time course of the initial substitution and subsequent rearrangements was monitored at 500-s intervals; see text and Figure 3 for details.

Carbonylation of 5. A sample of **5** (3 mg) was dissolved in 0.35 mL of CD_2Cl_2, sealed under ca. 200 KPa pressure of carbon monoxide in a 5-mm o.d. NMR tube, and allowed to stand at 273 K for 48 h. ^1H NMR analysis showed 50% unreacted **5** and four isomeric acyls **2a–d** in a ratio of 1:4.2:0.4:0.5, respectively.

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Registry No. **1**, 94203-64-2; **2**, 94203-65-3; **2a**, 94292-16-7; **2b**, 94292-17-8; **2c**, 94292-18-9; **2d**, 94292-19-0; **3**·BF_4, 94203-67-5; **3**·PF_6, 94203-68-6; **4**, 94203-70-0; **5**, 94203-71-1; **6**, 94203-72-2; **7a**·BF_4, 94203-74-4; **7a**·I, 94203-75-5; **7b**, 94292-21-4; $Fe(CO)_5$, 13463-40-6.

Correlation of Rate, Spectroscopic, and Structural Data for (Pyridine)- or (Triphenylphosphine)-bis(dimethylglyoximato)organocobalt Complexes

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The crystal and molecular structures of the complexes *trans-bis*(dimethylglyoximato)(R)(triphenylphosphine)cobalt(III) [R = CH_2CH_3 (**1**), 2-C_4H_9 (**2**), $CH_2C(CH_3)(CO_2C_2H_5)_2$ (**3**)] and *trans-bis*(dimethylglyoximato)($CH_2C(CH_3)(CO_2C_2H_5)_2$(pyridine)cobalt(III) (**4**) are reported. Crystal data for **1**: $P2_1/n$; $a = 10.346$ (1) Å, $b = 15.310$ (2) Å, $c = 18.516$ (3) Å, $\beta = 103.10$ (1)°; $Z = 4$; $R = 0.043$ for 4698 independent reflections. Crystal data for **2**: $P2_1/n$, $a = 11.157$ (5) Å, $b = 11.285$ (4) Å, $c = 24.356$ (9) Å, $\beta = 101.86$ (8)°; $Z = 4$, $R = 0.059$ for 2612 independent reflections. Crystal data for **3**: $P\bar{1}$, $a = 10.998$ (5) Å, $b = 10.564$ (5) Å, $c = 16.085$ (8) Å, $\alpha = 104.92$ (4)°, $\beta = 96.25$°, $\gamma = 94.74$ (5)°; $Z = 2$; $R = 0.033$ for 5084 independent reflections. Crystal data for **4**: $P2_1/n$, $a = 13.597$ (9) Å, $b = 22.47$ (1) Å, $c = 8.748$ (5) Å, $\beta = 93.98$ (5)°; $Z = 4$; $R = 0.035$ for 2237 independent reflections. The rate constants, k_1, of PPh_3 dissociation for **1–3** above and other structurally characterized compounds with R = CH_2CN, $CH(CH_3)CN$, CH_2CF_3, CH_2Br, CH_3, i-C_3H_7, and neo-C_5H_{11} were determined. Trends in ^{31}P and ^1H NMR spectra were examined for these and related acido (X = Cl, Br, I, NO_2) complexes. Good correlations were found between Co–P bond length, the sum of the CPC angles, log k_1, and ^1H NMR parameters. The ^{31}P NMR shifts were attenuated by opposing contributions from several different effects and did not correlate with other parameters. Distortions in the planarity of the bis(dimethylglyoximato)cobalt moiety appear to reflect both the bulk of the axial ligands and lattice effects. For **4**, the dihedral angle between the dioximato moieties (12.3°) is toward the pyridine and is the largest such angle in a pyridine complex of this type. No unusual distortions are observed in the alkyl group of **3** or **4**.

Introduction

A large body of structural, spectroscopic, dynamic, and thermodynamic data is now available for the class of organocobalt models of B_{12} coenzymes known as cobaloximes.[1-10] The four corrin ring equatorial N donors in B_{12} compounds are replaced by the four N atoms of a bis(dioximato) moiety in cobaloximes. Although several different dioximes have been employed,[1] the most thoroughly studied group of compounds is of the type $LCo(DH)_2X$, where L and X are neutral and mononegative monodentate axial ligands and DH is a monoanion of dimethylglyoxime.

X-ray structures of compounds of the type $LCo(DH)_2X$ are now more numerous than any other closely related group of organometallic compounds.[6,11-27] Since diverse

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types of chemical properties (bond lengths, reaction rates, NMR shifts, coupling constants, etc.) may be influenced differently by variations in L and/or X, a study of the class of compounds $LCo(DH)_2X$ offers the potential of achieving a deeper understanding of the relative importance of the many factors influencing any one property as the axial ligands are varied. Such knowledge has a broader application than organocobalt chemistry since we and others have demonstrated that the relative influences of ligand variations on a number of physical properties of a large number of series of both transition- and non-transition-metal compounds correlate well with trends followed by cobaloximes. Indeed, a parameter developed by us and based on the ^1H NMR spectra of cobaloximes[5] was found to correlate extremely well with a large number of physical properties examined in an exhaustive statistical survey of published data on metal compounds.[28]

In this report, we have examined more thoroughly compounds with L = triphenylphosphine and contrasted the findings with the more widely studied group of compounds with L = pyridine. The X groups employed here were CH_2CH_3, $2\text{-}C_4H_9$, and $CH_2C(CH_3)(CO_2C_2H_5)_2$. The latter alkyl group is of interest both as a bulky ligand with electron-withdrawing substituents and as a model for a ligand in an organocobalt intermediate in the B_{12}-catalyzed isomerization of methylmalonyl CoA to succinyl CoA.[29] Since the pyridine analogue has not been characterized, this compound was also studied.

Experimental Section

Reagents. Tributylphosphine (Aldrich) was distilled under vacuum before use. All other reagents were purchased from Aldrich and used without further purification.

Instrumentation. ^1H and ^{31}P NMR spectral measurements were made with a Varian EM390 (90 MHz, ^1H) and an IBM WP-200SY spectrometer (200.13 MHz, ^1H; 81.01 MHz, ^{31}P) equipped with a Bruker B-VT.1000 variable-temperature unit. Ligand exchange rates were monitored spectrophotometrically with a Cary 14 for the slow reactions ($k_{obsd} < 1.0\ s^{-1}$) and a Durrum-Gibson D-110 stopped-flow spectrophotometer for the fast reactions. Both instruments were equipped with thermostated compartments which maintained the reaction solution at 25.0 ± 0.04 °C.

Rate Measurements. Pseudo-first-order rate constants were determined for PPh_3 substitution from $PPh_3Co(DH)_2X$ by PBu_3 in CH_2Cl_2 (25 °C). The optimum wavelengths used to monitor the reaction rates were determined as described previously.[8] Absorbance data were collected over at least 3 half-lives. For fast reactions, the final absorbance was taken after ~10 half-lives. The final absorbance for slow reactions was calculated by using the Swinbourne treatment.[30]

Rate Data Analysis. The experimental absorbance vs. time rate data were treated with the standard integrated expression for a first-order process using linear least-squares analysis as described previously.[8] The rate constants are defined as follows ($M = Co(DH)_2R$):

$$PPh_3M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} M + PPh_3$$

$$PBu_3 + M \xrightarrow{k_2} PBu_3M$$

No dependence on $[PBu_3]$ was observed as expected for this reaction which conforms nicely to S_N1-LIM behavior.[8]

Preparations. The preparation and characterization of $PPh_3Co(DH)_2X$ (X = Cl, Br, NO_2) have been reported previously.[31]

All of the $PPh_3Co(DH)_2R$ complexes in Table VI and $pyCo(DH)_2CH_2C(CH_3)(CO_2C_2H_5)_2$ were prepared by published procedures[32] and have been characterized by single-crystal X-ray diffraction.

The alkylating agent for compounds III and IV, $BrCH_2C(CH_3)(CO_2C_2H_5)_2$, was prepared by using an adaptation of Rêtey's procedure[29] as follows: Diethyl methylmalonate (38 g, 0.218 mol) was added dropwise to a sodium ethoxide solution (prepared by addition of sodium (5 g, 0.217 mol) to ethanol (200 mL)) under nitrogen. The solution was stirred at 40 °C for 2 h, and then methylene bromide (40 g, 0.230 mol) was slowly added. The mixture was stirred at room temperature for 10 h. After filtration to remove a white precipitate which had formed upon addition of CH_2Br_2, the excess CH_2Br_2 was allowed to evaporate at reduced pressure. The resulting liquid was purified by vacuum distillation. The fraction which distilled at 60 °C (0.5 mmHg) was collected. This fraction contained a small amount of diethyl methylmalonate (by NMR) which did not pose problems in the preparation of alkylcobaloximes, yield 27 g (47%).

$PPh_3Co(DH)_2I$. To a suspension of $PPh_3Co(DH)_2Cl$ (3.0 g) in methanol (100 mL) was added NaI (3-fold molar excess). After the mixture was warmed and stirred ~15 min, everything dissolved. After an additional 15 min, the solution was removed from heat and ~150 mL H_2O added. Dark brown crystals formed upon cooling; yield 85%. Anal. Calcd for $C_{26}H_{29}IN_4O_4PCo$: C, 46.04; H, 4.31; N, 8.26. Found: C, 46.17; H, 4.37; N, 8.22.

Analytical data have been reported previously[8,31,33] for all of the other complexes presented here except the following: $PPh_3Co(DH)_2(neo\text{-}C_5H_{11})$. Anal. Calcd for $C_{31}H_{40}N_4O_4PCo$: C, 59.81; H, 6.48; N, 9.00. Found: C, 59.90; H, 6.53; N, 8.88. $PPh_3Co(DH)_2(2\text{-}C_4H_9)$. Anal. Calcd for $C_{30}H_{38}N_4O_4PCo$: C, 59.21, H, 6.29; N, 9.21. Found: C, 59.15; H, 6.29; N, 9.21. $PPh_3Co(DH)_2CH_2CF_3$. Anal. Calcd for $C_{28}F_3H_{31}N_4O_4$: C, 53.01; H, 4.93; N, 8.83. Found: C, 52.87; H, 4.93; N, 8.82. $PPh_3Co(DH)_2CH_2CN$. Anal. Calcd for $C_{28}H_{31}N_5O_4PCo$: C, 56.86; H, 5.28; N, 11.84. Found: C, 56.60; H, 5.32; N, 11.76. $PPh_3Co(DH)_2CH_2C(CH_3)(CO_2C_2H_5)_2$. Anal. Calcd for $C_{35}H_{44}N_4O_8PCo$: C, 56.91; H, 6.00; N, 7.58. Found: C, 57.04; H, 6.04; N, 7.55. $pyCo(DH)_2CH_2C(CH_3)(CO_2C_2H_5)_2$. Anal. Calcd for $C_{22}H_{34}N_5O_8Co$: C, 47.57; H, 6.17; N, 12.61. Found: C, 47.46; H, 6.20; N, 12.58. $PPh_3Co(DH)_2CH(CH_3)CN\cdot H_2O$. Anal. Calcd for $C_{29}H_{35}N_5O_5PCo$: C, 55.83; H, 5.66; N, 11.23. Found: C, 55.82; H, 5.69; N, 11.19.

Elemental Analyses. These were performed by Atlantic Microlabs, Inc. (Atlanta, GA).

Crystal Data. The crystals for compounds 1–4 were obtained by slow crystallization from acetone–water. Unit cell parameters of 1 were refined and intensities collected on a CAD4 diffractometer using graphite-monochromated Mo Kα radiation, whereas those of 2 were refined and collected, respectively, on a Philips PW1100 diffractometer using graphite-monochromated Mo Kα radiation. Cell dimensions of 3 and 4 were refined and intensities collected on a SIEMENS-AED diffractometer using filtered Mo Kα radiation. In all cases the intensities, having $I > 4\sigma(I)$ for 1 and $>3\sigma(I)$ for the others, were corrected for Lorentz and polarization factors. For 1, the anomalous dispersion correction for Co and P was also applied. No absorption correction was applied because of the small sizes of the crystals used and the

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Table I. Crystallographic Data for Compounds 1–4

	1	2	3	4
formula	$C_{28}H_{34}CoN_4O_4$	$C_{30}H_{38}CoN_4O_4P$	$C_{35}H_{44}CoO_8N_4P$	$C_{22}H_{34}CoO_8N_5$
mol wt	580.6	608.6	738.7	555.4
a, Å	10.346 (1)	11.157 (5)	10.998 (5)	13.597 (9)
b, Å	15.310 (2)	11.285 (4)	10.564 (5)	22.47 (1)
c, Å	18.516 (3)	24.356 (9)	16.085 (8)	8.748 (5)
α, deg			104.92 (5)	
β, deg	103.10 (1)	101.86 (8)	96.25	93.98 (5)
γ, deg			94.74 (5)	
V, Å^3	2735.7	3001.0	1749.1	2666.3
D(measd), g cm^{-3}	1.36 (1)	1.37 (1)	1.37 (1)	1.40 (1)
D(calcd), g cm^{-3}	1.35	1.35	1.38	1.37
Z	4	4	2	4
space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P2_1/n$
μ, cm^{-1} (Mo Kα)	7	7	6	7
cryst dimens, cm^3	0.02 × 0.02 × 0.03	0.01 × 0.01 × 0.03	0.06 × 0.03 × 0.05	0.02 × 0.02 × 0.03
no. of reflcts measd	7489	5147	9039	6987
no. of independent reflctns ($I > 3\sigma(I)$)	4698	2612	5084	2237
max 2θ, deg (Mo Kα)	56	56	56	56
R	0.043	0.059	0.033	0.035
R_w	0.065	0.072	0.045	0.041

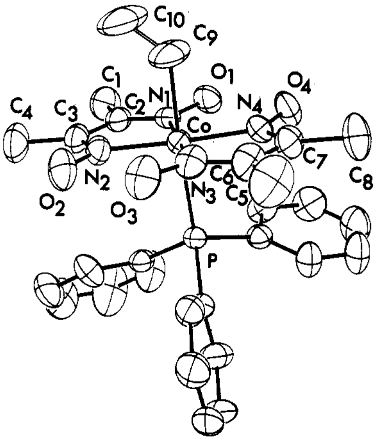

Figure 1. Structure and labeling scheme for the non-hydrogen atoms of 1 (thermal ellipsoids; 50% probability).

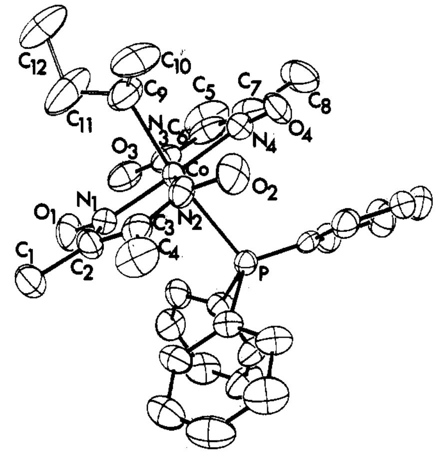

Figure 2. Structure and labeling scheme for the non-hydrogen atoms of 2 (thermal ellipsoids; 50% probability).

small values of the absorption coefficients. Crystal data of interest are given in Table I.

Structure Determination and Refinement. All the structures were solved by conventional Patterson and Fourier methods and refined by the full-matrix anisotropic least-squares method to the final values of *R* reported in Table I. The contribution of hydrogen atoms, held constant (B = 6 Å^2 for 1 and 5 Å^2 for the others), was included in the final refinement, excluding those attached to the C(10), C(11), and C(12) atoms of 2 and those belonging to the ethyl group attached to O(8) of 4. The final weighting scheme was $w = 1/(A + |F_o| + B|F_o|^2)$, where A = 14, 30, 10, and 23 for 1 through 4 and B = 0.004, 0.008, 0.006, and 0.016 for 1 through 4, respectively, were chosen so as to maintain $w(|F_o| - |F_c|)^2$ essentially constant over all range of F_o and $(\sin \theta)/\lambda$. Atomic scattering factors were those given in ref 34 and those given in ref 35 for the others. All calculations were done by using computer programs from CAD4-SDP suite for 1 and from X-ray 70[36] for the others. Final positional parameters are given in Tables II and III.

Results

Description and Discussion of the Structures of 1 and 2. The SHELXTL[37] drawing with the atom numbering scheme for 1 is given in Figure 1. Bond lengths and angles are given in Table IV. Values for the $Co(DH)_2$ unit are quite normal. The $P-Co-CH_2CH_3$ fragment is characterized by Co–P, Co–C, and C–C bond lengths of 2.415 (1), 2.045 (5), and 1.317 (9) Å, respectively, and P–Co–C and Co–C–C angles of 175.7 (3) and 126.2 (5)°, respectively. The geometry of the P–Co–C group does not differ significantly from that of the analogous methyl derivative,[18] in which the Co–P and Co–C distances and the P–Co–C angles are 2.418 (1) and 2.026 (6) Å and 175.4 (2)°, respectively. The value of the Co–C–C angle is very close to the values reported for cobaloximes with R = neo-C_5H_{11} (129.2 (7)°)[26] and R = CH_2Br (125.2 (9)°). The CH_2-CH_3 distance of 1.317 (9) Å is very far from the expected value of 1.54 Å. Such a shortening may be attributed only in part to the widening of the $Co-CH_2-CH_3$ angle, as observed in other cobaloximes containing $Co-CH_2R$ groups.[11] The high thermal motion of C(10) is probably largely responsible for the observed shortening. A similar value of 1.39 (1) Å was found in $pyCo(saloph)CH_2CH_3$ (saloph = dianion of bis(salicyclidene)-*o*-phenylenediamine) and attributed to the thermal motion of the terminal methyl group, whereas the $Co-CH_2-CH_3$ angle was found to be 117.3 (5)°.[38] In fact, in $4\text{-}CH_3OC(NH)\ pyCo(DH)_2CH_2CH_3$ the corresponding figures are 1.519 (8) Å and 117.8 (4)°.[17] The cobalt atom is displaced by 0.06 Å above the plane of the 4-N donors (coplanar within ±0.01 Å) toward PPh_3,

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Table II. Atomic Positional Parameters of Non-Hydrogen Atoms of **1** (×10⁵ for Co and P and ×10⁴ for the Others) and of **2** (×10⁴) with esd's in Parentheses

	x	*y*	*z*		*x*	*y*	*z*
			1				
Co	−708 (4)	21815 (2)	19392 (2)	C(10)	494 (7)	1320 (4)	3443 (2)
P	−10060 (6)	24512 (4)	6408 (3)	C(11)	−1927 (3)	3481 (2)	548 (1)
O(1)	879 (3)	488 (2)	1677 (2)	C(12)	−3126 (3)	3559 (2)	768 (2)
O(2)	−2561 (2)	2624 (2)	2268 (1)	C(13)	−3735 (4)	4373 (3)	767 (2)
O(3)	−981 (2)	3858 (1)	2295 (1)	C(14)	−3166 (4)	5106 (3)	555 (3)
O(4)	2519 (2)	1707 (2)	1783 (2)	C(15)	−1971 (4)	5047 (4)	352 (3)
N(1)	−0151 (3)	963 (2)	1810 (1)	C(16)	−1359 (3)	4240 (2)	341 (2)
N(2)	−1797 (3)	1989 (2)	2079 (1)	C(17)	6 (3)	2567 (2)	−54 (1)
N(3)	24 (3)	3393 (2)	2122 (1)	C(18)	−635 (4)	2798 (3)	−776 (2)
N(4)	1703 (3)	2367 (2)	1882 (2)	C(19)	65 (4)	2855 (3)	−1329 (2)
C(1)	−1475 (5)	−393 (2)	1755 (3)	C(20)	1400 (4)	2664 (2)	−1175 (2)
C(2)	−1249 (3)	576 (2)	1847 (2)	C(21)	2043 (4)	2437 (3)	−462 (2)
C(3)	−2244 (3)	1188 (2)	2007 (2)	C(22)	1346 (3)	2384 (2)	99 (2)
C(4)	−3572 (4)	920 (3)	2102 (2)	C(23)	−2147 (3)	1603 (2)	173 (1)
C(5)	1306 (4)	4752 (3)	2169 (3)	C(24)	−1590 (4)	783 (2)	116 (2)
C(6)	1116 (3)	3785 (2)	2075 (2)	C(25)	−2340 (5)	108 (3)	−259 (2)
C(7)	2116 (3)	3174 (2)	1934 (2)	C(26)	−3643 (5)	226 (3)	−573 (3)
C(8)	3480 (4)	3443 (3)	1872 (3)	C(27)	−4197 (5)	1022 (4)	−530 (4)
C(9)	627 (5)	2023 (3)	3056 (2)	C(28)	−3469 (4)	1716 (3)	−158 (3)
			2				
Co	−1642 (1)	1809 (1)	1417 (0)	C(11)	−3247 (13)	−379 (13)	1117 (7)
P	185 (2)	3033 (2)	1501 (1)	C(12)	−4534 (12)	−910 (13)	857 (6)
N(1)	−717 (6)	461 (6)	1692 (3)	C(13)	−236 (7)	4580 (6)	1332 (3)
N(2)	−1565 (6)	2042 (5)	2192 (3)	C(14)	−809 (8)	5265 (8)	1680 (4)
N(3)	−1736 (6)	1562 (6)	647 (3)	C(15)	−1178 (8)	6412 (8)	1523 (4)
N(4)	−2632 (6)	3110 (6)	1154 (3)	C(16)	−1035 (9)	6882 (9)	1019 (4)
O(1)	−310 (6)	−342 (5)	1354 (3)	C(17)	−531 (10)	6196 (9)	658 (4)
O(2)	−2027 (6)	3003 (5)	2405 (3)	C(18)	−106 (8)	5053 (8)	817 (4)
O(3)	−1247 (6)	642 (6)	439 (3)	C(19)	1160 (7)	2982 (7)	2208 (3)
O(4)	−3105 (5)	3835 (5)	1496 (3)	C(20)	1878 (7)	1975 (8)	2334 (3)
C(1)	189 (9)	−778 (9)	2517 (5)	C(21)	2662 (9)	1848 (10)	2855 (4)
C(2)	−471 (7)	296 (7)	2229 (3)	C(22)	2735 (9)	2724 (11)	3251 (4)
C(3)	−935 (7)	1254 (8)	2534 (3)	C(23)	2021 (9)	3720 (11)	3140 (4)
C(4)	−673 (9)	1360 (10)	3159 (4)	C(24)	1233 (8)	3864 (9)	2611 (3)
C(5)	−2412 (11)	2362 (13)	−304 (4)	C(25)	1385 (7)	2789 (7)	1096 (3)
C(6)	−2304 (8)	2413 (10)	317 (4)	C(26)	2406 (8)	3512 (8)	1188 (4)
C(7)	−2853 (7)	3303 (9)	619 (4)	C(27)	3354 (9)	3353 (10)	911 (4)
C(8)	−3560 (10)	4358 (11)	348 (6)	C(28)	3298 (9)	2406 (10)	546 (4)
C(9)	−3276 (9)	824 (9)	1327 (5)	C(29)	2288 (9)	1654 (9)	433 (4)
C(10)	−4031 (9)	1102 (12)	1760 (5)	C(30)	1359 (8)	1854 (8)	723 (4)

whereas the two DH units make an interplanar angle of 1.4°. As already observed in other cobaloximes containing the Co–CH_2–R grouping,[11,39] the C(9)–C(10) bond lies almost over one of the four equatorial nitrogen atoms, namely N(1).

The SHELXTL drawing with the atom numbering scheme for **2** is given in Figure 2. Bond lengths and angles are given in Table IV and are quite normal for the $Co(DH)_2$ unit.[11] The P–Co–C fragment is characterized by a P–Co–C angle of 177.1 (3)° and Co–P and Co–C bond lengths of 2.436 (2) and 2.11 (1) Å, respectively. The Co–C bond length does not differ significantly from the values found in the i-C_3H_7 analogue having the caged phosphite $P(OCH_2)_3CCH_3$ (2.12 (1) Å)[40] and pyridine (2.085 (3) Å)[15] as the trans ligand, but it is shorter than that of 2.22 (2) Å reported for $PPh_3Co(DH)_2(i\text{-}C_3H_7)$.[13] The Co–P distance in **2** is slightly longer than that of 2.412 (4) Å found in this i-C_3H_7 derivative. The 2-C_4H_9 group geometry shows a marked flattening of the C(9) tetrahedron. For example, the sum of the three angles at C(9) is 351 (1)° with a C(10)–C(9)–C(11) angle of 120 (1)°. These values must be compared with those found in the i-C_3H_7 analogue, which are 343 (2) and 113 (2)°, respectively, and with those found in $pyCo(DH)_2(i\text{-}C_3H_7)$, which are 340.6 (2)° and 112.3 (3)°. Disorder in the i-C_3H_7 group trans to the caged phosphite precludes any comparison. The cobalt atom in **2** is displaced by 0.03 Å out of the 4-N donor plane toward PPh_3 and the two DH units make an interplanar angle α of 5.5° away from the phosphine. The corresponding values for the i-C_3H_7 analogue are 0.17 Å and 14°, respectively.

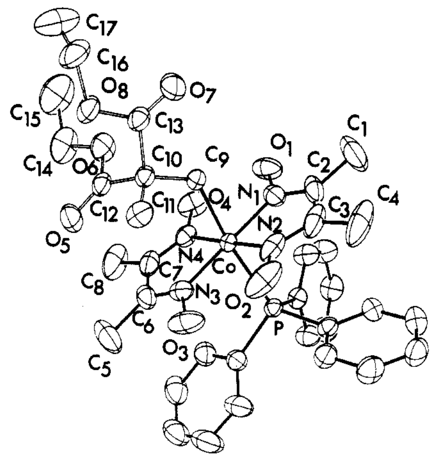

Figure 3. Structure and labeling scheme for the non-hydrogen atoms of **3** (thermal ellipsoids; 50% probability).

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(39) Randaccio, L.; Bresciani-Pahor, N.; Toscano, P. J.; Marzilli, L. G. *Inorg. Chem.* **1981**, *20*, 2722.

(40) Bresciani-Pahor, N.; Nardin, G.; Randaccio, L.; Zangrando, E. *Inorg. Chim. Acta* **1982**, *65*, L143.

Table III. Atomic Positional Parameters of Non-Hydrogen Atoms of 3 (×10^5 for Co and P and ×10^4 for the Others) and of 4 (×10^4) with esd's in Parentheses

	x	*y*	*z*		*x*	*y*	*z*
			3				
Co	14286 (3)	29002 (3)	27038 (2)	C(11)	802 (3)	635 (3)	4074 (2)
P	30808 (5)	43498 (6)	23866 (4)	C(12)	−1402 (2)	287 (2)	3509 (2)
O(1)	3330 (2)	2076 (3)	3711 (2)	C(13)	48 (2)	−604 (2)	2517 (2)
O(2)	427 (2)	1755 (2)	928 (1)	C(14)	−2745 (3)	−1369 (3)	3869 (2)
O(3)	−476 (2)	3733 (2)	1695 (2)	C(15)	−3597 (4)	−2034 (6)	3061 (3)
O(4)	2284 (2)	3892 (3)	4513 (1)	C(16)	−993 (4)	−1934 (3)	1145 (2)
O(5)	−2137 (2)	1058 (2)	3648 (2)	C(17)	−2295 (5)	−2336 (5)	824 (3)
O(6)	−1571 (2)	−947 (2)	3598 (2)	C(18)	2897 (2)	5065 (2)	1451 (2)
O(7)	868 (2)	−1288 (2)	2490 (1)	C(19)	3944 (3)	5544 (3)	1159 (2)
O(8)	−892 (2)	−773 (2)	1879 (1)	C(20)	3839 (3)	6106 (3)	463 (2)
N(1)	2617 (2)	1819 (2)	2936 (1)	C(21)	2689 (3)	6207 (3)	57 (2)
N(2)	1269 (2)	1693 (2)	1600 (1)	C(22)	1651 (3)	5771 (3)	357 (2)
N(3)	245 (2)	3993 (2)	2462 (2)	C(23)	1750 (3)	5196 (3)	1054 (2)
N(4)	1540 (2)	4046 (2)	3823 (1)	C(24)	3511 (2)	5830 (2)	3296 (2)
C(1)	3790 (4)	−26 (4)	2338 (3)	C(25)	3084 (2)	7018 (2)	3242 (2)
C(2)	2803 (3)	856 (3)	2286 (2)	C(26)	3325 (3)	8126 (3)	3950 (2)
C(3)	1984 (3)	768 (2)	1501 (2)	C(27)	4005 (3)	8073 (3)	4712 (2)
C(4)	1965 (4)	−287 (3)	669 (3)	C(28)	4404 (3)	6896 (3)	4785 (2)
C(5)	−779 (5)	5971 (4)	3048 (4)	C(29)	4145 (3)	5776 (3)	4086 (2)
C(6)	123 (3)	4997 (3)	3116 (3)	C(30)	4463 (2)	3523 (2)	2163 (2)
C(7)	911 (3)	5036 (3)	3908 (2)	C(31)	5556 (3)	3719 (4)	2737 (2)
C(8)	972 (5)	6128 (4)	4728 (3)	C(32)	6524 (3)	2991 (4)	2495 (3)
C(9)	−79 (2)	1865 (2)	2980 (2)	C(33)	6428 (3)	2083 (4)	1698 (3)
C(10)	−107 (2)	569 (2)	3264 (2)	C(34)	5365 (3)	1902 (3)	1125 (2)
				C(35)	4380 (3)	2613 (3)	1355 (2)
			4				
Co	−935 (0)	1447 (0)	1520 (1)	C(6)	−1815 (4)	1698 (2)	−1315 (6)
O(1)	−135 (3)	365 (1)	2801 (4)	C(7)	−1598 (4)	1062 (2)	−1318 (6)
O(2)	−829 (3)	2616 (2)	2803 (4)	C(8)	−1782 (4)	666 (3)	−2692 (7)
O(3)	−1703 (3)	2536 (2)	223 (5)	C(9)	−2274 (3)	1382 (2)	2539 (6)
O(4)	−977 (3)	294 (1)	159 (4)	C(10)	−2964 (4)	857 (2)	2365 (6)
O(5)	−3361 (3)	284 (2)	54 (4)	C(11)	−3386 (3)	750 (2)	731 (6)
O(6)	−3793 (3)	1249 (2)	122 (4)	C(12)	−3831 (4)	1006 (3)	3352 (7)
O(7)	−3770 (3)	1297 (2)	4499 (5)	C(13)	−2524 (4)	269 (2)	3029 (6)
O(8)	−4651 (3)	732 (3)	2841 (6)	C(14)	−4318 (4)	1186 (3)	−1398 (7)
N(1)	−290 (3)	953 (2)	3020 (5)	C(15)	−5328 (5)	930 (3)	−1269 (9)
N(2)	−589 (3)	2035 (2)	3004 (5)	C(16)[a]	−5501 (10)	650 (6)	3899 (16)
N(3)	−1553 (3)	1943 (2)	−3 (5)	C(161)	−5573 (13)	1020 (8)	3708 (21)
N(4)	−1235 (3)	872 (2)	−5 (4)	C(17)	−6131 (15)	1158 (9)	3034 (24)
N(5)	404 (3)	1570 (2)	562 (4)	C(171)	−6315 (15)	602 (9)	3290 (23)
C(1)	762 (5)	906 (3)	5439 (7)	C(18)	1016 (4)	1106 (2)	344 (7)
C(2)	115 (4)	1219 (2)	4227 (6)	C(19)	1902 (4)	1169 (3)	−338 (7)
C(3)	−74 (4)	1863 (2)	4224 (6)	C(20)	2177 (4)	1724 (3)	−812 (7)
C(4)	302 (5)	2276 (3)	5488 (7)	C(21)	1561 (4)	2202 (3)	−602 (7)
C(5)	−2274 (5)	2039 (3)	−2673 (7)	C(22)	683 (4)	2113 (2)	99 (6)

[a] This CH_2CH_3 group was disordered and the isotropic thermal parameters *B* ($Å^2$) were 5.7 (3), 8.0 (4), 9.9 (6), and 9.3 (5) for carbons 16, 161, 17, and 171, respectively.

Description and Discussion of Structures 3 and 4. SHELXTL and ORTEP drawings of the crystallographically independent molecules of 3 and 4 with the atom numbering scheme are shown in Figures 3 and 4, respectively. Bond lengths and angles are listed in Table V.

The geometry and orientation of the alkyl group in the two complexes is similar, with differences in the fine details.

The four N donors of the $Co(DH)_2$ unit are coplanar within ±0.01 Å in 4 and ±0.03 Å in 3. The cobalt atom is displaced by 0.03 Å toward C(9) in 4 and 0.02 Å toward P in 3. The $Co(DH)_2$ unit of 4 deviates from planarity with a bending angle α of 12.3° in the direction of the axial pyridine moiety, while the two DH units of 3 are tilted with respect to each other, with an interplanar angle of 5.2° so that the $Co(DH)_2$ moiety assumes a flat helical conformation. Such different distortions of the equatorial ligands, shown in Figure 5, may be attributed to the different bulk of py and PPh_3 ligands. The $CH_2C(CH_3)(CO_2C_2H_5)_2$ grouping in both compounds is arranged so that the nonhydrogen atoms of the CH_3CCOO moiety lie in a plane nearly parallel to the plane of the $(DH)_2$ ligand set (Figure 5) and the CH_2–C bond is almost over one Co-N(eq) bond, as observed in other cobaloximes containing $-CH_2CR_3$ groups σ bonded to cobalt with R = CH_3[14,26,41] or F.[42] Consequently the N(eq)–Co–C(9) angles (Table V) exhibit the usual pattern of values,[11] previously reported for the latter cobaloximes. The Co–C bond lengths are in the range observed for other cobaloximes containing either py or PPh_3 neutral ligands.[11] A comparison of Co–C bond lengths (Table VI) shows that in the PPh_3 derivatives this bond appears slightly but significantly longer than that of py analogues. The Co–N(axial) and Co–P bond lengths of 2.075 (4) and 2.460 (1) Å, respectively, are very close to the values of 2.081 (4) and 2.460 (1) Å, respectively, reported for the analogous neopentyl derivatives.[14,26] The large values of the Co–CH_2–C angles, close to 130°, have already been found in other cobaloximes containing

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(41) Bresciani-Pahor, N.; Calligaris, M.; Nardin, G.; Randaccio, L. *J. Chem. Soc., Dalton Trans.* 1982, 567.

(42) Bresciani-Pahor, N.; Calligaris, M.; Randaccio, L.; Zangrando, E., paper presented to the 16th Italian Meeting of Inorganic Chemistry, Ferrara, Italy, 1983.

Table IV. Bond Lengths (Å) and Bond Angles (deg) of 1 and 2 with Esd's in Parentheses

1

(a) Bond Lengths

Co-P	2.415 (1)	N(2)-O(2)	1.349 (5)	C(5)-C(6)	1.499 (7)
Co-N(1)	1.880 (4)	N(2)-C(3)	1.307 (5)	C(6)-C(7)	1.462 (8)
Co-N(2)	1.884 (4)	N(3)-O(3)	1.358 (5)	C(7)-C(8)	1.499 (7)
Co-N(3)	1.883 (4)	N(3)-C(6)	1.300 (5)	C(9)-C(10)	1.317 (9)
Co-N(4)	1.883 (4)	N(4)-O(4)	1.356 (5)	P-C(11)	1.830 (4)
Co-C(9)	2.045 (5)	N(4)-C(7)	1.304 (5)	P-C(17)	1.842 (4)
N(1)-O(1)	1.359 (5)	C(1)-C(2)	1.505 (7)	P-C(23)	1.834 (4)
N(1)-C(2)	1.297 (6)	C(2)-C(3)	1.470 (7)	C-C(phenyl,mean)	1.384 (10)
		C(3)-C(4)	1.482 (7)		

(b) Bond Angles

P-Co-C(9)	175.7 (3)	N(2)-Co-P	89.1 (1)	Co-C(9)-C(10)	126.2 (5)
N(1)-Co-N(2)	81.2 (2)	N(2)-Co-C(9)	88.3 (3)	Co-P-C(11)	108.8 (1)
N(1)-Co-N(3)	177.0 (2)	N(3)-Co-N(4)	81.4 (2)	Co-P-C(17)	123.3 (2)
N(1)-Co-N(4)	99.1 (2)	N(3)-Co-P	90.3 (1)	Co-P-C(23)	114.7 (1)
N(1)-Co-P	92.7 (1)	N(3)-Co-C(9)	86.8 (2)	C(11)-P-C(17)	102.6 (2)
N(1)-Co-C(9)	90.3 (2)	N(4)-Co-P	95.4 (1)	C(11)-P-C(23)	107.4 (2)
N(2)-Co-N(3)	98.1 (2)	N(4)-Co-C(9)	87.1 (3)	C(17)-P-C(23)	98.4 (2)
N(2)-Co-N(4)	175.4 (2)				

2

(a) Bond Lengths

Co-P	2.436 (2)	N(2)-C(3)	1.317 (1)	C(6)-C(7)	1.45 (1)
Co-C(9)	2.11 (1)	N(3)-O(3)	1.32 (1)	C(7)-C(8)	1.50 (2)
Co-N(1)	1.882 (6)	N(3)-C(6)	1.33 (1)	C(9)-C(10)	1.51 (2)
Co-N(2)	1.890 (7)	N(4)-O(4)	1.35 (1)	C(9)-C(11)	1.45 (2)
Co-N(3)	1.877 (7)	N(4)-C(7)	1.29 (1)	C(11)-C(11)	1.57 (2)
Co-N(4)	1.870 (7)	C(1)-C(2)	1.51 (1)	P-C(13)	1.833 (8)
N(1)-O(1)	1.36 (1)	C(2)-C(3)	1.47 (1)	P-C(19)	1.840 (7)
N(1)-C(2)	1.29 (1)	C(3)-C(4)	1.49 (1)	P-C(25)	1.839 (9)
N(2)-O(2)	1.350 (9)	C(5)-C(6)	1.49 (1)	C-C(phenyl,mean)	1.39 (2)

(b) Bond Angles

P-Co-C(9)	177.1 (3)	N(2)-Co-C(9)	92.2 (4)	C(10)-C(9)-C(11)	120 (1)
N(1)-Co-N(2)	81.3 (3)	N(3)-Co-N(4)	82.3 (3)	C(9)-C(11)-C(12)	115 (1)
N(1)-Co-N(3)	98.6 (3)	N(3)-Co-P	92.4 (2)	Co-P-C(13)	110.5 (2)
N(1)-Co-N(4)	177.0 (3)	N(3)-Co-C(9)	87.0 (4)	Co-P-C(19)	112.6 (3)
N(1)-Co-P	92.3 (2)	N(4)-Co-P	90.5 (2)	Co-P-C(25)	124.0 (3)
N(1)-Co-C(9)	90.6 (3)	N(4)-Co-C(9)	86.6 (4)	C(13)-P-C(19)	108.3 (3)
N(2)-Co-N(3)	179.2 (3)	Co-C(9)-C(10)	114.4 (7)	C(13)-P-C(25)	101.8 (4)
N(2)-Co-N(4)	97.8 (3)	Co-C(9)-C(11)	116.6 (9)	C(19)-P-C(25)	98.2 (4)
N(2)-Co-P	88.4 (2)				

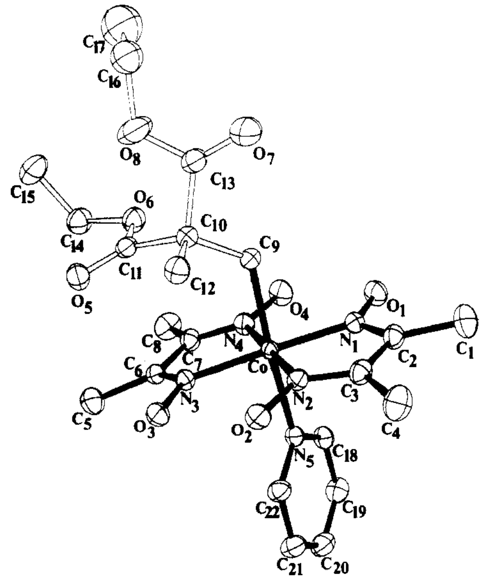

Figure 4. Structure and labeling scheme for the non-hydrogen atoms of 4 (thermal ellipsoids; 50% probability).

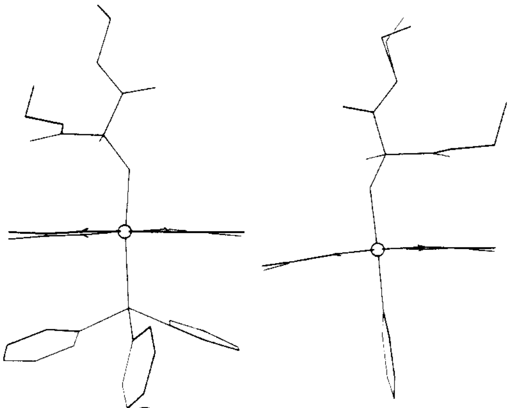

Figure 5. A side view of molecules 3 and 4 showing the distortions of the $(DH)_2$ ligand and the orientation of the axial ligands.

$-CH_2CR_3$ groups.[11,14,26,41] The C(9)–C(10) bond lengths of 1.537 (7) (**3**) and 1.550 (4) Å (**4**) are at the upper limit of the range of values found in neopentyl derivatives.[11,41]

Solution Studies. The results of the rate and NMR spectroscopic measurements, obtained as described in the Experimental Section, are summarized in Table VII.

Discussion

Trends in the Solid-State Data. The alkyl groups employed in this study include the following: a non-bulky good electron donor, CH_2CH_3; a bulky ligand with electron-withdrawing substituents, $CH_2C(CH_3)(CO_2C_2H_5)_2$; and a bulky ligand with a secondary carbon donor, 2-C_4H_9. Complexes of each alkyl with L = PPh_3 reveal the im-

Table V. Bond Lengths (Å) and Selected Bond Angles (deg) of 3 and 4 with Esd's in Parentheses

3

(a) Bond Lengths

Co-P	2.460 (1)	N(4)-C(7)	1.287 (4)	C(14)-O(6)	1.455 (4)
Co-C(9)	2.062 (2)	C(1)-C(2)	1.497 (5)	C(14)-C(15)	1.456 (6)
Co-N(1)	1.875 (2)	C(2)-C(3)	1.447 (4)	C(13)-O(7)	1.198 (3)
Co-N(2)	1.881 (2)	C(3)-C(4)	1.501 (5)	C(13)-O(8)	1.341 (3)
Co-N(3)	1.883 (2)	C(5)-C(6)	1.502 (6)	C(16)-O(8)	1.454 (4)
Co-N(4)	1.879 (2)	C(6)-C(7)	1.450 (5)	C(16)-C(17)	1.457 (7)
N(1)-O(1)	1.348 (3)	C(7)-C(8)	1.503 (5)	P-C(18)	1.849 (3)
N(1)-C(2)	1.305 (4)	C(9)-C(10)	1.550 (4)	P-C(24)	1.833 (2)
N(2)-O(2)	1.363 (3)	C(10)-C(11)	1.537 (4)	P-C(30)	1.838 (3)
N(2)-C(3)	1.293 (4)	C(10)-C(12)	1.544 (4)	C-C(phenyl,mean)	1.390 (5)
N(3)-O(3)	1.343 (3)	C(10)-C(13)	1.524 (4)	O(1)···O(4)	2.466 (3)
N(3)-C(6)	1.315 (4)	C(12)-O(5)	1.192 (3)	O(2)···O(3)	2.481 (3)
N(4)-O(4)	1.359 (3)	C(12)-O(6)	1.348 (3)		

(b) Bond Angles

P-Co-C(9)	173.32 (7)	N(4)-Co-P	89.25 (8)	O(6)-C(14)-C(15)	108.9 (3)
N(1)-Co-N(2)	81.11 (9)	N(4)-Co-C(9)	88.0 (1)	C(10)-C(13)-O(7)	126.5 (2)
N(1)-Co-N(3)	179.4 (1)	Co-C(9)-C(10)	127.2 (2)	C(10)-C(13)-O(8)	109.3 (2)
N(1)-Co-N(4)	98.5 (1)	C(9)-C(10)-C(11)	114.5 (2)	O(7)-C(13)-O(8)	124.2 (2)
N(1)-Co-P	88.23 (7)	C(9)-C(10)-C(12)	107.4 (2)	C(13)-O(8)-C(16)	118.0 (3)
N(1)-Co-C(9)	98.2 (1)	C(9)-C(10)-C(13)	111.6 (2)	O(8)-C(6)-C(17)	108.1 (3)
N(2)-Co-N(3)	98.7 (1)	C(11)-C(10)-C(12)	105.8 (2)	Co-P-C(18)	122.57 (8)
N(2)-Co-N(4)	177.3 (1)	C(11)-C(10)-C(13)	110.9 (2)	Co-P-C(24)	110.51 (9)
N(2)-Co-P	93.43 (7)	C(12)-C(10)-C(13)	106.0 (2)	Co-P-C(30)	112.49 (9)
N(2)-Co-C(9)	89.45 (9)	C(10)-C(12)-O(5)	125.8 (3)	C(18)-P-C(24)	101.7 (1)
N(3)-Co-N(4)	81.8 (1)	C(10)-C(12)-O(6)	110.4 (2)	C(18)-P-C(30)	99.5 (1)
N(3)-Co-P	91.22 (8)	O(5)-C(12)-O(6)	123.7 (3)	C(24)-P-C(30)	108.8 (1)
N(3)-Co-C(9)	82.4 (1)	C(12)-O(6)-C(14)	117.5 (2)		

4

(a) Bond Lengths

Co-N(1)	1.887 (4)	C(1)-C(2)	1.504 (8)	C(14)-O(6)	1.472 (7)
Co-N(2)	1.890 (4)	C(2)-C(3)	1.469 (8)	C(14)-C(15)	1.501 (9)
Co-N(3)	1.889 (4)	C(3)-C(4)	1.506 (8)	C(16)-C(17)	1.59 (3)
Co-N(4)	1.881 (4)	C(5)-C(6)	1.512 (8)	C(16)-O(8)	1.54 (2)
Co-N(5)	2.075 (4)	C(6)-C(7)	1.458 (7)	C(161)-C(171)	1.41 (3)
Co-C(9)	2.047 (5)	C(7)-C(8)	1.503 (8)	C(161)-O(8)	1.64 (2)
N(1)-O(1)	1.353 (5)	C(9)-C(10)	1.537 (7)	C(18)-N(5)	1.356 (6)
N(1)-C(2)	1.302 (6)	C(10)-C(11)	1.522 (7)	C(18)-C(19)	1.389 (8)
N(2)-O(2)	1.355 (5)	C(10)-C(12)	1.455 (8)	C(19)-C(20)	1.374 (9)
N(2)-C(3)	1.294 (6)	C(10)-C(13)	1.547 (7)	C(20)-C(21)	1.381 (8)
N(3)-O(3)	1.365 (5)	C(11)-O(5)	1.205 (6)	C(21)-C(22)	1.394 (8)
N(3)-C(6)	1.300 (7)	C(11)-O(6)	1.345 (6)	C(22)-N(5)	1.349 (6)
N(4)-O(4)	1.351 (5)	C(12)-O(7)	1.195 (8)	O(1)···O(4)	2.512 (3)
N(4)-C(7)	1.291 (6)	C(12)-O(8)	1.324 (7)	O(2)···O(3)	2.483 (5)

(b) Bond Angles

N(1)-Co-N(2)	81.5 (2)	N(5)-Co-C(9)	176.0 (2)	O(7)-C(12)-O(8)	123.1 (5)
N(1)-Co-N(3)	178.7 (2)	Co-C(9)-C(10)	125.4 (4)	C(11)-O(6)-C(14)	116.0 (4)
N(1)-Co-N(4)	99.0 (2)	C(9)-C(10)-C(11)	114.3 (4)	C(12)-O(8)-C(16)	120.1 (7)
N(1)-Co-N(5)	88.9 (2)	C(9)-C(10)-C(12)	106.6 (4)	C(12)-O(8)-C(161)	108.2 (8)
N(1)-Co-C(9)	91.8 (2)	C(9)-C(10)-C(13)	112.9 (4)	C(15)-C(14)-O(6)	111.0 (5)
N(2)-Co-N(3)	98.6 (2)	C(11)-C(10)-C(12)	107.9 (4)	C(17)-C(16)-O(8)	92 (2)
N(2)-Co-N(4)	177.6 (2)	C(11)-C(10)-C(13)	109.2 (4)	C(171)-C(161)-O(8)	100 (2)
N(2)-Co-N(5)	90.0 (2)	C(12)-C(10)-C(13)	105.5 (4)	C(18)-N(5)-C(22)	117.8 (4)
N(2)-Co-C(9)	86.1 (2)	C(10)-C(11)-O(5)	125.3 (5)	C(18)-C(19)-C(20)	119.0 (5)
N(3)-Co-N(4)	80.8 (2)	C(10)-C(11)-O(6)	111.0 (4)	C(19)-C(18)-N(5)	122.7 (5)
N(3)-Co-N(5)	89.8 (2)	O(5)-C(11)-O(6)	123.7 (5)	C(19)-C(20)-C(21)	119.0 (5)
N(3)-Co-C(9)	89.5 (2)	C(10)-C(12)-O(7)	125.2 (5)	C(20)-C(21)-C(22)	119.6 (5)
N(4)-Co-N(5)	87.6 (2)	C(10)-C(12)-O(8)	111.5 (5)	C(21)-C(22)-N(5)	121.9 (5)
N(4)-Co-C(9)	96.2 (2)				

portance of solid-state effects when comparisons are made to other structurally characterized compounds (Table VII). Three compounds in this table have relatively large α and d values. The alkyl groups (CH_2CN, CH_3, and i-C_3H_7) in these complexes almost span the range of electron donor ability in solution as judged by k_1 and ^1H NMR criteria (Table VII). For each compound, there is at least one complex with an alkyl ligand of similar donor ability and with α values (and to a lesser extent d values) which are significantly smaller. For example, the i-C_3H_7 and 2-C_4H_9 complexes have very similar k_1, ^{31}P and ^1H NMR shifts, $^5J_{PH}$, and $\sum C\hat{P}C$. Yet, the 2-C_4H_9 complex does not have large α or d values. The time-averaged structure of the two complexes in solution must be very similar. The structures of the compounds in the solid represent either different conformations which may exist to some extent in solution or conformations which exist only in the solid and which are influenced by intermolecular interactions. There are, however, no evident close contacts which readily explain the differences in the solid-state structures of the closely related compounds. Nevertheless, further support for the importance of solid-state effects is derived from the structural investigation of $P(OCH_3)_3Co(DH)_2Cl$ where the two crystallographically independent molecules have sig-

Table VI. Comparison of Co–C Bond Lengths (Å) in $\mathrm{pyCo(DH)_2R}$ and $\mathrm{PPh_3Co(DH)_2R}$

	py	PPh_3
CH_3	1.998 (5)[a]	2.026 (6)[b]
CH_2CF_3	2.010 (3)[c]	2.036 (3)[c]
C_2H_5	2.035 (5)[d]	2.045 (5)[e]
$CH_2C(CH_3)(CO_2C_2H_5)_2$	2.047 (5)[e]	2.062 (2)[e]
$CH(CH_3)CN$	2.053 (4)[j]	2.08 (1)[k]
neo-C_5H_{11}	2.060 (6)[f]	2.117 (9)[g]
i-C_3H_7	2.085 (3)[h]	2.22 (2)[i]

[a] Reference 25. [b] Reference 18. [c] Reference 16; the py ligand is actually 4-cyanopyridine. [d] Reference 17; the neutral ligand is 4-$CH_3OC(NH)$py. [e] Present results. [f] Reference 14. [g] Reference 25. [h] Reference 15. [i] Reference 13. [j] Reference 51. [k] Reference 50.

nificantly different geometries (e.g., Co–P = 2.165 (4) and 2.211 (4) Å and α = 7.0 and 1.0°, respectively).[43] Large α values, ~10°, are not observed unless one ligand is bulky, and solid-state effects probably modulate this parameter. In compound 4, the α value of −12.3° is the largest negative α value observed thus far (negative α values represent bending toward the neutral ligand).[14] This large value reflects the bulk of the $CH_2C(CH_3)(CO_2C_2H_5)_2$ group. Additionally, it provides further evidence that large α values arise partly from intramolecular interactions since the direction of the bending in this and other compounds with large α values is away from the bulky ligand.

For a regular tetrahedron, the value of $\sum \mathrm{C\hat{P}C}$ is 328.5°. In all cases in Table VII, the values observed are smaller. There is a clear break in values between non-alkyl and alkyl complexes. Within the alkyl complexes, a less distinctive and less significant division occurs with values of ~310° for complexes with an alkyl group containing electron-withdrawing substituents and smaller values for complexes with alkyl groups lacking such substituents. A clear break between non-alkyl and alkyl complexes is not evident in any other parameters listed in Table VII. As discussed below, $\sum \mathrm{C\hat{P}C}$ reflects electron acceptance by $\mathrm{Co(DH)_2X}$. Consistent with this trend, the value of $\sum \mathrm{C\hat{P}C}$ = 310° for $\mathrm{PPh_3Co(GH)_2CH_3}$ (where GH = monoanion of glyoxime) is larger than that for the DH analogue, as expected from the weaker electron donation by GH ligands.[24]

Trends in the NMR Data. (a) ^{1}H NMR. Trends in ^{1}H NMR spectra of cobaloximes as axial ligands are changed are reasonably well understood for both chemical shifts and ^{31}P–^{1}H coupling constants.[4] As the trans influence of the negative axial ligand increases, the ^{1}H resonance of the DH methyl group shifts upfield. This shift has been attributed to changes in the magnetic anisotropy at Co due to rehybridization of cobalt as the trans influence of the negative ligand (X) is increased.[4] Thus the changes in ^{1}H chemical shift as a function of X are dominated by the heavy-atom through-space effect of the Co.

Similarly, as the rehybridization occurs, the coupling between ^{1}H of the methyl group and ^{31}P is altered. This leads to an increase in the 5-bond ^{31}P–^{1}H coupling constants for complexes with ligands such as $P(OCH_3)_3$ and PBu_3.[4,5] The trend observed in Figure 6 and in Table VII is consistent.

Another important influence on the shift of the ^{1}H DH methyl resonance is observed when either axial ligand is anisotropic.[4] For example, the aromatic rings of PPh_3 induce an upfield shift. This upfield shift is not dependent on the trans influence of X since the difference in shift for X = Cl and X = CH_3 (~0.3 ppm) is about the same for

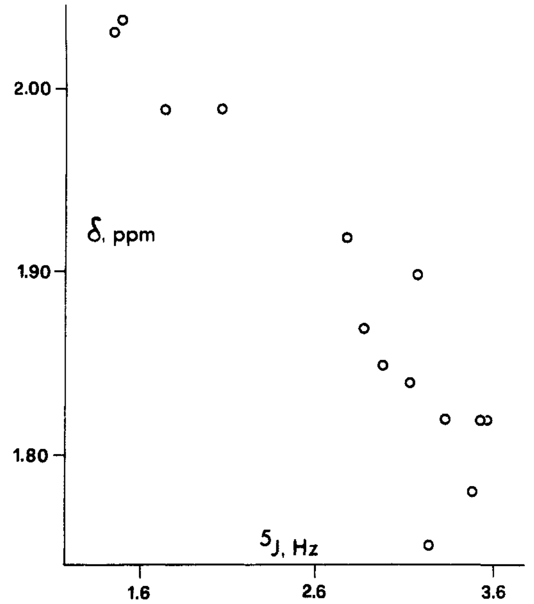

Figure 6. ^{1}H chemical shift (oxime CH_3) vs. $^5J_{PH}$ for the following $\mathrm{PPh_3Co(DH)_2X}$ compounds (left to right): X = Br, Cl, NO_2, I, CH_2CN, CH_2Br, CH_2CF_3, CH_3, $CH(CH_3)CN$, $CH_2C(CH_3)(CO_2C_2H_5)_2$, C_2H_5, neo-C_5H_{11}, *i*-C_3H_7, respectively. For references, see Table VII.

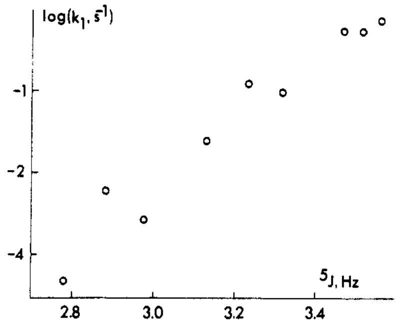

Figure 7. log k_1 (s^{-1}) vs. $^5J_{PH}$ for the following $\mathrm{PPh_3Co(DH)_2X}$ compounds (left to right): X = CH_2CN, CH_2Br, CH_2CF_3, CH_3, $CH_2C(CH_3)(CO_2C_2H_5)_2$, C_2H_5, neo-C_5H_{11}, *i*-C_3H_7, 2-C_4H_9, respectively. For references, see Table VII.

PPh_3 complexes as complexes with the non-anisotropic ligand, PBu_3.[4,5] In fact, this absence of an effect can be predicted from the magnitude of the changes in bond distances normally observed and the use of the dipolar relationship.[44]

(b) ^{31}P NMR. The changes in ^{1}H NMR shifts of cobaloximes are dominated by the remote heavy-atom effect of cobalt.[4,45] For nuclei with higher atomic numbers, such as ^{31}P and ^{13}C, the local paramagnetic contribution to the shifts usually dominates.[2,3] This local contribution can reflect both changes in bonding and structure across a series of related compounds such as $\mathrm{LCo(DH)_2X}$.[2,3,7] Even for such heavier nuclei, the remote effect of Co can be important for nuclei close to this heavy atom.[3] The ^{31}P NMR shifts of P donor ligands are sensitive to changes in bond angles at P.[2] Nevertheless, in an extensive study of the ^{31}P NMR spectra of cobaloximes several readily understood trends were found.[2] This study employed primarily small cone angle ligands such as $P(OCH_3)_3$ and PBu_3.[45,46] Examination of the ^{31}P NMR shift data in

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Table VII. X-ray Structural, Spectroscopic, and Kinetic Data for $PPh_3Co(DH)_2X$[a]

X	Co–P, Å	$\Sigma C\hat{P}C$,[b] deg	α, deg	*d*, Å	k_1,[c] s^{-1}	^1H NMR δ[e]	^{31}P NMR δ[f]	$^5J_{PH}$,[g] Hz
Cl	2.327 (2)	316.3	6.0	0.05		2.02	25.6	1.51
Br	2.331 (4)	315.2	7.0	0.07		2.03	30.4	1.47
I						1.99	32.5	2.05
NO_2	2.365 (4)	317.5	7.7	0.04		1.99	21.5	1.76
CH_2CN	2.391 (1)	310.1	11.1	0.08	$(2.4 \pm 0.3) \times 10^{-5}$ [d]	1.92	23.0	2.78
$CH(CH_3)CN$	2.410 (3)	307.8	9.4	0.03	*h*	1.90	23.1	3.18
CH_2CF_3	2.383 (1)	311.0	1.7	0.04	$(8.9 \pm 0.3) \times 10^{-4}$ [d]	1.85	21.2	2.98
CH_2Br	2.399 (3)	309.8	2.7	0.07	$(3.8 \pm 0.1) \times 10^{-3}$	1.87	20.0	2.88
CH_3	2.418 (1)	307.0	14.0	0.11	$(4.5 \pm 0.2) \times 10^{-2}$	1.84	20.4	3.13
C_2H_5	2.415 (1)	308.4	1.4	0.06	1.4 ± 0.1	1.82	20.9	3.32
i-C_3H_7	2.412 (4)	308.8	14.0	0.17	$(3.9 \pm 0.2) \times 10^1$	1.82	22.7	3.52
2-C_4H_9	2.436 (2)	308.3	5.5	0.03	$(6.5 \pm 0.3) \times 10^1$	1.82	21.4	3.56
neo-C_5H_{11}	2.460 (1)	305.7	2.2	0.04	$(3.4 \pm 0.1) \times 10^1$	1.78	17.2	3.47
$CH_2C(CH)_3(CO_2C_2H_5)_2$	2.460 (1)	310.0	5.2	0.02	1.5 ± 0.1	1.75	20.0	3.23

[a] $CDCl_3$ was the solvent for NMR studies; ^1H and ^{31}P chemical shifts were referenced to internal Me_4Si and external H_3PO_4, respectively. Data for solution studies are from the present work; references for solid-state studies are as follows: Cl, ref 20; Br, ref 19; NO_2, ref 22 and 23; CH_2CN, ref 21; $CH(CH_3)CN$, ref 50; CH_2CF_3, ref 16; CH_2Br, ref 21; CH_3, ref 18; C_2H_5, present results; i-C_3H_7, ref 13; 2-C_4H_9, present results; neo-C_5H_{11}, ref 26; $CH_2C(CO_2C_2H_5)_2$, present results. [b] Sum of the C–P–C angles; 328.5° is expected for a regular tetrahedron. [c] See text for details. [d] Swinbourne treatment was employed. [e] Chemical shifts for the oxime ($N{=}CCH_3$); 90 MHz. [f] 81.01 MHz. [g] Coupling between PPh_3 and the oxime CH_3 groups; 200.13 MHz. Values for compounds with $k_1 > 1.0\ s^{-1}$ were determined from low temperature, stopped-exchange spectra. [h] Plots of ln *A* vs. *t* showed curvature. NMR measurements indicate that some of the PPh_3 is displaced by the nitrile of the X groups. Further studies are in progress.

Table VII reveals considerable scatter. For example, the CH_2CN and i-C_3H_7 complexes have alkyl ligands near the extremes of electron donor ability, yet these compounds have similar ^{31}P NMR shifts. This scatter evidently reflects the contribution of several opposing effects, and ^{31}P NMR shifts for PPh_3 cobaloximes do not appear to be a useful parameter for assessing trends.

Trends in the Rate Data. In general, the ^1H NMR shift and coupling constant data and the ligand exchange rates trend in parallel. These parameters reflect the electron donor ability of the alkyl ligand. The better rate correlation is found between coupling constant and log k_1 (Figure 7) since the shift is sometimes influenced by the anisotropy of the alkyl group, especially for $CH_2C(CH_3)(CO_2C_2H_5)_2$.

Correlation of Structural and Solution Studies. Except for ^{31}P NMR shifts and α and *d* values, the other parameters in Table VII, including both solid-state and solution measurements, trend in parallel. One correlation between a solid-state parameter, Co–P distance, and a solution parameter, ^1H NMR shift, is shown in Figure 8. In general, one might expect the Co–P distance to increase as the trans influence of X increases, the steric interaction between the PPh_3 and the equatorial ligand should increase. In turn the $\sum C\hat{P}C$ should decrease to minimize repulsions. *The opposite trend in* $\sum C\hat{P}C$ *is observed.* A possible explanation of the observed trend is as follows: The $Co(DH)_2X$ moiety is a better electron acceptor when X is a weak trans influence ligand. The P donor may then utilize more p character in its bonding to Co. The bonding between P and the phenyl groups would then involve more s orbital character, which requires larger C–P–C angles.

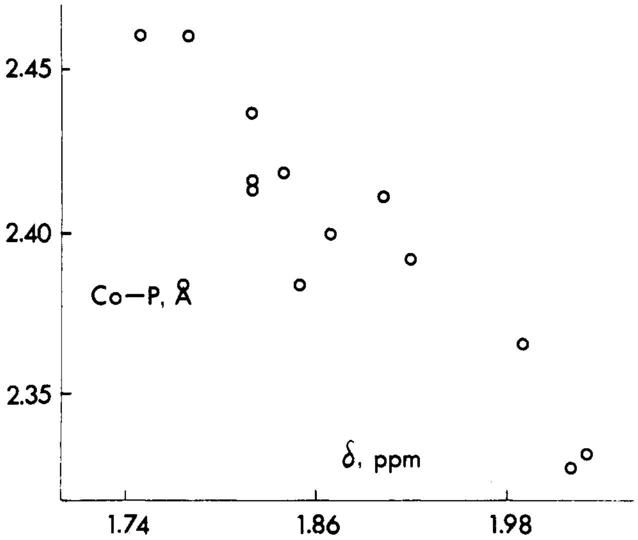

Figure 8. Co–P distance (Å) vs. ^1H chemical shift (oxime CH_3) for the following $PPh_3Co(DH)_2X$ compounds (top to bottom): X = $CH_2C(CH_3)(CO_2C_2H_5)_2$ and neo-C_5H_{11} (left to right, respectively), 2-C_4H_9, CH_3, C_2H_5, i-C_3H_7, $CH(CH_3)CN$, CH_2Br, CH_2CN, CH_2CF_3, NO_2, Br, Cl, respectively. For references, see Table VII.

A Final Word on 3 and 4. The $CH_2C(CH_3)(CO_2C_2H_5)_2$ grouping has been used to model the B_{12}-dependent, enzyme-catalyzed carbon skeleton rearrangement of methylmalonyl CoA to succinyl CoA.[29] We wished to determined whether there was any unusual strain in the carbon skeleton and if increasing the bulk of the trans ligand from py to PPh_3 increased the strain. The answer to both questions is a disappointing no. The principal change in going from 4 to 3 is a slight increase in the Co–C9–C10 bond angle from 125.4 (4) to 127.2 (2)°, but this change is not significant. Strain may not be involved in the rearrangements or, alternatively, the greater steric requirements of the cobalamin system may be required to promote the rearrangement.[1,12] Indeed, the cobalamin with this bulky alkyl is relatively unstable and difficult to isolate.[29,47] Finke[48] and Costa[49] have shown that the Costa B_{12} model (with Schiff base and oxime N donors) has electronic properties similar to cobalamins. The system probably has similar steric requirements to the cobaloximes

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and preparation and study of complexes with the Costa model containing $CH_2C(CH_3)(CO_2C_2H_5)_2$ may elucidate the relative importance of steric and electronic contributions to instability. It is also possible that, during the catalysis, the organic intermediates do not form a direct Co to C bond.[1] Alternatively, a bond between Co and a secondary or tertiary carbon in the alkyl could provide the strain necessary to drive a carbon skeleton rearrangement. Increased strain was observed, as discussed above, in going from $PPh_3(DH)_2(i\text{-}C_3H_7)$ to $PPh_3Co(DH)_2(2\text{-}C_4H_9)$.

The $CH_2C(CH_3)(CO_2C_2H_5)_2$ ligand[29,52] is interesting in that it is a bulky alkyl with electron-withholding substituents. The structural consequences of this have been mentioned above. The Co–P bond length in **3** is anomalously long and may reflect the steric bulk of the alkyl. Steric interactions may be made more serious by the relatively large value of $\sum C\hat{P}C$ for this alkyl. Complexes with bulky alkyl groups bearing electron-withdrawing substituents appear worthy of further study.[53]

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Registry No. **1**, 38141-58-1; **2**, 94202-45-6; **3**, 94202-46-7; 4, 57620-61-8; $PPh_3Co(DH)_2Cl$, 23295-34-3; $PPh_3Co(DH)_2Br$, 33988-32-8; $PPh_3Co(DH)_2I$, 33988-34-0; $PPh_3Co(DH)_2NO_2$, 39038-45-2; $PPh_3Co(DH)_2CH_2CN$, 84662-76-0; $PPh_3Co(DH)_2CH(CH_3)CN$, 94292-13-4; $PPh_3Co(DH)_2CH_2CF_3$, 17567-52-1; $PPh_3Co(DH)_2CH_2Br$, 84662-75-9; $PPh_3Co(DH)_2CH_3$, 15977-37-4; $PPh_3Co(DH)_2(i\text{-}C_3H_7)$, 60293-65-4; $PPh_3Co(DH)_2(\text{neo-}C_5H_{11})$, 82405-10-5; PBu_3, 998-40-3; $BrCH_2C(CH_3)(CO_2C_2H_5)_2$, 75511-41-0; CH_2Br_2, 74-95-3; diethyl methylmalonate, 609-08-5.

Supplementary Material Available: A listing of structure factors and tables of anisotropic thermal parameters and hydrogen atom parameters (74 pages). Ordering information is given on any current masthead page.

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(53) A reviewer has suggested that the ^{31}P NMR can be correlated by a two-parameter fit with Co–P bond distance and $\sum CPC$. We are examining this issue.

Aryldiazenido (N_2Ar) Complexes. Carboxylate, Formate, Hydroxycarbonyl, and Hydride Derivatives of $[(\eta\text{-}C_5H_5)Re(CO)_2(N_2Ar)][BF_4]$ and $[(\eta\text{-}C_5Me_5)Re(CO)_2(N_2Ar)][BF_4]$

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The aryldiazenido complexes $[(\eta\text{-}C_5H_5)Re(CO)_2(p\text{-}N_2C_6H_4R)][BF_4]$ (**1**: **a**, R = Me; **b**, R = OMe; **c**, R = NEt_2) and $[(\eta\text{-}C_5Me_5)Re(CO)_2(p\text{-}N_2C_6H_4R)][BF_4]$ (**7**, R = OMe) react with a stoichiometric amount of 0.1 M aqueous NaOH to give the air-stable, microcrystalline, golden yellow hydroxycarbonyl complexes $(\eta\text{-}C_5H_5)Re(CO)(p\text{-}N_2C_6H_4R)(COOH)$ (**2**) and $(\eta\text{-}C_5Me_5)Re(CO)(p\text{-}N_2C_6H_4R)(COOH)$ (**8**). These complexes dissolve in excess aqueous hydroxide to give bright yellow solutions of the respective carboxylate complex anions $[(\eta\text{-}C_5H_5)Re(CO)(p\text{-}N_2C_6H_4R)(CO_2)]^-$ (**4**) and $[(\eta\text{-}C_5Me_5)Re(CO)(p\text{-}N_2C_6H_4R)(CO_2)]^-$ (**10**), which have been isolated as lithium or calcium salts. Under specified conditions, which are discussed, decarboxylation occurs to yield the yellow hydride complexes $(\eta\text{-}C_5H_5)ReH(CO)(p\text{-}N_2C_6H_4R)$ (**3**) and $(\eta\text{-}C_5Me_5)ReH(CO)(p\text{-}N_2C_6H_4R)$ (**9**). Formate complexes $(\eta\text{-}C_5H_5)Re(CO)(p\text{-}N_2C_6H_4R)(OCHO)$ (**5**) and $(\eta\text{-}C_5Me_5)Re(CO)(p\text{-}N_2C_6H_4R)(OCHO)$ (**11**), isomeric with the hydroxycarbonyl complexes, have also been synthesized for comparison.

Introduction

Recent work in this laboratory on the characterization and study of complexes containing the aryldiazenido ligand (N_2Ar; Ar = aryl) has centered on the cationic dicarbonylcyclopentadienylrhenium derivatives $[(\eta\text{-}C_5H_5)Re(CO)_2(N_2Ar)]^+$ (**1**).[1] These compounds have been particularly interesting to us because, in contrast with most aryldiazenido complexes, the N_2Ar ligand reacts readily with various nucleophiles and thereby can be transformed, for example, to a dinitrogen ligand[1] (eq 1) or to substituted diazene or hydrazide ligands[2] (eq 2).

$$\mathbf{1} + NaI \rightarrow (\eta\text{-}C_5H_5)Re(CO)_2(N_2) \qquad (1)$$

$$\mathbf{1} + CH_3Li \rightarrow (\eta\text{-}C_5H_5)Re(CO)_2[NN(CH_3)Ar] \qquad (2)$$

Although there is a well-known formal analogy between nitrosyl (NO) and organodiazenido ligands, it is notable that in reactions of the corresponding rhenium nitrosyl cation $[(\eta\text{-}C_5H_5)Re(CO)_2(NO)]^+$ with nucleophiles, it never appears that the nitrosyl ligand is transformed. Instead, this nitrosyl complex and the triphenylphosphine analogue

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(1) Barrientos-Penna, C. F.; Einstein, F. W. B.; Sutton, D.; Willis, A. C. *Inorg. Chem.* **1980**, *19*, 2740.

(2) Barrientos-Penna, C. F.; Einstein, F. W. B.; Jones, T.; Sutton, D. *Inorg. Chem.* **1982**, *21*, 2578.