl$, 87155-62-2; $(CH_3O)_3PCo(GH)_2Cl$, 87155-63-3; $Bu_3PCo(GH)_2Cl$, 87155-64-4; $pyCo(GH)_2CH_3$, 27073-09-2; $pyCo(GH)_2C_2H_5$, 87155-65-5; $pyCo(GH)_2$-*i*-C_3H_7, 87155-66-6; 4-*t*-$BupyCo(GH)_2CH_3$, 87155-67-7; $H_2OCo(GH)_2CH_3$, 87155-68-8; $(c\text{-}C_6H_{11})_3PCo(GH)_2CH_3$, 87155-71-3; $H_2OCo(GH)_2C_2H_5$, 87155-72-4; $(CH_3O)_3PCo(GH_2)C_2H_5$, 87155-73-5; $H_2OCo(GH)_2P(O)(OCH_3)_2$, 87174-15-0; $(CH_3O)_3PCo(GH)_2P(O)(OCH_3)_2$, 87174-16-1; 1-methylimidazole, 616-47-7.

Supplementary Material Available: Tables of anisotropic thermal parameters, bond lengths and relevant bond angles, equations of least-squares planes for the non-hydrogen atoms, parameters for the hydrogen atoms, and calculated and observed structure factor amplitudes (24 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry, University of California at Davis, Davis, California 95616

A Compound with Severely Distorted Geometry at Ligated Carbon: Synthesis and X-ray Crystal Structure of $Bi[CH(SiMe_3)_2]_3$, a Trialkylbismuth Complex with High Thermal Stability†

BRENDAN MURRAY, JAN HVOSLEF, HÅKON HOPE, and PHILIP P. POWER*

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The high-yield synthesis and the X-ray crystal structure of $Bi[CH(SiMe_3)_2]_3$ are described. At 140 K the crystals are monoclinic, space group $P2_1/c$, $Z = 4$, with $a = 8.351$ (3) Å, $b = 21.615$ (12) Å, $c = 19.060$ (7) Å, and $\beta = 94.47$ (3)°. This is the first reported example of a crystal structure determination of a bismuth trialkyl. The geometry at bismuth is trigonal pyramidal with an average Bi–C distance of 2.328 (±0.013) Å and an average C–Bi–C angle of 102.9 (±0.5)°. Both the Bi–C distance and the angle at bismuth are large compared with those of the few previously reported structures containing Bi–C bonds. An outstanding feature of the structure is the severe distortion found in the geometry of the ligand, particularly at the carbon atom attched to bismuth. An average difference of about 14° in the two Bi–C–Si angles in each alkyl substituent is observed, whereas the distortion at the Si atoms amounts to 5°. The average C–Si distance is 1.874 (±0.014) Å. The compound has high thermal stability, not decomposing until 148 °C.

Introduction

Antimony and bismuth are among the least studied heavier main-group elements. The chemical and physical properties of their compounds are less well-known than those involving tin, lead, indium, thallium, or tellurium. The lack of interest is particularly striking compared with the large volume of publications on the lighter group 5A elements.[1] Recent publications on the use of organobismuth compounds to provide mobile functional groups in organic synthesis,[2] as well as the revival of interest in main-group metal clusters,[3] may indicate increasing interest in the area. Nevertheless, basic information

† No reprints available.

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