Preparation of Arsinocobaloximes and the Crystal Structure of $[(CH_3)(C_6H_5)As(O)Co^{III}(dmgH)(dmg)]_2Co^{II}$

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Abstract: The Co(I) cobaloxime $(C_4H_9)_3PCo(dmgH)_2$ reacts with $(CH_3)_2AsCl$, $(CH_3)_2AsI$, $C_6H_5AsCl_2$, $(C_6H_5)(CH_3)AsCl$, and $(C_6H_5)_2AsCl$ to give solutions of the air-sensitive species $R'R''AsCo(dmgH)_2P(C_4H_9)_3$. When $R' = R'' = CH_3$ and $R' = C_6H_5$, $R'' = Cl$, the ultimate product is $\{[(C_4H_9)_3P]_2Co(dmgH)_2\}^+ X^-$ ($X = Cl, I$). When $R' = C_6H_5$ and $R'' = C_6H_5, CH_3$, a red solid can be isolated of formula $[R'R''As(O)Co(dmg_2H)P(C_4H_9)_3]_2Co$ which is hydrated ($2H_2O$) in the case $R' = C_6H_5$, $R'' = CH_3$. The crystal structure of a hydrated complex (final $R_1 = 0.102$) consists of two $(C_6H_5)(CH_3)AsO$-$Co(dmg_2H)P(C_4H_9)_3$ units which are bonded in a *fac* configuration to a central Co(II) atom through the arsenyl O and two adjacent dmg O atoms. The average Co(II)–O bond length (six bonds) is 2.08 Å. The two Co(III) atoms are axially bound to $(C_4H_9)_3P$ and $(C_6H_5)(CH_3)As(O)$ units. The molecule has approximate (noncrystallographic) twofold symmetry and is dissymmetric. Solutions of $(CH_3)_2AsCo(dmgH)_2P(C_4H_9)_3$ react with CH_3I and $CH_3Co(dmgH)_2C_5H_5N$ to give $(CH_3)_3As$ and methyl-cobalt complexes. The CH_3 group of $CH_3Co(dmgH)_2C_5H_5N$ is not transferred to arsenic on reaction with AsH_3 (CH_4 is evolved) or AsX_3 ($[CH_3Co(dmgH_2)_2C_5H_5N]^{2+}2X^-$, $X = Cl$ or I, is produced). The relevance of these reactions to models for the biological methylation of arsenic is discussed.

Introduction

Although it has yet to be proven, methylcobalamin has been implicated in the biological methylation of many elements[2] including mercury,[3] arsenic,[4,5] tin,[6] lead,[7] selenium,[8] and thallium.[9] As a consequence, during the past few years there has been an extensive investigation of alkyl transfer reactions between alkyl-cobalt complexes and metal electrophiles such as Hg(II), Pt(II), Au(I), Cu(II), Cr(II), Tl(III), Pb(II), Cd(II), and Zn(II).[10] In the case of arsenic, Schrauzer and co-workers[5] have reported that the arsines $(CH_3)_nH_{3-n}As$ ($n = 0$–3) are obtained by reacting methylcobaloximes with As_2O_3 in the presence of thiols (or NH_4Cl/Zn) as reducing agents. A very speculative mechanism for this reaction was advanced which embraced the possibility of intermediates with cobalt-arsenic σ bonds being involved.

We have recently presented evidence[11] which indicates that the biological methylation of arsenic to trimethylarsine by aerobic microorganisms proceeds by a series of oxidation-reduction steps involving carbonium ions (probably from *S*-adenosylmethionine) as suggested some time ago by Challenger (reaction 1).[12]

$$CH_3^+ + \overset{..}{As}(III) \rightarrow CH_3As(V) \xrightarrow{2e^-} CH_3\overset{..}{As}(III) \qquad (1)$$

$$CH_3\overset{..}{As}(III) \xrightarrow[\text{(b) } 2e^-]{\text{(a) } CH_3^+} (CH_3)_2\overset{..}{As}(III) \xrightarrow[\text{(b) } 2e^-]{\text{(a) } CH_3^+} (CH_3)_3As$$

Nevertheless the original work by McBride and Wolfe[4] on cell-free extracts of *Methanobacterium* strain M.O.H. indicates that methylcobalamin does transfer its CH_3 group to arsenic to give $(CH_3)_2AsH$ (from arsenate).[13] Thus the possibility exists that anaerobic methylation of arsenic could involve alkyl-cobalt intermediates.

With this in mind we have prepared some compounds with the Co–$\overset{..}{As}R_2$ moiety and studied their properties.

Experimental Section

All reactions were carried out under a nitrogen or argon atmosphere. Infrared spectra were recorded on a Perkin-Elmer 457 spectrometer and calibrated by using polystyrene. NMR spectra were run on Varian T-60 and XL-100 instruments. Chemical shifts are given in ppm downfield from internal Me_4Si. Ultraviolet and visible spectra were recorded on a Cary 17-D spectrophotometer. Gas samples were monitored by GLC by using a Varian 1520 instrument fitted with a 6-ft 5% SE 30, stainless steel column. Microanalyses were performed by Mr. Peter Borda (U.B.C.). Arsenic compounds were prepared by using methods described in the literature: $(CH_3)_2AsCl$,[14] $(CH_3)_2AsI$,[15] CH_3AsCl_2,[15] $(CH_3)(C_6H_5)AsCl$,[16] $C_6H_5AsCl_2$,[16] AsI_3,[17] and AsH_3.[18] $AsCl_3$, As_2O_3, $(CH_3)_2AsO(OH)$, and $C_6H_5AsO(OH)_2$ were commercial products.

Bromo(dimethyl sulfide)cobaloxime was prepared by the method of Hill and Morallee[19] by using dimethyl sulfide as the base. Bromo(4-*tert*-butylpyridine)cobaloxime $[Br(4\text{-}t\text{-}C_4H_9C_5H_5N)\text{-}Co(dmgH)_2$ where dmgH = dimethylglyoximato monoanion] and $Br[(n\text{-}C_4H_9)_3P]Co(dmgH)_2$ were prepared from the corresponding (dimethyl sulfide)cobaloxime.[20]

Reaction of Bromo(4-*tert*-butylpyridine)cobaloxime with Iododimethylarsine. $NaBH_4$ (0.05 g; 1.3 mmol) was added to a deoxygenated methanol solution (25 mL) of the cobaloxime (0.135 g; 0.27 mmol) at 0 °C. The color changed immediately from red-brown to deep blue. Acetone (5 mL) was added to remove the excess $NaBH_4$. The arsine (0.062 g; 0.27 mmol) in methanol (2 mL) was added dropwise producing a red-brown solution and precipitate. The reaction mixture was allowed to warm to room temperature, the precipitate was filtered, washed with water, methanol, and acetone, and dried in vacuo (yield ~60% on the basis of the empirical formula given below).

Anal. Calcd for $(C_{10}H_{20}N_4O_4AsCo\cdot CH_3OH)_x$: C, 31.0; H, 5.40; N, 13.2. Found: C, 32.9; H, 5.35; N, 13.2.

Reaction of Bromo(tri-*n*-butylphosphine)cobaloxime with Iododimethylarsine, Chlorodimethylarsine, and Dichlorophenylarsine. The following general procedure was used. An excess (5×) of $NaBH_4$ was first added to a deoxygenated methanol solution of the cobaloxime (0.5 mmol) at 0 °C, then acetone (5 mL). *Slow dropwise* addition of an equimolar amount of the haloarsine in methanol produced a color change from deep blue to green. The ice bath was removed and the solution stirred at room temperature (10 h) after which time the color had reverted to red-brown. The solution was concentrated (2–3 mL), degassed water (25 mL) was added, and the resulting red-brown solid filtered. Recrystallization of the solid, under an argon atmosphere, from a 1:5 benzene-petroleum ether (bp 30–60 °C) mixture at 25 °C gave dark red-brown crystals of $(Co(dmgH)_2[P(C_4H_9)_3]_2)^+X^-$ ($X = I, Cl$)[21] in 35–45% yield.

Anal. Calcd for $C_{32}H_{68}CoIN_4O_4P_2$: C, 46.8; H, 8.29; N, 6.83; I, 15.5. Found: C, 46.6; H, 8.23; N, 6.59; I, 15.0. Calcd for $C_{32}H_{68}ClCoN_4O_4P_2$: C, 52.8; H, 9.34; N, 7.69. Found: C, 52.5; H, 9.10; N, 7.40.

The NMR spectrum ($CDCl_3$ solution) of the iodide complex consisted of a triplet centered at 2.43 ($dmgH\text{-}CH_3$, $J(H,P) = 3.0$ Hz) and broad multiplets centered at 1.30 and 0.90 ($P(C_4H_9)_3$). The NMR

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spectrum ($CDCl_3$) of the chloride complex exhibited a triplet centered at 2.33 (dmgH-CH_3, J(H,P) = 2.5 Hz) and multiplets centered at 1.33 and 0.90 ($P(C_4H_9)_3$).

Reaction of Bromo(tri-*n*-butylphosphine)cobaloxime with Chloromethylphenylarsine. $NaBH_4$ (0.16 g; 4.2 mmol) was added to a red-brown degassed methanol solution (25 mL) of the cobaloxime (0.48 g; 0.84 mmol) at 0 °C. Acetone (5 mL) was added to the blue solution, followed by the *slow dropwise* addition of $Cl(CH_3)(C_6H_5)As$ (0.17 g; 0.84 mmol) in methanol (3 mL). The green solution was stirred at 0 °C for 1.5 h. After stirring at room temperature for a further 6.5 h, the color had changed to red-brown. The solution was concentrated (2-3 mL) and degassed water (25 mL) was added. The water-insoluble oil was recrystallized from a degassed methanol-water mixture at ~25 °C affording metallic brown plates of B: yield, 0.030 g (~5%).

Anal. Calcd for $C_{54}H_{96}As_2Co_3N_8O_{10}P_2 \cdot 2H_2O$: C, 45.0; H, 6.94; N, 7.77; As, 10.4. Found: C, 45.2; H, 7.15; N, 7.59; As, 10.1.

The ^1H NMR spectrum ($CDCl_3$ solution) consisted of singlets at 7.30 (As-C_6H_5) and 1.60 (As-CH_3), doublets centered at 2.20 (dmgH-CH_3 J(H,P) = 2.6 Hz) and 1.94 (dmgH-CH_3, J(H,P) = 2.7 Hz), and broad multiplets centered at 1.28 and 0.90 ($P(C_4H_9)_3$). The structure of this material B was determined by X-ray techniques as described below.

Reaction of Bromo(tri-*n*-butylphosphine)cobaloxime with Chlorodiphenylarsine. $NaBH_4$ (0.12 g; 3.2 mmol) was added to a red-brown degassed methanol solution (50 mL) of the cobaloxime (0.350 g; 0.61 mmol) at 0 °C. Acetone (5 mL) was added to the blue solution, followed by, *slowly* and *dropwise*, a solution of $As(C_6H_5)_2Cl$ (0.16 g; 0.61 mmol) in methanol (5 mL). The green solution was stirred at 0 °C for 0.5 h and then at room temperature for a further 3 h. The red-brown solution was evaporated to dryness. The residue was washed with water and recrystallized from a degassed acetone-water mixture at 25 °C affording brown crystals of the diphenylarsino analogue of B: yield, 0.032 g (~10%).

Anal. Calcd for $C_{64}H_{100}As_2Co_3N_8O_{10}P_2$: C, 50.23; H, 6.54; N, 7.33. Found: C, 50.28; H, 6.60; N, 7.10.

The ^1H NMR spectrum ($CDCl_3$ solution) consisted of very broad peaks.

Alkylation Reactions. These were carried out using Schlenk type apparatus. Solid $NaBH_4$ (0.010 g; 0.26 mmol) was added to a degassed methanol solution (3 mL) of $Br[P(C_4H_9)_3]Co(dmgH)_2$ (0.045 g; 0.08 mmol) followed by acetone (1.5 mL). A methanol solution (1 mL) of $(CH_3)_2AsI$ (0.018 g; 0.08 mmol) was slowly added to the blue solution. Upon addition of CH_3I (0.16 mmol) the color changed from green to yellow-orange. A sample of the head space in the tube was found to contain $As(CH_3)_3$ on examination by GLC. Solvents were removed in vacuo leaving an orange solid which was identified as $CH_3[P(C_4H_9)_3]Co(dmgH)_2$ of known ^1H NMR spectrum.[22] In another experiment after the addition of excess CH_3I (0.81 mmol) solvents were removed in vacuo leaving an oily orange solid. The water-soluble material was shown to contain $As(CH_3)_4I$ of known ultraviolet spectrum and melting point (330 °C, lit. 325-326 °C[23]). ^1H NMR spectrum (D_2O solution) singlet 172 Hz upfield of H_2O. The water-insoluble material was identified as $CH_3[P(C_4H_9)_3]$-$Co(dmgH)_2$.

Reaction of Methylaquocobaloxime with Arsine. Methylaquocobaloxime (0.434 g, 1.34 mmol), deoxygenated water (3 mL), and arsine (0.586 g, 7.5 mmol) were allowed to mix in a sealed Carius tube. The tube was warmed to 20 °C (from −196 °C) and agitated in the dark for 4 days. The tube was opened and the noncondensible gas was identified as a mixture of CH_4 and H_2 by means of its infrared spectrum and by GLC. No condensible gases were obtained when the tube was warmed. Addition of dithioerythritol (0.2 g) to the reaction mixture made no difference to the course of the reaction.

Reaction of Arsenic Trichloride with Methylpyridinecobaloxime. Freshly distilled $AsCl_3$ (72 μL, 0.9 mmol) was added to a degassed suspension of the cobaloxime (0.360 g; 0.9 mmol) in methanol (10 mL). The solution cleared, turned bright red, and later (10 min) an orange precipitate formed. The suspension was stirred for a further hour. The solvent was removed in vacuo and the orange solid identified as D recrystallized from methylene chloride-hexane as orange needles: yield, 89%.

Anal. Calcd for $C_{14}H_{24}N_5O_4Cl_2Co$: C, 36.84; H, 5.26; N, 15.35; Cl, 15.57. Found: C, 36.71; H, 5.28; N, 15.06; Cl, 14.98.

The ^1H NMR spectrum ($CDCl_3$ solution) consisted of a broad peak centered at 10.36 (dmgH_2-O*H*), multiplets centered at 8.90, 8.33, and 7.96 (C_5H_5N), and singlets at 2.26 (dmgH_2-CH_3) and 1.13 (Co-CH_3).

Table I. Crystal Data

$C_{54}H_{100}As_2Co_3N_4O_{12}P_2$		F_w	1442.0
space group	$P\bar{1}$	ρ_0[a]	1.39 g cm^{-3}
a	11.77 (2) Å	ρ_c (Z = 2)	1.40 g cm^{-3}
b	13.65 (2) Å	μ	18.75 cm^{-1}
c	21.90 (4) Å	Mo Kα_1 radiation	λ = 0.70926 Å
α	96.06 (8)°	unique reflections	2755
β	92.80 (7)°	reflections $I > 2.3\sigma_I$	1619
γ	101.10 (7)°	final R_1[b]	0.102
U	3423 Å^3	final R_2[c]	0.111

[a] Flotation in aqueous $ZnBr_2$ solution. [b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma F_o^2)^{1/2}$.

The identical compound was obtained by using dry $CHCl_3$ or toluene as solvents.

Reaction of Methylpyridinecobaloxime with Arsenic Triiodide or Dichloromethylarsine. CH_3AsCl_2 (0.084 g; 0.52 mmol) in degassed $CDCl_3$ (1 mL) was added to a degassed $CDCl_3$ solution (2 mL) of $(CH_3)(C_5H_5N)Co(dmgH)_2$ (0.200 g; 0.52 mmol). The solution was stirred for 1 h after which time the NMR spectrum revealed only starting materials. AsI_3 reacted slowly with $CH_3(C_5H_5N)Co(dmgH)_2$ in THF at 20 °C to give a solid whose NMR spectrum was identical with that of D.

X-Ray Crystallography. Very thin plates of B were obtained from methanol/water. The best formed and thickest crystals were selected under a microscope, removed from the mother liquor, and immediately transferred to Lindeman tubes (containing small amounts of the solvent) which were then sealed. Despite numerous attempts only one crystal was found which did not give a multiple diffraction pattern or show decomposition; even so the reflections were weak and not well defined. Since there seemed little possibility of finding a substantially better crystal, intensity data were collected on this one. It was recognized that the data set would be of poor quality but we were sure that solving the structure would be worthwhile in view of its chemical interest.

Cell dimensions were determined by least squares from the setting angles of 9 reflections with $2\theta > 20°$ which were centered on a Picker FACS-1 four circle diffractometer employing monochromated Mo $K\alpha_1$ radiation (T = 295 K). Crystal data are given in Table I. A θ-2θ scan was used to collect intensity data. The scan rate was 2° min^{-1} and the scan width $(1.4 + 0.692 \tan\theta)°$. Stationary-crystal stationary-counter background counts of 20 s were taken at each side of the scan. The intensities of 2755 unique reflections with $2\theta \leq 30°$ were measured and of these 1619 with $I > 2.3\sigma_I$ (σ_I is the standard deviation of the intensity derived from counting statistics and a precision factor of 0.03) were regarded as observed and were used in structure solution and refinement. Data were not collected beyond $2\theta = 30°$ as the percentage of reflections classified as "observed" decreased rapidly. Two standard reflections were measured at regular intervals to scale the data.

The structure was solved by heavy-atom procedures. Full-matrix least-squares refinement of the nonhydrogen atoms with isotropic temperature factors yielded a value of 0.124 for R_1 $(=\Sigma||F_o| - |F_c||/\Sigma|F_o|)$. The As, Co, and P atoms were assigned anisotropic temperature factors in further refinement which gave $R_1 = 0.103$, but the most prominent features in a difference map still remained in the vicinity of the heavy atoms. The 4 As-Co and Co-P vectors are of similar length and direction so it was possible that the structure had refined to a false minimum. In order to overcome such a possibility various adjustments were made to the heavy atom coordinates, but in each case further least-squares cycles returned the atoms to their original positions. The coordinates of the nonmethyl H atoms were determined geometrically (r_{C-H} 0.95 Å, sp^2 or sp^3 geometry at C atoms) and the alkyl H atoms were assigned the average temperature factor of C(31)-C(33), C(41)-C(42), and C(51)-C(53) and the phenyl H atoms of C(62)-C(66). The H atom scattering contribution was included in future least squares, the parameters being recalculated after each set of cycles. The methyl H atoms were not located. Several C atoms exhibited high temperature factors suggesting that there might be some degree of disorder in the *n*-butyl groups which was not resolved on account of the poor data. Isotropic temperature factors

Table II. Final Positional and Thermal Parameters for $Co[(C_4H_9)_3PCo(dmg_2H)As(O)(CH_3)(C_6H_5)]_2 \cdot 2H_2O$[a,b]

atom	x	y	z	U	x	y	z	U
Co(2)	−0.1063(5)	−0.0254(5)	0.2445(3)	c				
		ligand 1				ligand 2		
Co(1)	−0.1430(4)	0.2129(5)	0.3266(3)	c	−0.0838(4)	−0.2709(4)	0.1628(3)	c
As(1)	−0.1623(4)	0.1968(4)	0.2206(2)	c	−0.1080(4)	−0.2606(4)	0.2680(2)	c
P(1)	−0.1171(10)	0.2020(11)	0.4291(6)	c	−0.0635(9)	−0.2531(9)	0.0626(5)	c
O(11)	0.010(2)	0.072(2)	0.307(1)	47(8)	0.027(2)	−0.059(2)	0.189(1)	47(8)
N(12)	0.002(3)	0.165(3)	0.316(1)	43(10)	0.032(2)	−0.158(2)	0.183(1)	20(9)
C(13)	0.092(4)	0.237(3)	0.315(2)	56(14)	0.143(4)	−0.172(3)	0.196(2)	55(14)
C(13A)	0.212(3)	0.218(3)	0.302(2)	61(14)	0.246(3)	−0.086(3)	0.218(2)	71(15)
C(14)	0.067(4)	0.345(3)	0.320(2)	52(13)	0.139(4)	−0.274(3)	0.189(2)	57(14)
C(14A)	0.158(3)	0.432(3)	0.324(2)	50(13)	0.254(3)	−0.320(3)	0.201(2)	70(14)
N(15)	−0.041(2)	0.334(2)	0.333(1)	30(9)	0.039(3)	−0.338 (3)	0.169(1)	63(11)
O(16)	−0.076(2)	0.442(2)	0.340(1)	65(9)	0.032(2)	−0.435(2)	0.164(1)	69(9)
O(21)	−0.239(2)	0.000(2)	0.301(1)	68(9)	−0.224(2)	−0.115(2)	0.177(1)	46(8)
N(22)	−0.254(3)	0.093(2)	0.314(1)	38(9)	−0.218(3)	−0.207(3)	0.164(1)	61(11)
C(23)	−0.367(4)	0.099(3)	0.325(2)	63(14)	−0.313(4)	−0.277(4)	0.147(2)	57(14)
C(23A)	−0.463(4)	−0.005(3)	0.312(2)	87(16)	−0.434(3)	−0.247(3)	0.144(2)	72(14)
C(24)	−0.374(4)	0.199(3)	0.339(2)	50(13)	−0.308(3)	−0.376(3)	0.136(2)	42(12)
C(24A)	−0.489(3)	0.249(3)	0.348(2)	73(14)	−0.404(3)	−0.472(3)	0.116(2)	78(15)
N(25)	−0.284(3)	0.261(3)	0.339(2)	82(13)	−0.194(3)	−0.387(3)	0.144(1)	49(10)
O(26)	−0.277(2)	0.363(2)	0.350(1)	86(10)	−0.175(2)	−0.483(2)	0.136(1)	73(9)
C(31)	0.016(4)	0.259(4)	0.468(2)	121(19)	0.080(4)	−0.245(4)	0.033(2)	110(18)
C(32)	0.050(5)	0.369(4)	0.478(2)	139(22)	0.122(4)	−0.341(4)	0.029(2)	94(16)
C(33)	0.193(9)	0.425(7)	0.502(5)	335(56)	0.273(5)	−0.320(4)	0.013(3)	151(24)
C(34)	0.213(6)	0.399(6)	0.547(4)	216(35)	0.299(6)	−0.283(6)	−0.036(4)	234(36)
C(41)	−0.123(4)	0.074(4)	0.445(2)	103(18)	−0.088(4)	−0.138(3)	0.047(2)	87(16)
C(42)	−0.235(4)	0.007(4)	0.455(2)	94(17)	−0.217(4)	−0.127(4)	0.030(2)	94(17)
C(43)	−0.241(7)	−0.117(7)	0.470(4)	267(39)	−0.246(7)	−0.015(6)	0.021(4)	274(39)
C(44)	−0.342(6)	−0.164(5)	0.498(3)	230(33)	−0.365(5)	0.012(5)	0.007(3)	197(28)
C(51)	−0.228(3)	0.253(3)	0.472(2)	82(15)	−0.161(3)	−0.350(3)	0.010(2)	58(13)
C(52)	−0.208(5)	0.252(4)	0.543(3)	153(22)	−0.151(3)	−0.338(3)	−0.062(2)	56(13)
C(53)	−0.320(4)	0.259(4)	0.581(2)	131(20)	−0.264(3)	−0.393(3)	−0.097(2)	55(13)
C(54)	−0.394(7)	0.343(7)	0.547(4)	312(44)	−0.257(3)	−0.389(3)	−0.163(2)	78(15)
O(1)	−0.118(2)	0.092(2)	0.194(1)	59(8)	−0.086(2)	−0.141(2)	0.291(1)	52(8)
C(1)	−0.074(3)	0.309(3)	0.187(1)	39(12)	−0.001(3)	−0.325(3)	0.319(2)	78(15)
C(61)	−0.331(3)	0.204(3)	0.185(2)	43(12)	−0.261(3)	−0.342(3)	0.289(2)	34(12)
C(62)	−0.378(4)	0.078(3)	0.169(2)	80(15)	−0.336(4)	−0.254(3)	0.296(2)	90(17)
C(63)	−0.500(4)	0.062(4)	0.151(2)	110(18)	−0.449(5)	−0.291(4)	0.305(2)	131(21)
C(64)	−0.545(3)	0.161(3)	0.152(2)	72(14)	−0.482(4)	−0.398(2)	0.304(2)	97(17)
C(65)	−0.494(4)	0.261(4)	0.170(2)	98(17)	−0.413(5)	−0.485(4)	0.279(2)	133(21)
C(66)	−0.381(4)	0.284(4)	0.189(2)	134(21)	−0.297(5)	−0.442(5)	0.297(2)	140(22)
OW(1)	0.087(3)	0.126(3)	0.137(1)	136(13)	0.110(3)	−0.067(3)	0.372(2)	172(16)
H(31A)	0.075	0.236	0.446		0.134	−0.195	0.059	
H(31B)	0.017	0.237	0.508		0.076	−0.224	−0.008	
H(32A)	−0.004	0.388	0.505		0.077	−0.386	−0.003	
H(32B)	0.032	0.388	0.438		0.113	−0.367	0.067	
H(33A)	0.175	0.497	0.510		0.297	−0.383	0.010	
H(33B)	0.228	0.420	0.479		0.317	−0.276	0.046	
H(41A)	−0.074	0.077	0.481		−0.044	−0.120	0.013	
H(41B)	−0.092	0.042	0.411		−0.059	−0.091	0.082	
H(42A)	−0.284	0.004	0.419		−0.262	−0.152	0.062	
H(42B)	−0.265	0.039	0.489		−0.242	−0.168	−0.008	
H(43A)	−0.174	−0.117	0.495		−0.201	0.008	−0.011	
H(43B)	−0.238	−0.155	0.431		−0.217	0.026	0.059	
H(51A)	−0.301	0.213	0.458		−0.239	−0.348	0.020	
H(51B)	−0.224	0.320	0.463		−0.144	−0.414	0.017	
H(52A)	−0.149	0.308	0.559		−0.089	−0.366	−0.077	
H(52B)	−0.184	0.192	0.550		−0.139	−0.268	−0.068	
H(53A)	−0.297	0.283	0.623		−0.325	−0.362	−0.084	
H(53B)	−0.369	0.194	0.578		−0.278	−0.461	−0.089	
H(62)	−0.334	0.027	0.172		−0.305	−0.185	0.294	
H(63)	−0.548	−0.003	0.139		−0.503	−0.248	0.311	
H(64)	−0.624	0.152	0.137		−0.562	−0.421	0.309	
H(65)	−0.538	0.312	0.168		−0.440	−0.554	0.301	
H(66)	−0.341	0.350	0.204		−0.249	−0.483	0.261	

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co(2)	41(4)	83(6)	70(5)	25(4)	4(4)	−3(4)
			ligand 1			
Co(1)	31(4)	50(5)	75(5)	19(4)	6(3)	1(4)
As(1)	28(3)	86(5)	75(4)	21(3)	0(3)	8(4)
P(1)	43(10)	102(13)	61(11)	15(9)	0(8)	−14(10)

Table II (*Continued*)

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
			ligand 2			
Co(1)	27(4)	37(5)	86(5)	23(4)	3(3)	4(4)
As(1)	38(4)	66(5)	80(4)	21(3)	−7(3)	10(4)
P(1)	28(9)	55(11)	76(11)	20(8)	17(8)	−21(9)

[a] Estimated standard deviations of the least significant figures are given in parentheses here and in succeeding tables. [b] The values of the thermal parameters (in Å^2) are multiplied by 10^3. U is 0.108 for H(61)–H(66) and 0.130 for the other H atoms. [c] Anisotropic temperature factors in the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{22}klb^*c^*)]$.

were retained for the O, N, and C atoms as the maximum peaks and troughs in a final difference map ($\pm$ 0.90–0.53 $e^- \text{Å}^{-3}$; $\sigma_p = 0.15$ $e^- \text{Å}^{-3}$) were around the As, Co and P atoms. In addition the observations/parameters ratio was low (1619/360 = 4.5).

Neutral scattering factors[24] were used throughout and anomalous dispersion corrections were applied for As, Co, and P.[25] A weighting scheme of the form $w = 1/\sigma_F{}^2$ was employed in the final stages of refinement. In the final cycle, all shift-to-error ratios were <0.2. Final R_1 was 0.102.

The atomic coordinates and associated thermal parameters are listed in Table II. Figure 1 shows the atom labeling scheme and some of the more important bond lengths and angles.

Results and Discussion

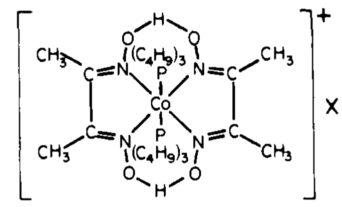
Compounds containing arsenic σ bonded to transition metals are not well known[26-31] and there is little information available about the properties of derivatives containing $M\text{-}AsR_2$ or $M\text{-}AsR\text{-}$ moieties (R = alkyl or aryl). Early work[31] showed that tetrakistrifluoromethyldiarsine reacts with compounds with metal-metal bonds to give for example $(\eta^5\text{-}C_5H_5)\text{-}Fe(CO)_2As(CF_3)_2$. More conventional routes have been developed by using metal carbonyl anions and haloarsines[27-30] and the compounds $(CH_3)_2As\text{-}M(CO)_n(C_5H_5\text{-}\eta^5)$ (e.g., M = Fe, n = 2; M = Mo, n = 3) have been found to be unexpectedly stable. This route using anions is the most obvious preparative one for cobaloxime compounds since reactions of the easily obtained powerful nucleophilic Co(I) species are very well documented.[32]

Thus Schrauzer and Kratel[33] used this approach to obtain cobaloxime derivatives of $\text{-}M(C_6H_5)_3$ (M = Si, Ge, Sn) and $\text{-}M'(C_6H_5)_2$ (M′ = Sb, Bi). We have employed essentially the same procedure in our study of the reaction of haloarsines with cobaloximes.[34]

Reaction of iododimethylarsine with (4-*tert*-butylpyridine)cobaloxime(I) gave a red solid that was insoluble in a wide range of solvents. Microanalysis indicated that the formula approximates to $[Co(dmgH)_2As(CH_3)_2]CH_3OH$. Schrauzer and Kratel[33] obtained a similar substance from chlorodimethylarsine and pyridinecobaloxime(I) and postulated a similar formula in spite of equally bad analytical data. There seems little doubt that both compounds are closely related and are probably polymers composed of $\text{-}AsMe_2 \rightarrow Co(dmgH)_2\text{-}$ units. Presumably facile displacement of the weaker pyridine bases by the arsine results in polymer formation. Such arsenido-bridged products are commonly encountered[27-31] and the carbonyl derivative $(CO)_4Co\text{-}As(CH_3)_2$ is apparently also unstable in this regard.[35]

In an attempt to block the polymerization reaction, tri-*n*-butylphosphinecobaloxime(I) was used as nucleophile. Slow dropwise addition of the haloarsines $(CH_3)_2AsCl$, $(CH_3)_2AsI$, $C_6H_5AsCl_2$, and $(R)(C_6H_5)AsCl$ (R = CH_3, C_6H_5) to the blue cobaloxime(I) solution produces a dark-green oxygen-sensitive solution which slowly (~6 h) changes to red-brown. Microanalyses and ^{1}H NMR spectra of the red-brown products from the first three reactants indicate that they have the known structure A[21] (X = Cl, I). Thus, the ^{1}H NMR spectrum of A exhibits a triplet because of spin-spin coupling of the in-plane methyl groups with two equivalent phosphorus atoms in mutually trans positions.

A



In contrast, the reaction involving $(CH_3)(C_6H_5)AsCl$ ultimately gives a product B that contains arsenic. The ^{1}H NMR spectrum shows two sets of equivalent resonances in the dmgH-methyl region and a singlet in the $As\text{-}CH_3$ region; however, the latter signal is sufficiently downfield to be in the As(V) region if oxygen is also bound to arsenic.[36] This information was taken to indicate that B contains an $\text{-}As(C_6H_5)\text{-}(CH_3)(O)$ moiety which has an asymmetric arsenic atom and which could give rise to two sets of ligand methyl resonances such as is found for $(C_5H_5N)Co(dmgH)_2(CH(CN)(CH_3))$[37] and $CH_3Co(dmgH)_2NH(CH_3)CH_2C_6H_5$.[38] In spite of external appearances, it proved to be very difficult to find a crystal of B suitable for X-ray analyses; however, one of very poor quality, *but the best available*, was eventually selected. The structure of the complex is shown in Figure 1. It does contain the anticipated $(C_6H_5)(CH_3)As(O)$ group and the

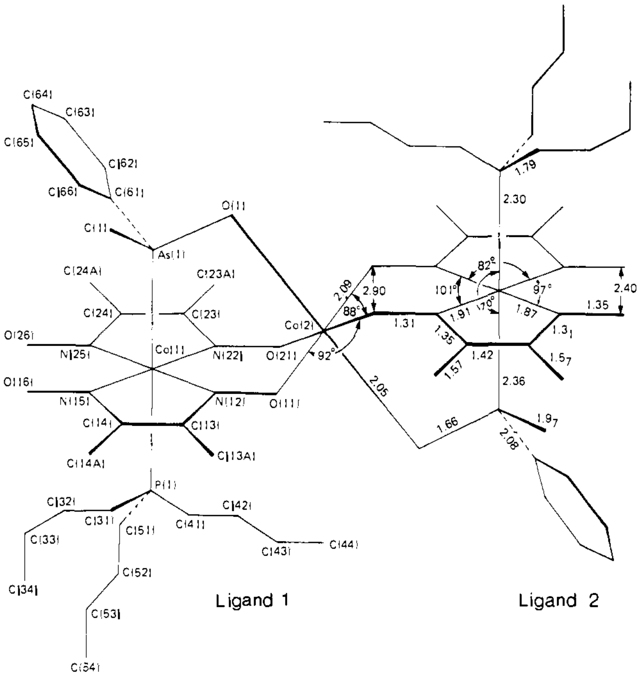


Figure 1. A formalized view of the molecule B showing the atom labeling scheme. Ligand 2 is related to ligand 1 by approximate twofold symmetry. Each atom in ligand 2 is given the same index as the corresponding atom in ligand 1 with a subscript 1 or 2 being added, when necessary, to denote the ligand number. Some averaged bond lengths (Å) and angles (deg) are also shown.

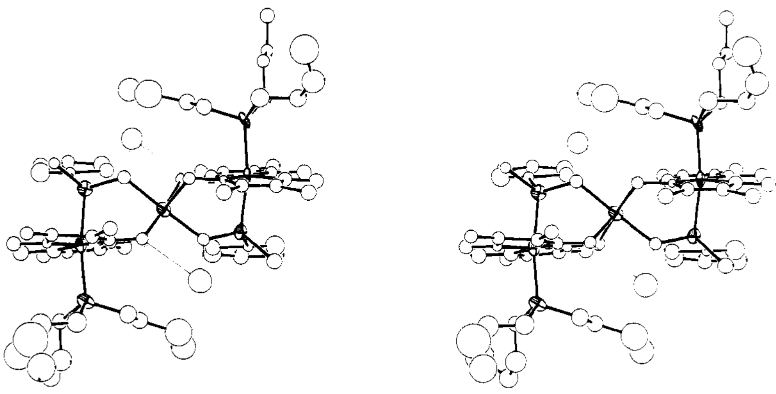


Figure 2. Stereoscopic view of the $Co[(C_4H_9)_3PCo(dmg_2H)As(O)(CH)_3(C_6H_5)]_2$ (B) molecule and water molecules down the approximate (noncrystallographic) twofold axis. Probability ellipsoids are shown at the 25% level. Hydrogen atoms are not included.

chiral molecule shown should have only one $As-CH_3$ resonance. It seems that the meso isomer is not formed.

Description of the Structure. A stereoscopic drawing of the molecule is shown in Figure 2. The molecule consists of two $(n-C_4H_9)_3PCo(dmg_2H)-As(O)(CH_3)(C_6H_5)$ units which may be considered to act as tridentate ligands bonded in a *fac* configuration to a central Co atom through two adjacent dmg O atoms and the arsenyl O. The molecule as a whole possesses approximate (noncrystallographic) twofold symmetry and is disymmetric. The unit cell contains a racemic mixture of these molecules.

The central Co atom, Co(2), has an octahedral environment with the Co-O distances averaging 2.08 Å, consistent with Co(II).[39,40] The two water molecules are each hydrogen bonded to two of the O atoms of the coordination sphere.

Within the accuracy of this structure determination, the two independent tridentate ligands appear to be chemically equivalent. In each the Co(1) atom is bonded to two dmg groups; the Co and four N atoms are coplanar within 0.06 Å. The Co-N bond lengths (1.84-1.96 (3) Å) and N-Co-N "bite" angles (79-84 (2)°) are comparable with the values reported for $Co^{III}(dmgH)_2XY$ compounds (~1.89 Å and ~81°).[41-45] The oxime O···O intramolecular contacts in these compounds are usually ~2.48 Å, indicating the presence of hydrogen bonding. In B the replacement of the O(12)/O(22) H atom by Co causes O(12)···O(22) to open to 2.90 (3) Å which in turn allows O(16)···O(26) to shorten to an average of 2.39 Å. Two other complexes have been reported where the two O···O distances are significantly different due to the breaking of an O···H···O contact. In $(C_2H_5)Co(dmgH)(dmgH_2)Cl$ (O···O distances 2.43 and 2.71 (1) Å), it was thought to arise from additional protonation[46] while in $Co(dmg_2H)py_2$ (2.45 and 2.92 Å) it was ascribed to the loss of a proton.[47] In both cases the O atoms of the long contact are involved in *inter*molecular hydrogen bonding.

Axially each Co(1) atom is bonded to an As and a P. The Co-As distance (2.36 Å) is similar to previously reported values for Co^n-As (n = 0 to III).[48] The Co-P bond length averages 2.30 Å and falls in the range observed for Co^{III}-P in $(n-C_4H_9)_3PCo(dmgH)_2(4\text{-pyridyl})$ (2.342 (1) Å),[42] $(C_6H_5)_3PCo(dmgH)_2Cl$ (2.327 (4) Å),[43] and $(n-C_4H_9)_3PCo(dmgH)_2(\text{xanthinate})$ (2.285 (2) Å).[44] The deviations from the sum of the covalent radii (2.32 Å)[49] were attributed to trans effects. Examination of a model constructed with the observed bond lengths shows that the bonding of O(1) to Co(2) causes strain at angles As(1)-O(1)-Co(2) and N(12)-Co(1)-As(1) which is reflected in the observed averaged values of 127 and 83°, respectively. The Co-As-C and Co-P-C angles are all >111° to minimize steric interactions with the atoms of the equatorial plane.

There is some evidence for a weak π-type interaction between the phenyl ring and the adjacent dmg group. The plane of atoms C(61)-C(66) is tilted toward the equatorial plane (As(1) is ~0.18 Å out of the phenyl plane) so the phenyl C atoms lie at distances of 3.2 Å (C(61)) to 4.0 Å (C(64)) from the equatorial plane and the angle between the planes is only 19.6°. The asymmetry of the As-C-C angles (As(1)-C(61)-C(62) average 98°, As(1)-C(61)-C(66) average 128°) allows the phenyl ring to assume a more favorable orientation for the interaction than it would otherwise have.[45]

The n-butyl groups $C(31)_1$-$C(34)_1$, $C(31)_2$-$C(34)_2$, and $C(51)_1$-$C(54)_1$ have gauche conformations rather than anti, presumably due to packing considerations; the torsion angles are respectively 61(12), 59(8), and 39(8)°.

A compound analogous to B but with $(C_6H_5)_2As(O)$ replacing the $(C_6H_5)(CH_3)As(O)$ groups can be obtained by reacting the Co(I) complex with $(C_6H_5)_2AsCl$. In this case the paramagnetism of the central Co(II) atom broadens the ^1H NMR spectrum so that no sharp resonances are observed.

Characterization and Chemistry of the "Green Solutions". We believe that the green solutions initially observed when the cobaloxime(I) reacts with the haloarsines are due to the presence of the previously unknown air-sensitive Co-As σ-bonded complexes C ($R' = R'' = CH_3$; $R' = R'' = C_6H_5$, $R' = CH_3$, $R'' = C_6H_5$; $R' = C_6H_5$, $R'' = Cl$). The isolation of complex B (Figure 1) gives strong support to this since it can be regarded as a decomposition product of C which is formed after or during oxidation.

C

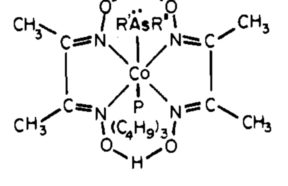
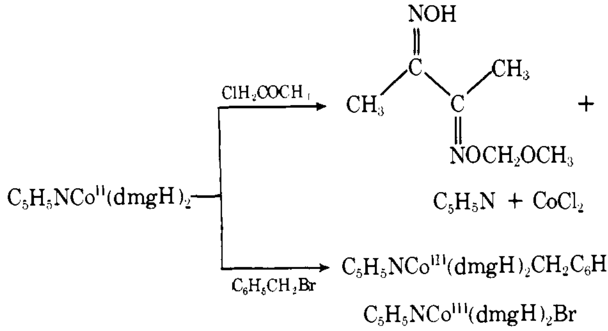


Figure 3 shows the visible spectrum of $P(C_4H_9)_3Co^I(dmgH)_2$ and the reaction product which we formulate as $P(C_4H_9)_3Co(dmgH)_2As(CH_3)_2$, C ($R' = R'' = CH_3$). Clearly a new species has been formed. The spectrum of the Co(I) species is identical with that reported by Schrauzer and co-workers;[50] however, that of C is not typical of a Co(III) cobaloxime. The $RCo(dmgH)_2B$ derivatives normally have λ_{max} in the range 410-450 nm. Only $HCo(dmgH)_2P(C_4H_9)_3$ is reported to have a band at longer wavelengths (λ_{max} 615 nm).[51] The NMR spectrum of C ($R' = R'' = CH_3$) is also similar to that of the hydride[51] in that the resonance associated with the equatorial ligand is at much higher field than usual indicating a build up of electron density on the $Co(dmgH)_2P(C_4H_9)_3$ moiety.[52] This ^1H spectrum of C broadens as the temperature is lowered. The ^{31}P NMR spectrum of the same species at 35 °C shows one broader than usual signal. These features are probably due to a base-on-base-off equilibrium.[32]

The ESR spectrum of solutions of C (R′ = C_6H_5, R″ = CH_3) quenched at 77 K shows the presence of base-on Co(II) and another paramagnetic species which is probably $(C_6H_5)(CH_3)As$. Little is known about the spectra of either species[53,54] so this interesting result is being actively investigated.

Reactions of cobalamins and cobaloximes are very dependent on the electron density at cobalt and the attacking reagent. For example, the Co(II) derivative $C_5H_5NCo(dmgH)_2$ is alkylated at the periphery (reaction 2a) rather than at cobalt as might have been expected from reaction 2b[55]



(2a)
(2b)

and even the ligand substitution pattern of Co(III) cobalamins is altered by changes in the axial ligands.[55] Thus it is possible that the chemistry of C is dependent on the nature of R′ and R″.

A can be envisaged as being formed by a redistribution reaction illustrated in reaction 3

$$2R_3PCo(dmgH)_2AsR'R'' \rightarrow [R_3PCo(dmgH)_2PR_3]^+ + [R'R''AsCo(dmgH)_2AsR'R'']^- \quad (3)$$

where the anionic species is unstable. This exchange could occur via a base-on ⇌ base-off reaction.[32] The cationic species A are not formed when R′ = CH_3 or C_6H_5 and R″ = C_6H_5, and in this case it seems that C is more stable in solution and does not undergo reaction 3. Slow oxidation results in production of the Co-As(R′)(R″)(O) compound which, although unstable itself is stabilized by its decomposition product, free Co(II), to produce B.

Further evidence for the formulation of C (R′ = R″ = CH_3) is provided by its reactions with sources of methyl carbonium ion and carbanion. Thus the interaction with 2 equiv of CH_3I gives $As(CH_3)_3$ (identified by GLC and mass spectroscopy) and $P(C_4H_9)_3Co(dmgH)_2CH_3$. In the presence of excess CH_3I, $As(CH_3)_4I$ is produced.

It is surprising to find *both* arsenic and cobalt alkylation in this essentially quantitative reaction.[58]

Although it is not unusual for CH_3I to cleave As-M bonds (eq 4)[59]

$$(CH_3)_2As\text{-}As(CH_3)_2 + 2CH_3I \rightarrow (CH_3)_4AsI + IAs(CH_3)_2 \quad (4)$$

The results of Malisch and co-workers[27-29] indicate that, given the choice, CH_3I will attack the arsenic nucleophile (eq 5)

$$(\eta^5\text{-}C_5H_5)Mo(CO)_3As(CH_3)_2 + CH_3I \rightarrow [(\eta^5\text{-}C_5H_5)Mo(CO)_3{}^+As(CH_3)_3]I^- \quad (5)$$

and subsequent loss of trimethylarsine from such an intermediate in the present case should lead to the formation of $P(C_4H_9)_3Co(dmgH)_2I$, but this compound is not detected. Perhaps it is the buildup of charge on the cobalt atom of C (R′ = R″ = CH_3) as seen in the ^1H NMR spectrum described above which renders this atom susceptible to electrophilic attack. But in view of the ESR results for C (R′ = CH_3, R″ = C_6H_5) it is also conceivable that homolytic fission of the Co-As bond occurs to give Co(II).[58] This could give the $Co^{III}\text{-}CH_3$ species via a reaction like that shown in eq 2b but the other products should include $(CH_3)_2AsI$.[59]

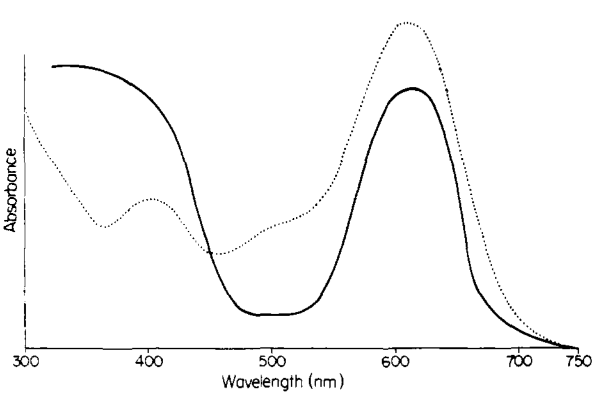


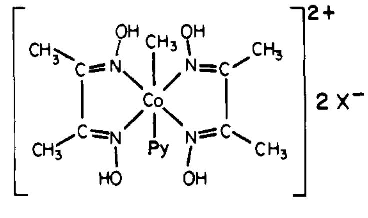
Figure 3. Absorption spectrum of tri-*n*-butylphosphinecobaloxime(I) (---) treated with iododimethylarsine (—).

Similarly methyl(pyridine)cobaloxime(III), a potential source of CH_3^-, reacts with C to give $(CH_3)_3As$. Thus again the possibility of free radical reactions must be considered.[62]

Models for Biological Alkylation. In a typical experiment described by Schrauzer and co-workers[5,61] $CH_3(H_2O)Co(dmgH)_2$, As_2O_3, and dithioerythritol (DTE) reacted to give low yields of CH_4 (109 μmol), CH_3AsH_2 (134 μmol), CH_3AsH_2 (2 μmol), and AsH_3 (290 μmol). Similar results were reported if NH_4Cl/Zn replaced the DTE as reductant. In our hands we have found that methylarsines are produced, although in variable and concentration-dependent amounts. At low concentrations, the major volatile product is CH_4; AsH_3 is not observed. Our results indicate that it is unlikely that AsH_3 would be stable in the presence of a methylcobaloxime since the two react to form methane very readily. It is reported that in the absence of reducing agent methylcobaloximes do not react with arsenate or arsenite.[5] The present results show that methyl transfer from cobaloximes to arsenic via electrophilic attack by arsenic halides does not readily occur since $AsCl_3$, AsI_3, and CH_3AsCl_2 fail to react with $CH_3(C_5H_5N)Co(dmgH)_2$ to give CH_3-As species.

The initial investigation of the reaction of this same cobaloxime with $AsCl_3$ in CH_3OH solution indicated a successful transfer since a shift of the NMR signal associated with the Co-CH_3 moiety was observed. However, the product, in high yield, seems to be the cationic derivative D (X = Cl). It is easy to envisage that D is formed by attack of HCl, produced by solvolysis of the $AsCl_3$, on the cobaloxime, but this generally results in monoprotonation.[63] Thus 3 M HCl in CH_3OH/H_2O monoprotonates $R(H_2O)Co(dmgH)_2$ (R = alkyl). Furthermore even when dry toluene is used as solvent the diprotonated product D (X = Cl) is isolated in high yield from the reaction of $AsCl_3$ and $CH_3(C_5H_5N)Co(dmgH)_2$. When AsI_3 is used to interact with the same cobaloxime, a similar complex D (X = I) is slowly formed in methanol and THF. Since AsI_3 is generally regarded as being stable to hydrolysis, it is unlikely to be the direct source of HI for protonation. Thus these reactions are not as simple as they seem at first sight.

D



The results with solutions containing C indicate that compounds containing Co–As bonds can be alkylated by Co^{III}–R species. Hence such compounds could well be intermediates in *model* alkyl transfer reactions.[5] They may also be involved in arsine production as suggested[5] but we are unable to comment on this aspect at the moment.

We are continuing to investigate the chemistry of these and related complexes with Co–AsR_2 moieties.

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Supplementary Material Available: A listing of structure factor amplitudes (16 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) University of British Columbia. (b) Simon Fraser University. (c) University of Saskatchewan, Saskatoon.

(2) W. P. Ridley, L. J. Dizikes, and J. M. Wood, *Science*, **197**, 329 (1977).

(3) J. M. Wood, *Science*, **183**, 1049 (1974).

(4) B. C. McBride and R. S. Wolfe, *Biochemistry*, **10**, 4312 (1971).

(5) G. N. Schrauzer, J. A. Seck, R. J. Holland, T. M. Beckham, E. M. Rubin, and J. W. Sibert, *Bioinorg. Chem.*, **2**, 93 (1972).

(6) L. J. Dizikes, W. P. Ridley, and J. M. Wood, *J. Am. Chem. Soc.*, **100**, 1010 (1978).

(7) U. Schmidt and F. Huber, *Nature (London)*, **259**, 157 (1976).

(8) Y. K. Chau, P. T. S. Wong, B. A. Silverberg, P. L. Luxon, and G. A. Bengert, *Science*, **192**, 1130 (1976).

(9) F. Huber and H. Kirchmann, *Inorg. Chim. Acta*, **29**, L249 (1978).

(10) (a) W. M. Scovell, *J. Am. Chem. Soc.*, **96**, 3451 (1974); (b) P. J. Craig and S. F. Morton, *J. Organomet. Chem.*, **145**, 79 (1978); (c) G. Agnes, S. Bendle, H. A. O. Hill, F. R. Williams, and R. J. P. Williams, *J. Chem. Soc., Chem. Commun.*, 850 (1971); (d) J. H. Espenson, W. R. Bushey, and M. E. Chmielewski, *Inorg. Chem.*, **14**, 1302 (1975); (e) P. Abley, E. R. Dockal, and J. Halpern, *J. Am. Chem. Soc.*, **95**, 3166 (1973); (f) J. H. Espenson and T. D. Sellers, *ibid.*, **96**, 94 (1974); (g) S. Tauzer, R. Dreos, G. Costa, and M. Green, *J. Organomet. Chem.*, **81**, 107 (1974); (h) M. W. Witman and J. H. Weber, *Inorg. Chem.*, **15**, 2375 (1976); **16**, 2512 (1977); (i) V. C. W. Chu and D. W. Gruenwedel, *Bioinorg. Chem.*, **7**, 169 (1977).

(11) W. R. Cullen, C. L. Froese, A. Lui, B. C. McBride, D. J. Patmore, and M. Reimer, *J. Organomet. Chem.*, **139**, 61 (1977).

(12) F. Challenger, *Adv. Enzymol.*, **12**, 429 (1951).

(13) It has been pointed out by C. D. Taylor and R. S. Wolfe, *J. Biol. Chem.*, **249**, 4886 (1973), that "it is not established that methylcobalamin is involved as a natural carrier in hydrogen-grown *Methanobacterium*".

(14) W. Steinkkopf and W. Mieg, *Ber.*, **53B**, 1013 (1920).

(15) A. E. Goddard, "A Text-Book of Inorganic Chemistry", Vol. XI, Part II, Charles Griffin & Co., London, 1930.

(16) E. J. Cragoe, R. J. Andres, R. F. Coles, B. Elpern, J. F. Morgan, and C. S. Hamilton, *J. Am. Chem. Soc.*, **69**, 925 (1947).

(17) G. Brauer, Ed., "Handbook of Preparative Inorganic Chemistry", Vol. I, Academic Press, London, 1963, p 598.

(18) W. L. Jolly and J. E. Drake, *Inorg. Synth.*, 7, 34 (1963).

(19) H. A. O. Hill and K. G. Morallee, *J. Chem. Soc. A*, 554 (1969).

(20) R. B. Silverman, Ph.D. Thesis, Harvard University, 1974, pp 180, 181.

(21) C. W. Smith, G. W. Van Loon, and M. C. Baird, *Can. J. Chem.*, **54**, 1875 (1976).

(22) G. N. Schrauzer and R. J. Windgassen, *J. Am. Chem. Soc.*, **88**, 3738 (1966).

(23) R. Armstrong, N. A. Gibson, J. W. Hosking, and D. C. Weatherburn, *Aust. J. Chem.*, **20**, 2771 (1967).

(24) "International Tables for X-ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974; R. S. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(25) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).

(26) W. R. Cullen, D. J. Patmore, and J. R. Sams, *Inorg. Chem.*, **12**, 867 (1973), and references therein.

(27) W. Malisch, H. Rössner, K. Keller, and R. Janta, *J. Organomet. Chem.*, **133**, C21 (1977).

(28) P. Panster and W. Malisch, *Chem. Ber.*, **109**, 3842 (1976).

(29) W. Malisch and M. Kuhn, *Angew. Chem., Int. Ed. Engl.* **13**, 84 (1974).

(30) R. Mueller and H. Vahrenkamp, *Chem. Ber.*, **110**, 3910 (1977).

(31) W. R. Cullen and R. G. Hayter, *J. Am. Chem. Soc.*, **86**, 1030 (1964).

(32) D. Dodd and M. D. Johnson, *J. Organomet. Chem.*, **52**, 1 (1973).

(33) G. N. Schrauzer and G. Kratel, *Chem. Ber.*, **102**, 2392 (1969).

(34) Prior to haloarsine addition, acetone was added to remove the excess borohydride thus preventing reduction of the haloarsine.

(35) Y. L. Baay and A. G. McDairmid, *Inorg. Nucl. Chem. Lett.*, **3**, 159 (1967).

(36) T. Antonio, A. K. Chopra, W. R. Cullen, and D. H. Dolphin, *J. Inorg. Nucl. Chem.*, **41**, 2221 (1979).

(37) M. Naumberg, K. N. V. Duong, F. Gaudemer, and A. Gaudemer, *C.R. Acad. Sci., Ser. C*, **270**, 1301 (1970).

(38) A. Gaudemer, F. Gaudemer, and L. Diep, *Bull. Soc. Chim. Fr.*, 884 (1972).

(39) Lj. Manojlović-Muir and K. W. Muir, "Molecular Structure by Diffraction Methods", Vol. 3, The Chemical Society, London, 1975, Chapter 11.

(40) The magnetic moment of **B**, $\mu_{\text{eff}} = 4.99\ \mu_B$, is typical of high spin Co(II) and indicates that the spin density is localized on the central cobalt atom.

(41) (a) P. G. Lenhert, *Chem. Commun.*, 980 (1967); (b) A. Chiaroni and C. Pascard-Billy, *Bull. Soc. Chim. Fr., Part 2*, 781 (1973); (c) V. Ohashi, Y. Sasada, Y. Tashiro, Y. Ohgo, S. Takeuchi, and J. Yoshimura, *Bull. Chem. Soc. Jpn.*, **46**, 2589 (1973); (d) D. L. McFadden and A. T. McPhail, *J. Chem. Soc., Dalton Trans.*, 363 (1974); D. Ginderow, *Acta Crystallogr., Sect. B*, **31**, 1092 (1975); (e) D. A. Stotter, G. M. Sheldrick, and R. Taylor, *J. Chem. Soc., Dalton Trans.*, 2124 (1975); (f) L. P. Battaglia, A. B. Corradi, C. G. Palmieri, M. Nardelli, and M. E. V. Tani, *Acta Crystallogr., Sect. B*, **30**, 1114 (1974); (g) M. M. Botoshanskii, Yu. A. Simonov, T. I. Malinovskii, A. V. Ablov, and O. A. Bologa, *Dokl. Akad. Nauk SSSR*, **225**, 323 (1975); (h) A. Bigotto, E. Zangrando, and L. Randaccio, *J. Chem. Soc., Dalton Trans.*, 96 (1976); (i) D. Dodd, M. D. Johnson, I. P. Steeples, and E. D. McKenzie, *J. Am. Chem. Soc.*, **98**, 6399 (1976); (j) Y. Ohashi and Y. Sasada, *Bull. Chem. Soc. Jpn.*, **50**, 1710 (1977); (k) Y. Ohashi and Y. Sasada, *ibid.*, **50**, 2863 (1977); (l) W. Pannhorst, *Acta Crystallog., Sect. B*, **33**, 2384 (1977).

(42) W. W. Adams and P. G. Lenhert, *Acta Crystallogr., Sect. B*, **29**, 2412 (1973).

(43) S. Brückner and L. Randaccio, *J. Chem. Soc., Dalton Trans.*, 1017 (1974).

(44) L. G. Marzilli, L. A. Epps, T. Sorrell, and T. J. Kistenmacher, *J. Am. Chem. Soc.*, **97**, 3351 (1975).

(45) G. J. Palenik, D. A. Sullivan, and D. V. Naik, *J. Am. Chem. Soc.*, **98, 1177** (1976).

(46) A. L. Crumbliss, J. T. Bowman, P. L. Gaus, and A. T. McPhail, *J. Chem. Soc., Chem. Commun.*, 415 (1973).

(47) A. V. Ablov, A. A. Dvorkin, Yu. A. Simonov, O. A. Bologa, and T. I. Malinovskii, *Dokl. Akad. Nauk SSSR*, **217**, 89 (1974). This paper reports the structure of $[Co^{III}(dmgH)_2py_2]^+OH^- \cdot 2[Co^{III}(dmg_2H)py_2] \cdot 5H_2O$. The cation is centrosymmetric with a long O···O contact of 2.64 Å. The Co–N_{oxime} bonds are unusually long in both molecular species (mean value 1.94 (2) Å).

(48) (a) P. J. Pauling, D. W. Porter, and G. B. Robertson, *J. Chem. Soc. A*, 2728 (1970); (b) W. Harrison and J. Trotter, *ibid.*, 1607 (1971); (c) F. W. B. Einstein and R. D. G. Jones, *Inorg. Chem.*, **11**, 395 (1972); (d) F. W. B. Einstein and R. D. G. Jones, *J. Chem. Soc., Dalton Trans.*, 2568 (1972); (e) P. K. Bernstein, G. A. Rodley, R. Marsh, and H. B. Gray, *Inorg. Chem.*, **11**, 3040 (1972); (f) J. H. Enemark, R. D. Feltham, J. Riker-Nappier, and K. F. Bizot, *ibid.*, **14**, 624 (1975); (g) P. D. Dapporto, S. Midollini, and L. Sacconi, *ibid.*, **14**, 1643 (1975).

(49) L. Pauling, "The Nature of the Chemical Bond", Cornell University Press, Ithaca, New York, 1960.

(50) G. N. Schrauzer, R. J. Windgassen, and J. Kohnle, *Chem. Ber.*, **98**, 3324 (1965).

(51) G. N. Schrauzer and R. J. Holland, *J. Am. Chem. Soc.*, **93**, 1505 (1971).

(52) The dmg-CH_3 resonance is underneath those of $P(C_4H_9)_3$ (0.95 and 1.37 ppm). The As-CH_3 resonance lies outside the normal range at 2.37 ppm again indicating considerable charge transfer to cobalt.

(53) C. Giannotti and J. R. Bolton, *J. Organomet. Chem.*, **110**, 383 (1976), and references therein.

(54) J. R. Preer, F.-D. Tsang, and H. B. Gray, *J. Am. Chem. Soc.*, **94**, 1875 (1972).

(55) R. B. Silverman and D. Dolphin, *Can. J. Chem.*, **54**, 1425 (1976).

(56) No other arsenic or cobalt derivative was detected in the ^{1}H NMR spectrum of the reaction mixture.

(57) W. R. Cullen, *Can. J. Chem.*, **38**, 439 (1960), and references therein.

(58) J. M. Pratt, "Inorganic Chemistry of Vitamin B_{12}", Academic Press, New York, 1972, pp 233–235.

(59) Co(II) species react with CH_3I to give Co^{III}–CH_3, but not Co^{III}–I. The mechanism is not established.[58]

(60) Homolytic cleavage of cobalt–carbon bonds on free radical attack has been postulated as being the key step in transfer of a methyl group from methylcobalamin to a thiol, coenzyme M. J. M. Wood in "Biological Aspects of Inorganic Chemistry", A. W. Addison, W. R. Cullen, D. Dolphin, and B. R. James, Eds., Wiley-Interscience, New York, 1977, p 283. See also: L. J. Dizikes, W. P. Ridley, and J. M. Wood, *J. Am. Chem. Soc.*, **100**, 1010 (1978).

(61) Note that the quantity of reagents used was given in the original thesis[62] as 2.7 mmol of each in 3 mL of water. This appears to have been misquoted in the subsequent publication.[5]

(62) J. A. Seck, Ph.D. Thesis, University of California, San Diego, Calif., 1973.

(63) A. L. Crumbliss and P. L. Gaus, *Inorg. Chem.*, **14**, 486 (1975).