# Steric Influences of Phosphorus-donor Ligands on the Structure and Ligand-exchange Rates of Cobaloximes

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The crystal structures of two cobaloximes, $[CoMe(Hdmg)_2(PMe_3)]$ (1) and $[CoMe(Hdmg)_2\{P(C_6H_{11})_3\}]$ (2) ($H_2dmg$ = dimethylglyoxime), are reported and discussed. Compound (1) crystallizes in the space group $P\bar{1}$ with cell parameters $a$ = 15.830(8), $b$ = 12.279(7), $c$ = 12.257 Å, $\alpha$ = 94.85(7), $\beta$ = 84.49(8), $\gamma$ = 130.07(9)°, and $Z$ = 4; (2) crystallizes in the space group $P2_12_12_1$ with $a$ = 18.50(1), $b$ = 16.83(1), $c$ = 9.943(8) Å, and $Z$ = 4. Both structures have been solved by Patterson and Fourier methods and refined by block-diagonal anisotropic least-squares methods to final $R$ values of 0.037 (1) and 0.038 (2), using 4 812(1) and 2 710(2) independent reflections. The Me–Co–P fragment of (1) is characterized by a C–Co–P angle of 178.9(2)° (mean) and Co–P and Co–C bond lengths of 2.293(1) (mean) and 2.015(3) Å (mean); the corresponding figures for (2) are 179.1(2)°, 2.463(1), and 2.016(5) Å respectively. The value of 2.463(1) Å is the largest so far reported for a $Co^{III}$–P bond length. The two nearly planar Hdmg units make a mean interplanar angle of 4° in (1) and are bent towards the axial methyl group. A similar but more pronounced bending is observed in (2). The trend in Co–P distances in these and other similar complexes $[CoX(Hdmg)_2(PR_3)]$ (X = Cl or Me; R = OMe, Me, $Bu^n$, Ph, or $C_6H_{11}$) is discussed and compared with $^{31}P$ and $^1H$ chemical shifts. Deformations observed in the geometry of these octahedral cobalt(III) complexes are interpreted in terms of 'steric' and 'electronic' influences. Finally, kinetic measurements of the conversion of $[CoMe(Hdmg)_2\{P(C_6H_{11})_3\}]$ to $[CoMe(Hdmg)_2(py)]$ (py = pyridine) give no indication of a significant contribution from steric effects on the rate of the five- to six-co-ordinate step. However, the relatively high rate of displacement of the $P(C_6H_{11})_3$ ligand compared to other phosphines of smaller cone angle almost certainly arises from the steric interaction of the $C_6H_{11}$ rings with the $Co(Hdmg)_2$ moiety.

WE are attempting to evaluate steric effects in vitamin $B_{12}$ models in order to probe the feasibility of the mechanochemical mechanism of Co–C bond cleavage during substrate to product catalysis by the $B_{12}$ coenzyme–enzyme complex.[1-5] Such a study also has some bearing on steric effects of $P$-donor ligands since such ligands are used to generate steric distortions in model compounds.[6-8] These distortions are suggested to occur in the coenzyme, caused by enzyme side chains.[1-5] In addition to ground-state structural effects (referred to here as 'influences'), steric factors play some role in modifying reaction rates (referred to as 'effects').[9,10]

The cobaloximes (cobalt complexes containing two 'coplanar' dioxime ligands) have proved to be useful in evaluating the influence of bulky groups on ground-state structural parameters. We recently demonstrated that the Co–C bond length in the compound $[CoPr^i(Hdmg)_2(py)]$ (where Hdmg = monoanion of dimethylglyoxime and py = pyridine) was approximately 0.1 Å longer than in the parent $[CoMe(Hdmg)_2(py)]$.[11] We also found that a further increase of 0.1 Å could be achieved by substituting the bulky triphenylphosphine ligand for pyridine in the isopropyl derivative.[8] We argued that these steric influences were not indirectly caused by electronic changes in the bonding accompanying distortion of the cobalt co-ordination sphere.

In this report, structural analyses of two cobaloximes $[CoMe(Hdmg)_2(PMe_3)]$ (1) and $[CoMe(Hdmg)_2\{P(C_6H_{11})_3\}]$ (2) ($C_6H_{11}$ = cyclohexyl), which contain $P$-donor ligands of similar basicity[12,13] but of widely different steric bulk,[14] are presented. Furthermore, the ability of the bulky $P(C_6H_{11})_3$ phosphine to interact with the five-co-ordinate intermediate believed to be formed during substitution reactions of cobaloximes[9,10,15,16] is also evaluated.

## EXPERIMENTAL

*Kinetic Measurements.*—Pyridine was used only after distillation. Tricyclohexylphosphine was obtained from Strem Chemical Co. and used without further purification. It was stored in a freezer at approximately −10 °C when not in use.

The compound $[CoMe(Hdmg)_2\{P(C_6H_{11})_3\}]$ (2) was prepared by the previously outlined method[17] and characterized by $^1H$ n.m.r. measurement, $X$-ray structural determination, and elemental analysis (Found: C, 55.7; H, 8.7; Co, 9.7. Calc. for $C_{27}H_{50}CoN_4O_4P$: C, 55.5; H, 8.6; Co, 10.1%).

The rate determinations were made at 25 °C on a Durrum–Gibson D-110 stopped-flow spectrophotometer. All measurements were made using reagent-grade $CH_2Cl_2$ as solvent and at 500 nm. The complex concentration after mixing was 0.01 mol $dm^{-3}$ with pyridine being maintained constantly at 0.1 mol $dm^{-3}$ and $P(C_6H_{11})_3$ varied to produce the required change in ligand ratio.

*Crystal Data.*—Crystals of (1) and of (2) were obtained from the starting material by crystallization from $CH_2Cl_2$–n-heptane at 0—5 °C. The cell parameters were determined from Weissenberg and precession photographs and refined on a Siemens AED single-crystal diffractometer. The crystal data are given in Table 1.

One check reflection intensity, in both collections of diffraction data, was measured every 100 reflections and did not show any systematic variation throughout the data recording. The intensities for which $I > 3\sigma(I)$ were corrected for Lorentz and polarization factors but not for absorption.

*Solution and Refinement of Structures.*—The structures

TABLE 1

Crystallographic data for compounds (1) and (2)

| | (1) | (2) |
|---|---|---|
| Formula | $C_{12}H_{26}CoN_4O_4P$ | $C_{27}H_{50}CoN_4O_4P$ |
| $M$ | 380.3 | 584.7 |
| $a$ (Å) | 15.830(8) | 18.50 (1) |
| $b$ (Å) | 12.279(7) | 16.83(1) |
| $c$ (Å) | 12.257(7) | 9.943(8) |
| α (°) | 94.85(7) | |
| β (°) | 84.49(8) | |
| γ (°) | 130.07(9) | |
| $U$(Å$^3$) | 1 814.1 | 3 095.8 |
| $D_m$ (g cm$^{-3}$) | 1.40 | 1.27 |
| $D_c$ (g cm$^{-3}$) | 1.39 | 1.25 |
| $Z$ | 4 | 4 |
| Space group | $P\bar{1}$ | $P2_12_12_1$ |
| μ (cm$^{-1}$) | 10.9 | 6.7 |
| λ(Å) | 0.7109 | 0.7109 |
| $F$(000) | 800 | 1 256 |
| Crystal size (cm) | 0.05 × 0.06 × 0.05 | 0.05 × 0.03 × 0.06 |
| No. of measured reflections | 7 739 | 4 224 |
| No. of independent reflections | 4 812 | 2 710 |
| $2\theta_{max.}$ (°) (Mo-$K_\alpha$) | 56 | 56 |
| $R$ | 0.037 | 0.038 |

were solved by conventional Patterson and Fourier methods and refined by block-diagonal anisotropic least-squares methods to a final $R$ value of 0.037(1) and 0.038(2) respectively.

The contribution from hydrogen atoms was held constant ($B$ = 5 Å$^2$) in both structures. In the final refinements, the weighting scheme was $w = 1/(A + |F_o| + B|F_o|^2)$, where $A$ = 3.9(1) and 8.0(2) and $B$ = 0.006 were chosen so as to maintain $w(|F_o| - |F_o|)^2$ essentially constant over all ranges of $|F_o|$ and (sin θ)/λ. Atomic scattering factors were those given in ref. 18. All the calculations were done using a standard set of computer programs.[19]

Final positional parameters are collected in Tables 2 and 3. Anisotropic thermal parameters as well as final calculated and observed structure factors are listed in Supplementary Publication No. SUP 23151 (27 pp.).*

## RESULTS

*Descriptions of the Structures*.—The numbering schemes for compounds (1) and (2) are shown in Figures 1 and 2

TABLE 2

Positional parameters (× $10^4$) for the atoms of compounds (1) and (2) with estimated standard deviations in parentheses. Hydrogen-atom co-ordinates are multiplied by $10^3$

(*a*) Compound (1)

| | Molecule A | | | | Molecule B | | |
|---|---|---|---|---|---|---|---|
| Atom | $x$ | $y$ | $z$ | Atom | $x$ | $y$ | $z$ |
| Co | 184(0) | 2 390(0) | 2 649(0) | Co | 3 973(0) | 6 815(0) | 7 595(0) |
| P | 1 776(1) | 4 717(1) | 2 685(1) | P | 5 869(1) | 8 435(1) | 7 549(1) |
| O(1) | 1 314(2) | 1 653(2) | 1 270(3) | O(1) | 4 010(2) | 5 556(3) | 5 546(2) |
| O(2) | −1 033(2) | 3 189(3) | 2 029(3) | O(2) | 3 841(2) | 5 991(3) | 9 753(2) |
| O(3) | −956(2) | 3 107(3) | 4 017(3) | O(3) | 3 816(2) | 7 976(3) | 9 645(3) |
| O(4) | 1 376(2) | 1 551(2) | 3 264(3) | O(4) | 4 051(2) | 7 596(3) | 5 443(3) |
| N(1) | 680(2) | 2 041(3) | 1 316(3) | N(1) | 3 983(2) | 5 531(3) | 6 650(3) |
| N(2) | −451(2) | 2 757(3) | 1 678(3) | N(2) | 3 892(2) | 5 728(3) | 8 659(3) |
| N(3) | −356(2) | 2 674(3) | 3 974(3) | N(3) | 3 854(2) | 8 008(3) | 8 533(3) |
| N(4) | 769(2) | 1 946(3) | 3 621(3) | N(4) | 3 970(2) | 7 837(3) | 6 535(3) |
| C(1) | 686(4) | 1 906(5) | −711(4) | C(1) | 3 969(3) | 3 505(4) | 6 486(5) |
| C(2) | 377(3) | 2 175(4) | 409(4) | C(2) | 3 949(3) | 4 583(3) | 7 117(4) |
| C(3) | −292(3) | 2 606(4) | 635(3) | C(3) | 3 886(3) | 4 700(4) | 8 315(4) |
| C(4) | −720(4) | 2 881(5) | −255(5) | C(4) | 3 800(3) | 3 704(4) | 9 040(5) |
| C(5) | −446(4) | 2 690(6) | 6 010(5) | C(5) | 3 731(3) | 9 915(4) | 8 711(5) |
| C(6) | −96(3) | 2 473(4) | 4 882(4) | C(6) | 3 811(3) | 8 893(3) | 8 080(4) |
| C(7) | 583(3) | 2 063(4) | 4 672(4) | C(7) | 3 866(3) | 8 775(4) | 6 883(4) |
| C(8) | 1 041(4) | 1 813(5) | 5 540(5) | C(8) | 3 809(3) | 9 622(4) | 6 130(5) |
| C(9) | −1 203(3) | 339(4) | 2 626(4) | C(9) | 2 306(3) | 5 404(4) | 7 595(4) |
| C(10) | 1 902(4) | 5 790(4) | 1 645(5) | C(10) | 6 541(3) | 8 466(5) | 6 244(4) |
| C(11) | 3 041(3) | 4 972(5) | 2 477(6) | C(11) | 6 464(3) | 10 288(4) | 7 775(5) |
| C(12) | 1 964(4) | 5 695(5) | 3 957(5) | C(12) | 6 509(3) | 8 201(4) | 8 553(4) |
| H(1) | 130 | 155 | 230 | H(1) | 410 | 680 | 530 |
| H(2) | −110 | 315 | 300 | H(2) | 370 | 680 | 1 000 |
| H(1)C(1) | 112 | 158 | −66 | H(1)C(1) | 400 | 364 | 566 |
| H(2)C(1) | 111 | 276 | −116 | H(2)C(1) | 325 | 251 | 664 |
| H(3)C(1) | −2 | 110 | −111 | H(3)C(1) | 460 | 358 | 664 |
| H(1)C(4) | −114 | 320 | 9 | H(1)C(4) | 380 | 403 | 985 |
| H(2)C(4) | −119 | 204 | −72 | H(2)C(4) | 451 | 383 | 893 |
| H(3)C(4) | −6 | 370 | −70 | H(3)C(4) | 316 | 274 | 893 |
| H(1)C(5) | −91 | 296 | 596 | H(1)C(5) | 372 | 978 | 954 |
| H(2)C(5) | 23 | 347 | 642 | H(2)C(5) | 306 | 976 | 857 |
| H(3)C(5) | −88 | 179 | 643 | H(3)C(5) | 441 | 1 093 | 856 |
| H(1)C(8) | 153 | 158 | 519 | H(1)C(8) | 384 | 933 | 533 |
| H(2)C(8) | 48 | 107 | 603 | H(2)C(8) | 440 | 1 065 | 622 |
| H(3)C(8) | 158 | 275 | 599 | H(3)C(8) | 306 | 939 | 625 |
| H(1)C(9) | −171 | 14 | 328 | H(1)C(9) | 197 | 576 | 805 |
| H(2)C(9) | −102 | −30 | 261 | H(2)C(9) | 200 | 445 | 786 |
| H(3)C(9) | −161 | 12 | 194 | H(3)C(9) | 206 | 524 | 681 |
| H(1)C(10) | 263 | 680 | 173 | H(1)C(10) | 737 | 920 | 630 |
| H(2)C(10) | 128 | 582 | 176 | H(2)C(10) | 632 | 871 | 565 |
| H(3)C(10) | 190 | 541 | 91 | H(3)C(10) | 634 | 751 | 608 |
| H(1)C(11) | 371 | 603 | 253 | H(1)C(11) | 728 | 1 092 | 776 |

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

TABLE 2 (*continued*)

(*a*) Compound (1) (*continued*)

| | Molecule A | | |
|---|---|---|---|
| Atom | *x* | *y* | *z* |
| H(2)C(11) | 309 | 457 | 177 |
| H(3)C(11) | 310 | 451 | 309 |
| H(1)C(12) | 270 | 671 | 392 |
| H(2)C(12) | 201 | 524 | 459 |
| H(3)C(12) | 136 | 573 | 414 |

| | Molecule B | | |
|---|---|---|---|
| Atom | *x* | *y* | *z* |
| H(2)C(11) | 619 | 1 040 | 854 |
| H(3)C(11) | 622 | 1 057 | 722 |
| H(1)C(12) | 732 | 892 | 848 |
| H(2)C(12) | 628 | 721 | 843 |
| H(3)C(12) | 623 | 825 | 931 |

(*b*) Compound (2)

| Atom | *x* | *y* | *z* | *B*/Å$^2$ |
|---|---|---|---|---|
| Co | 2 444(0) | 2 448(0) | 1 640(1) | |
| P | 3 767(1) | 2 291(1) | 1 573(1) | |
| O(1) | 2 186(2) | 897(2) | 2 686(4) | |
| O(2) | 2 328(2) | 2 953(2) | −1 118(3) | |
| O(3) | 2 505(2) | 4 025(2) | 591(4) | |
| O(4) | 2 236(2) | 1 980(2) | 4 393(4) | |
| N(1) | 2 259(2) | 1 347(2) | 1 575(4) | |
| N(2) | 2 349(2) | 2 332(2) | −248(3) | |
| N(3) | 2 509(2) | 3 567(2) | 1 708(4) | |
| N(4) | 2 395(2) | 2 584(2) | 3 528(3) | |
| C(1) | 1 967(4) | 180(3) | 186(7) | |
| C(2) | 2 167(3) | 1 036(3) | 391(5) | |
| C(3) | 2 216(3) | 1 621(3) | −691(5) | |
| C(4) | 2 077(4) | 1 443(5) | −2 151(6) | |
| C(5) | 2 543(5) | 4 776(3) | 3 082(7) | |
| C(6) | 2 509(4) | 3 887(3) | 2 878(5) | |
| C(7) | 2 429(3) | 3 309(3) | 3 970(5) | |
| C(8) | 2 363(5) | 3 511(4) | 5 442(6) | |
| C(9) | 1 362(3) | 2 587(4) | 1 666(6) | |
| C(10) | 4 190(2) | 2 301(2) | 3 274(5) | |
| C(11) | 3 949(3) | 1 616(3) | 4 206(5) | |
| C(12) | 4 150(3) | 1 803(3) | 5 692(5) | |
| C(13) | 4 947(4) | 1 946(4) | 5 847(6) | |
| C(14) | 5 226(3) | 2 575(4) | 4 845(7) | |
| C(15) | 5 018(3) | 2 392(3) | 3 386(6) | |
| C(16) | 4 286(3) | 3 092(2) | 711(5) | |
| C(17) | 4 258(3) | 3 906(3) | 1 411(6) | |
| C(18) | 4 774(3) | 4 487(3) | 746(8) | |
| C(19) | 4 610(4) | 4 587(3) | −748(7) | |
| C(20) | 4 588(4) | 3 781(3) | −1 491(7) | |
| C(21) | 4 073(3) | 3 201(3) | −781(5) | |
| C(22) | 4 073(3) | 1 386(2) | 617(5) | |
| C(23) | 3 925(3) | 589(3) | 1 316(5) | |
| C(24) | 4 018(4) | −97(3) | 329(6) | |
| C(25) | 4 792(4) | −115(3) | −191(7) | |
| C(26) | 4 981(4) | 684(4) | −858(7) | |
| C(27) | 4 853(3) | 1 377(3) | 123(7) | |
| H(1) | 208(5) | 132(5) | 339(9) | 7(2) |
| H(2) | 243(4) | 356(5) | −3(8) | 5(2) |
| H(1)C(1) | 197 | −11 | 107 | |
| H(2)C(1) | 232 | −9 | −43 | |
| H(3)C(1) | 147 | 14 | −22 | |
| H(1)C(4) | 215 | 195 | −280 | |
| H(2)C(4) | 157 | 126 | −239 | |
| H(3)C(4) | 242 | 104 | −259 | |
| H(1)C(5) | 258 | 505 | 200 | |
| H(2)C(5) | 295 | 496 | 348 | |
| H(3)C(5) | 207 | 500 | 335 | |
| H(1)C(8) | 232 | 301 | 597 | |
| H(2)C(8) | 192 | 385 | 558 | |
| H(3)C(8) | 280 | 381 | 572 | |
| H(1)C(9) | 123 | 316 | 190 | |
| H(2)C(9) | 119 | 231 | 269 | |
| H(3)C(9) | 110 | 234 | 106 | |
| HC(10) | 401 | 279 | 363 | |
| H(1)C(11) | 342 | 153 | 406 | |
| H(2)C(11) | 421 | 111 | 389 | |
| H(1)C(12) | 386 | 229 | 603 | |
| H(2)C(12) | 399 | 134 | 632 | |
| H(1)C(13) | 505 | 213 | 682 | |
| H(2)C(13) | 521 | 144 | 572 | |
| H(1)C(14) | 500 | 310 | 511 | |
| H(2)C(14) | 576 | 262 | 497 | |
| H(1)C(15) | 519 | 283 | 262 | |

(*b*) Compound (2) (*continued*)

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| H(2)C(15) | 527 | 188 | 292 |
| HC(16) | 480 | 292 | 77 |
| H(1)C(17) | 375 | 412 | 140 |
| H(2)C(17) | 439 | 384 | 243 |
| H(1)C(18) | 476 | 502 | 123 |
| H(2)C(18) | 529 | 427 | 87 |
| H(1)C(19) | 412 | 486 | −85 |
| H(2)C(19) | 499 | 495 | −118 |
| H(1)C(20) | 434 | 385 | −262 |
| H(2)C(20) | 506 | 352 | −186 |
| H(1)C(21) | 357 | 342 | −85 |
| H(2)C(21) | 408 | 266 | −124 |
| HC(22) | 376 | 137 | −22 |
| H(1)C(23) | 428 | 50 | 209 |
| H(2)C(23) | 342 | 58 | 173 |
| H(1)C(24) | 386 | −62 | 68 |
| H(2)C(24) | 369 | 1 | −52 |
| H(1)C(25) | 512 | −15 | 68 |
| H(2)C(25) | 491 | −58 | −74 |
| H(1)C(26) | 545 | 70 | −130 |
| H(2)C(26) | 459 | 76 | −166 |
| H(1)C(27) | 520 | 130 | 91 |
| H(2)C(27) | 499 | 191 | −31 |

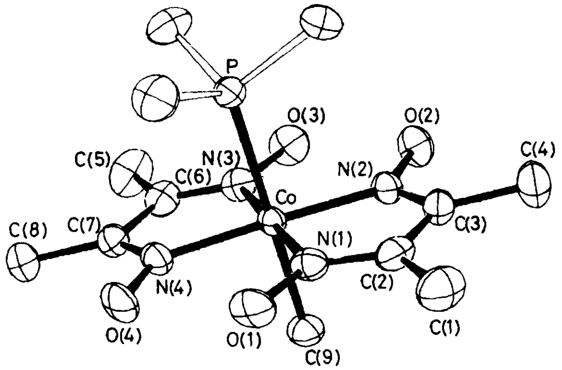

FIGURE 1 ORTEP drawing and numbering scheme for [CoMe(Hdmg)$_2$(PMe$_3$)] (1)

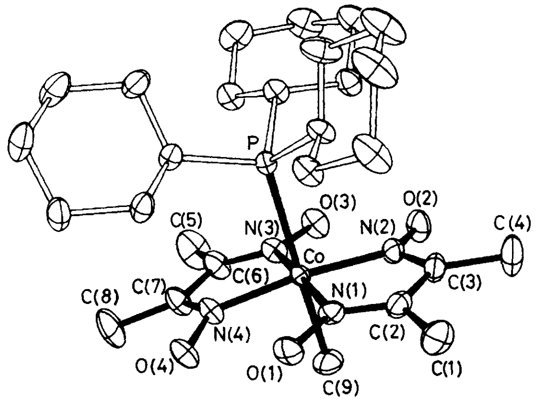

FIGURE 2 ORTEP drawing and numbering scheme for [CoMe(Hdmg)$_2${P(C$_6$H$_{11}$)$_3$}] (2)

respectively, and relevant bond lengths and angles are reported in Table 3.

TABLE 3

Bond lengths (Å) and relevant bond angles (°)

| | (1) | | |
|---|---|---|---|
| | Molecule A | Molecule B | (2) |
| Co–P | 2.291(1) | 2.295(1) | 2.463(1) |
| Co–C(9) | 2.011(3) | 2.019(3) | 2.016(5) |
| Co–N(1) | 1.882(4) | 1.884(4) | 1.885(3) |
| Co–N(2) | 1.879(4) | 1.882(4) | 1.895(4) |
| Co–N(3) | 1.874(4) | 1.879(4) | 1.889(3) |
| Co–N(4) | 1.883(4) | 1.883(4) | 1.894(3) |
| N(1)–O(1) | 1.355(6) | 1.352(4) | 1.345(5) |
| N(1)–C(2) | 1.315(6) | 1.309(7) | 1.300(7) |
| N(2)–O(2) | 1.353(6) | 1.360(5) | 1.358(5) |
| N(2)–C(3) | 1.300(6) | 1.290(6) | 1.299(7) |
| N(3)–O(3) | 1.352(6) | 1.361(5) | 1.352(5) |
| N(3)–C(6) | 1.316(7) | 1.305(7) | 1.282(6) |
| N(4)–O(4) | 1.354(5) | 1.358(5) | 1.364(5) |
| N(4)–C(7) | 1.311(6) | 1.297(7) | 1.298(6) |
| C(1)–C(2) | 1.495(7) | 1.492(8) | 1.501(8) |
| C(2)–C(3) | 1.455(8) | 1.463(6) | 1.460(7) |
| C(3)–C(4) | 1.505(9) | 1.500(8) | 1.505(8) |
| C(5)–C(6) | 1.506(8) | 1.486(8) | 1.511(7) |
| C(6)–C(7) | 1.449(8) | 1.462(7) | 1.465(7) |
| C(7)–C(8) | 1.497(9) | 1.497(8) | 1.507(8) |
| P–C (mean) | 1.812(6) | 1.820(6) | 1.870(5) |
| C–C (cyclohexyl) (mean) | | | 1.536(9) |
| N(1)–Co–N(2) | 81.2(2) | 81.3(2) | 81.3(2) |
| N(1)–Co–N(3) | 178.1(1) | 176.0(1) | 173.2(2) |
| N(1)–Co–N(4) | 98.8(2) | 98.8(2) | 98.3(2) |
| N(1)–Co–P | 90.8(1) | 91.9(1) | 94.2(1) |
| N(1)–Co–C(9) | 89.1(2) | 87.7(2) | 86.3(2) |
| N(2)–Co–N(3) | 98.7(2) | 98.8(2) | 98.3(2) |
| N(2)–Co–N(4) | 177.7(1) | 176.9(1) | 171.9(2) |
| N(2)–Co–P | 92.5(1) | 92.9(1) | 93.1(1) |
| N(2)–Co–C(9) | 88.3(2) | 88.5(2) | 86.1(2) |
| N(3)–Co–N(4) | 81.3(2) | 80.9(2) | 81.2(2) |
| N(3)–Co–P | 91.1(1) | 92.1(1) | 92.5(1) |
| N(3)–Co–C(9) | 89.0(2) | 88.3(2) | 87.0(2) |
| N(4)–Co–P | 89.8(1) | 90.2(1) | 95.0(1) |
| N(4)–Co–C(9) | 89.5(2) | 88.5(2) | 85.8(2) |
| P–Co–C(9) | 179.2(2) | 178.5(2) | 179.1(2) |
| Co–P–C (mean) | 114.7(2) | 115.0(2) | 114.4(1) |
| C–P–C (mean) | 103.8(3) | 103.4(3) | 104.2(2) |

The two crystallographically independent molecules of (1), A and B, have the four nitrogen atoms of the $(Hdmg)_2$ unit coplanar within ±0.003 and ±0.008 Å respectively. The cobalt atom is displaced by 0.035 and 0.058 Å respectively above these mean planes towards the phosphine ligand. The two Hdmg units are slightly bent towards the axial methyl group making an interplanar angle of 2 and 6° respectively. A side view of the molecule is shown in Figure 3. Bond lengths and angles of the $Co(Hdmg)_2$ moiety are quite normal.[6-8] The $H_3C$–Co–$PMe_3$ fragments of the two crystallographically independent molecules are characterized by C–Co–P angles of 179.2(2) and 178.5(2)°, Co–P bond lengths of 2.291(1) and 2.295(1) Å, and Co–C bond lengths of 2.011(3) and 2.019(3) Å respectively. In compound (2) the four *N*-donors are coplanar within ±0.011 Å. The cobalt atom is displaced by 0.123 Å above this mean plane towards $P(C_6H_{11})_3$. The two Hdmg units make an interplanar angle of 12°, bending far away from the phosphine ligand. A side view is shown in Figure 3. Bond lengths and angles in the $Co(Hdmg)_2$ moiety are quite normal.[6-8]

The $H_3C$–Co–$P(C_6H_{11})_3$ fragment is characterized by a C–Co–P angle of 179.1(2)° and Co–P and Co–C bond lengths of 2.463(1) and 2.016(5) Å respectively. This Co–P bond length is the longest so far reported for $Co^{III}$ and can be compared to the value of 2.369(5) Å found in the analogous chloro-derivative.[6] The geometry of the $H_3C$–Co–P fragment in $[CoMe(Hdmg)_2(PR_3)]$ compounds is compared in Table 4.

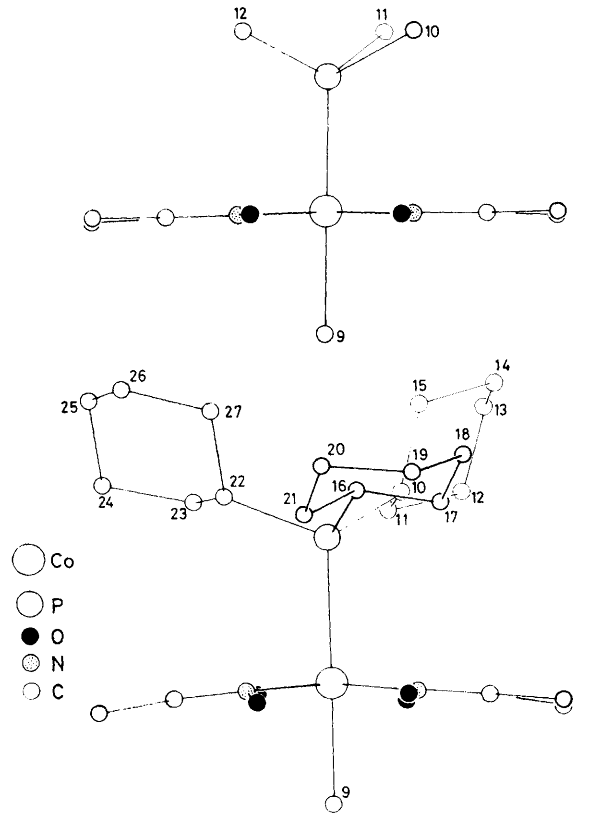

FIGURE 3 Side views with a numbering scheme of the phosphine carbon atoms for (1) (above) and for (2) (below)

*Kinetics*.—As described previously, ligand-exchange reactions of cobaloximes in non-co-ordinating solvents such as $CH_2Cl_2$ proceed by an $S_N1$ limiting mechanism.[9, 10] Mass-law rate retardation allows the evaluation of the competition between the leaving ligand and an incoming ligand for the supposed five-co-ordinate species. In general, regardless of the nucleophilicity of the incoming and leaving ligands, the competition ratio was found to be *ca.* 1 : 1.[9] Only in the cases of bulky phosphines with long alkyl chains was a ratio of more than 1 : 1 observed. This

TABLE 4

Geometry of the $H_3C$–Co–P fragment in $[CoMe(Hdmg)_2(PR_3)]$ complexes. *d* (Å) is the displacement of Co above the equatorial co-ordination plane towards the phosphine ligand and α(°) is the bending angle between the two Hdmg units

| R | Co–P(Å) | Co–C(Å) | P–Co–C (°) | *d* (Å) | α (°) |
|---|---|---|---|---|---|
| OMe [a] | 2.256(4) | 2.014(14) | 177.2(5) | 0.10 | 10 |
| Me [b] | 2.293(1) | 2.015(3) | 178.9(2) | 0.05 | 4 |
| $Bu^n$ [c] | 2.342(1) | 1.983(1) [e] | 179.2(2) | 0.03 | 5 |
| Ph [d] | 2.418(1) | 2.026(6) | 175.4(2) | 0.11 | 14 |
| $C_6H_{11}$ [b] | 2.463(1) | 2.016(5) | 179.1(2) | 0.12 | 12 |

[a] G. Stucky and J. S. Swanson, personal communication. [b] This work. [c] W. W. Adams and P. G. Lenhert, *Acta Crystallogr., Sect. B*, 1973, **29**, 2412. [d] Ref. 6. [e] This value refers to a Co–C ($sp^2$) bond in $[Co(C_5H_4N)(Hdmg)_2(PBu^n{}_3)]$.

was found for $PBu^n_3$ and $P(C_8H_{17})_3$. Since $P(C_6H_{11})_3$ is the *P*-donor ligand with the largest cone angle we could co-ordinate to these complexes, we determined the competition ratio for this ligand against a standard ligand (py) which is known to compete equally with other small ligands, including $PMe_3$.[9] The results are presented in Table 5 and Figure 4.

TABLE 5

Competition data [a]

| $[P(C_6H_{11})_3]/[py]$ | $k_{obs.}$ ($s^{-1}$) [b] | $1/k_{obs.}$ (s) [c] |
|---|---|---|
| 0.0 | 0.25 | 4.0 |
| 0.7 | 0.23 | 4.4 |
| 1.4 | 0.22 | 4.6 |
| 1.8 | 0.22 | 4.6 |
| 2.1 | 0.20 | 5.0 |
| 2.1 | 0.19 | 5.3 |
| 2.4 | 0.19 | 5.3 |
| 2.7 | 0.17 | 5.8 |
| 2.9 | 0.17 | 5.8 |
| 3.2 | 0.17 | 5.8 |
| 3.3 | 0.19 | 5.3 |
| 3.6 | 0.16 | 6.2 |
| 4.7 | 0.13 | 7.5 |
| 4.9 | 0.15 | 6.6 |

[a] $[CoMe(Hdmg)_2\{P(C_6H_{11})_3\}] = 0.01$ mol $dm^{-3}$; $[py] = 0.1$ mol $dm^{-3}$. $k_1 = 0.26 \pm 0.03$ $s^{-1}$; $k_2/k_{-1} = 6.0 \pm 1.5$; correlation coefficient for data = 0.94. [b] Error range for $k_{obs.} = \pm 0.01$. [c] Error range for $1/k_{obs.} = \pm 0.1$.

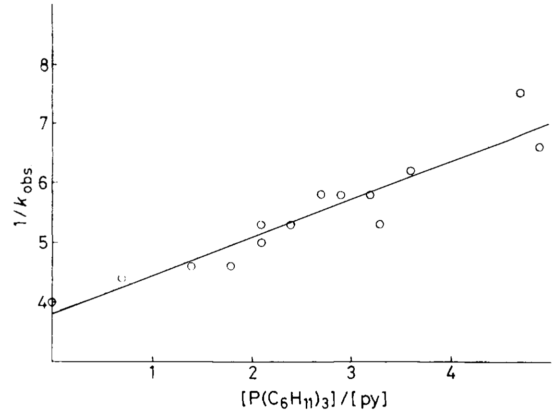

FIGURE 4 Plot of $1/k_{obs.}$ (s) against $[P(C_6H_{11})_3]/[py]$ for the reaction: $[CoMe(Hdmg)_2\{P(C_6H_{11})_3\}] \xrightarrow{py} [CoMe(Hdmg)_2(py)] + P(C_6H_{11})_3$

DISCUSSION

It has already been shown [7] that for the series $[CoX(Hdmg)_2(PR_3)]$ (X = Cl or Me; R = OMe, $Bu^n$, Ph, or $C_6H_{11}$) the Co–P bond lengths increase with increasing bulkiness of the phosphines rather than their basicity. The present Co–P distances agree with this finding. In addition, if Co–P bond lengths in $[CoMe(Hdmg)_2(PR_3)]$ are plotted against those in $[CoCl(Hdmg)_2(PR_3)]$,[21] a linear relationship is obtained (Figure 5). This relationship corresponds to that found in the $[CoX(Hdmg)_2(PR_3)]$ (X = Cl or Me) series for the difference Δ, of $^{31}P$ chemical shifts between the co-ordinated and the free phosphines, although in the bond-length correlation the $P(C_6H_{11})_3$ derivatives do not show any exception as was found in the values of Δ.[20] No correlation however is observed between Co–P bond lengths and $^{31}P$ chemical shifts.[21]

On the contrary, a good correlation is found with $^1H$ chemical shifts of the $CH_3$ group of co-ordinated methanol in the series $CH_3(H)O–Co(Hdmg)_2(PR_3)$.[22]

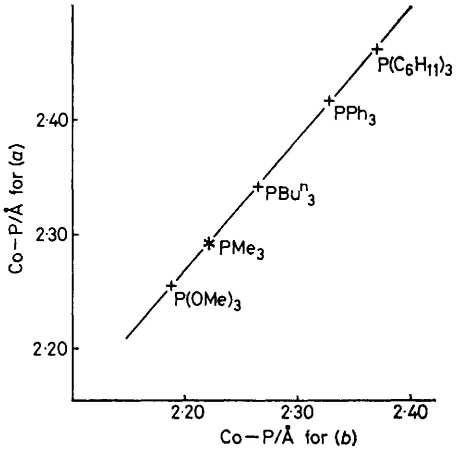

FIGURE 5 Correlation between Co–P bond length in $[CoMe(Hdmg)_2(PR_3)]$ (*a*) and $[CoCl(Hdmg)_2(PR_3)]$ (*b*). Estimated standard deviations are approximately represented by the arms of the crosses. The asterisk indicates the expected position for the $PMe_3$ derivative

The linear correlation in Figure 5 can be represented by the equation $Co–P_{Me} = 1.15.Co–P_{Cl} - 0.25$ with a correlation coefficient $r = 0.9998$. This value of $r$ leads us confidently to expect (Figure 3) a value close to 2.22 Å for the Co–P distance in the $[CoCl(Hdmg)_2(PMe_3)]$ derivative, which has not been structurally characterized.

The slope of 1.15, which corresponds to an angle of 4° between this line and that of $y = x + a$, indicates that the lengthening due to the greater *trans*-influencing power of $CH_3$ is little influenced by the bulk of the phosphorus ligand. In fact if the two effects were completely uncorrelated a slope of unity would be expected. On the contrary, values $>1$ indicate that the *trans* influence of the $CH_3$ group increases with the increasing bulkiness of the phosphine; values $<1$ would indicate an opposite trend. It is of interest that the point for the phosphite ligand, $P(OCH_3)_3$, falls on the line established by phosphine complexes (see below).

Finally, the Co–C bond lengths, which range from 2.011(3) to 2.026(6) Å, do not vary significantly (Table 4) suggesting that binding to the methyl group is relatively insensitive to the nature of the *P*-donor ligands used here. As the bulk of the phosphorus ligands increases the steric interaction between the phosphine and the $(Hdmg)_2$ equatorial ligand appears to provoke a ' regular ' lengthening of the Co–P distance as well as an increase in the displacement of the cobalt out of the co-ordination plane. This effect, observed also for Co–C bond lengths in the compounds $[Co(CHMe_2)(Hdmg)_2(py)]$ [2.085(3) Å] and $[CoMe(Hdmg)_2(py)]$[23] [1.966(6) Å], may be called the ' steric *cis* influence ', which in the present case merely adds to the usual *trans* influence or 'electronic *trans* influence'. In cobaloximes, the '*cis* steric influence' may provoke, in addition to bond lengthening, significant variations of the geometry of the group interacting with the $(Hdmg)_2$ ligands as found in $[Co(CH_2XMe_3)(Hdmg)_2(py)]$ compounds (X = C or Si).[24] Since the two Hdmg halves may be bent out of coplanarity by this interaction with a very bulky phosphine (Table 4), these in turn may sterically interact with the other (*trans*) axial ligand. If this group is itself bulky, its bonding to the metal may be weakened. Such a steric effect, on a *trans* ligand through the equatorial one, may be called 'steric *trans* influence'. This appears to happen in the $[Co(CHMe_2)(Hdmg)_2(PPh_3)]$ complex where the Co–C bond lengthens to 2.22(2) Å.[8] Geometry modifications associated with these effects are sketched in Figure 6.

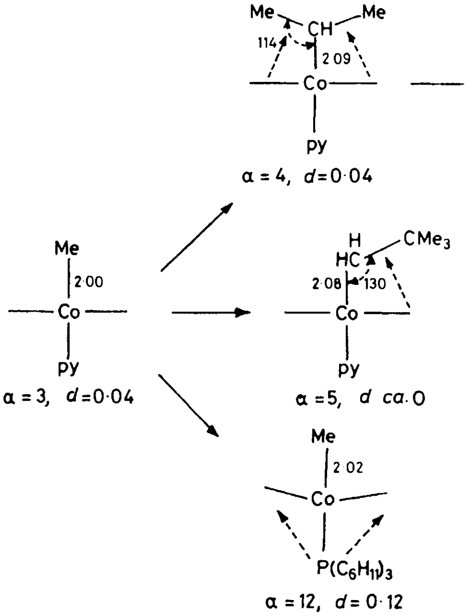

FIGURE 6 A sketch of the geometrical deformations arising from steric interactions between equatorial and axial ligands (*d* in Å, angles in degrees)

The conversion of $[CoMe(Hdmg)_2\{P(C_6H_{11})_3\}]$ into $[CoMe(Hdmg)_2(py)]$ is accompanied by conversion of a non-planar system into a more planar system. The distortion induced by the $P(C_6H_{11})_3$ ligand might be sufficient to slow down considerably the rate of reaction of the reputed five-co-ordinate species with $P(C_6H_{11})_3$ leading to a large rate ratio. However, the value obtained in this study is only approximately six and it appears that the requisite distortion needed to proceed to the ground-state species is either not energetically large or does not take place until after the transition state between the five-co-ordinate intermediate and the six-co-ordinate product. The value of six can be entirely attributed to the bulk of the cyclohexyl ring blocking the lone pair of the phosphorus ligand. The value for $PBu^n_3$, for example, is five.

From the data obtained in this study, we conclude that there is no indication of a significant contribution of steric effects to the rate of the five- to six-co-ordinate step in the ligand-exchange reaction. However, the relatively high rate of displacement of the $P(C_6H_{11})_3$ ligand compared to phosphines of small cone angle (such as $PBu^n_3$ and $PMe_3$, which are not readily displaced by any other ligand) almost certainly arises from the steric interaction of the $C_6H_{11}$ rings with the equatorial $Co(Hdmg)_2$ group.

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