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# Structures of the Intermediate Complex, $\{CpCo(dppe)[P(OMe)_3]\}^{2+}$, and Final Product, $\{CpCo(dppe)[P(O)(OMe)_2]\}^+$, from an Arbuzov Transformation. A Comment on the Lewis Basicity of the Phosphoryl Oxygen Atom

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## Abstract

The intermediate phosphite complex, $\{CpCo(dppe)[P(OMe)_3]\}^{2+}$, and the final product of dealkylation by the Arbuzov reaction, $\{CpCo(dppe)[P(O)(OMe)_2]\}^+$, have been characterized by X-ray crystallography. Crystal data for $\{CpCo(dppe)[P(OMe)_3]\}(PF_6)_2\cdot Me_2CO$: monoclinic, $P2_1/c$, $a = 13.007(2)$, $b = 15.906(6)$, $c = 21.937(4)$ Å, $\beta = 105.59°$, $V = 4371.4(18)$ Å$^3$, $Z = 4$, $R_F = 0.055$. $\{CpCo(dppe)[P(O)(OMe)_2]\}HgI_3$: triclinic, $P\bar{1}$, $a = 10.820(3)$, $b = 14.152(3)$, $c = 14.537(4)$ Å, $\alpha = 114.48(2)$, $\beta = 104.65(2)$, $\gamma = 71.91(2)°$, $V = 1905.7(9)$, $Z = 2$, $R_F = 0.047$. Unlike other complexes of this type, the phosphoryl group does not coordinate Lewis acids [$HgX_2$ (X = Cl, Br, I), $ZnX_2$ (X = Cl, Br), and $AlCl_3$ were tested], probably because of steric hindrance by the phenyl rings of dppe. The P=O group also could not be protonated, perhaps because of the unit positive charge on the reactant complex.

## Introduction

Phosphorus-bound alkyl phosphonate metal complexes, $M-P(O)(OR)_2$, can be prepared by adding $HP(O)(OCH_3)_2$ to various metal complexes [1–3], or, in certain instances, by a Michaelis–Arbuzov-like rearrangement represented in general by reaction (1) [4]:

$$L_nM-X + P(OR)_3 \longrightarrow L_nM-P(O)(OR)_2 + RX \qquad (1)$$

The mechanism of reaction (1) has been extensively investigated where $L_nM-X = [CpCo(dppe)I]^+$ ≠ [5–7]. The reaction follows an ionic pathway described by reactions (2) and (3):

$$[CpCo(dppe)I]^+ + P(OMe)_3 \rightleftharpoons \underset{\mathbf{1}}{\{CpCo(dppe)[P(OMe)_3]\}^{2+}} + I^- \qquad (2)$$

$$\{CpCo(dppe)[P(OMe)_3]\}^{2+} + I^- \longrightarrow \underset{\mathbf{2}}{\{CpCo(dppe)[P(O)(OMe)_2]\}^+} + CH_3I \qquad (3)$$

The intermediate phosphite complex, **1**, can be isolated in the absence of strong nucleophiles [6].

Two aspects of reactions (2) and (3) are addressed in this paper. First, the structural details of an intermediate phosphite complex have never been compared to the product phosphonate complex resulting from the Arbuzov rearrangement. This void has been filled by determining the structures of $\{CpCo(dppe)[P(OMe)_3]\}(PF_6)_2\cdot Me_2CO$, **1**, and $\{CpCo(dppe)[P(O)(OMe)_2]\}HgI_3$, **2**. Second, the phosphoryl oxygen atom of related phosphonate complexes has been demonstrated to coordinate metal ions, $H^+$, and $H_2O$ [8–20]. With an occasional exception [19, 20], two or three phosphonate ligands become involved so that the complex acts as a chelating ligand. Unsuccessful attempts to coordinate the single phosphoryl oxygen atom of $\{CoCo(dppc)[P(O)(OMe)_2]\}^+$ to $H^+$ and Lewis acids, such as $HgX_2$ (X = Cl, Br, I), $ZnX_2$ (X = Cl, Br) and $AlCl_3$, are described in this paper.

## Experimental

### *Synthesis and Reactions*

Yellow, crystalline $\{CpCo(dppe)[P(OMe)_3]\}(PF_6)_2\cdot Me_2CO$, **1**, was prepared by procedures discussed elsewhere [6]. Crystals were grown by allowing an acetone–ether solution to remain at 0 °C for several days. $\{CpCo(dppe)[P(O)(OMe)_2]\}HgI_3$, **2**, was obtained by refluxing equimolar amounts of $\{CpCo(dppe)[P(O)(OMe)_2]\}I$ [5] and $HgI_2$ in MeOH for four hours. The residue remaining after solvent removal was dissolved in $CH_2Cl_2$. Slow evaporation

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≠Abbreviations used: Cp = $\eta^5$-$C_5H_5$, dppe = bis(diphenylphosphino)ethane, Me = $CH_3$.

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TABLE I. Crystal Parameters, Data Collection and Refinement Procedures and Results for 1 and 2

| | {CpCo(dppe)[P(OMe)$_3$]}-(PF$_6$)$_2$·Me$_2$CO (1) | {CpCo(dppe)[P(O)(OMe)$_2$]}-HgI$_3$ (2) |
|---|---|---|
| formula | $C_{37}H_{44}CoF_{12}O_4P_5$ | $C_{33}H_{35}CoHgI_3O_3P_3$ |
| crystal system | $P2_1/c$, monoclinic | $P\bar{1}$, triclinic |
| $a$ (Å) | 13.007(2) | 10.820(3) |
| $b$ (Å) | 15.906(6) | 14.152(3) |
| $c$ (Å) | 21.937(4) | 14.537(4) |
| $\alpha$ (deg) | 90 | 114.48(2) |
| $\beta$ (deg) | 105.59(2) | 104.65(2) |
| $\gamma$ (deg) | 90 | 71.91(2) |
| $V$ (Å$^3$) | 4371.4(18) | 1905.7(9) |
| $Z$ | 4 | 2 |
| $D$ (calc.) (g cm$^{-3}$) | 1.422 | 2.113 |
| crystal size (mm) | 0.28 × 0.30 × 0.34 | 0.12 × 0.24 × 0.24 |
| $\mu$ (cm$^{-1}$) | 6.51 | 71.0 |
| temperature (°C) | 23 | 22 |
| diffractometer | Nicolet R3 | |
| radiation | Mo K$_\alpha$ ($\lambda$ = 0.71073 Å) | |
| monochromator | highly oriented graphite | |
| scan technique | $\theta/2\theta$ | $\omega$ |
| scan range, data | $4° \leqslant 2\theta \leqslant 44°$; $\pm h, +k, +l$ | $4° \leqslant 2\theta \leqslant 43°$; $\pm h, \pm h, +l$ |
| transmission (max/min) | 0.513/0.478 | 0.950/0.537 |
| scan speed (deg min$^{-1}$) | var. 4–20 | var. 4–20 |
| unique data | 5392 (5811 collected) | 3599 (4596 collected) |
| unique data, $F_o \geqslant n\sigma(F_o)$ | 3740 ($n$ = 3) | 3496 ($n$ = 3) |
| $R$, av. redund. data | 0.017 | 0.032 |
| std. reflns | 3 std/97 data (no decay) | 3std/197 data (no decay) |
| $R_F$,[a] $R_{wF}$,[b] GOF[c] | 0.0554, 0.0562, 1.417 | 0.0466, 0.0395, 1.418 |
| $g$[d] | 0.00080 | 0.0015 |
| no L.S. parameters | 532 | 195 |
| highest peak, final diff. map (e Å$^{-3}$) | 0.41 (1.5 Å from P(4)) | 0.91 (1.2 Å from Hg) |
| mean shift/esd max last cycle | 0.120 | 0.019 |

[a] $R_F = \Sigma|\Delta|/\Sigma|F_o|$; $\Delta = |F_o| - |F_c|$. [b] $R_{wF} = \Sigma(|\Delta|w^{1/2})/\Sigma(|F_o|w^{1/2})$. [c] $\mathrm{GOF} = [\Sigma w(\Delta^2)/(N_{obs} - N_{par})]^{1/2}$. [d] $w^{-1} = \sigma^2(F_o) + gF_o^2$.

yielded golden crystals, MP = 82–84 °C. The analogous $HgBr_2I^-$ salt (MP = 217–220 °C) and $HgCl_2I^-$ salt (MP ~ 75 °C) can be prepared in a like manner.

### *Crystal Structure Determination*

Crystals of both 1 and 2 were mounted on glass fibers. Preliminary photography showed $2/m$ and $\bar{1}$ Laue symmetry for 1 and 2, respectively. The unit-cell parameters provided in Table I were obtained from the least squares fit of the angular settings of 25 well-centered reflections, $22° \leqslant 2\theta \leqslant 30°$; Table I also provides details on the collection of data and refinement. Corrections for $Lp$ effects and absorption (empirical) were applied to the data along with a peak profile analysis to improve the accuracy in the measurement of weak reflections. Wilson plots were used to place the data on an approximately absolute scale. For 1, systematic absences in the reflection data uniquely defined the space group; for 2, the centrosymmetric alternative, $P\bar{1}$, was suggested by the statistical distribution of $E$-values and proved correct by the reasonable solution and well behaved refinement of the structure.

1 was solved by direct methods (SOLV) which provided locations for the Co and five P atoms. 2 resisted solution by direct methods and was solved by an automatic Patterson interpretation procedure which straightforwardly provided locations for the Hg, three I, Co and three P atoms. This procedure and all others used in the data reduction, solution, refinement, and graphics are parts of the SHELXTL library (4.1) written by G. Sheldrick and distributed by the Nicolet Corporation, Madison, Wis.

For both structures, blocked-cascade refinement with anisotropic temperature factors for all non-hydrogen atoms except for the Cp and phenyl rings in 2 which were refined isotropically, converged at the $R$ values given in Table I. Additionally, the Cp and phenyl rings for 2 were constrained to rigid-body geometries. For both cases the hydrogen atoms were incorporated as fixed, idealized and updated contributions: $d$(C–H) = 0.96 Å and $U$ = 1.2 $U$

attached C. The $PF_6^-$ anions in **1** were well behaved without octahedral constraint, but a molecule of acetone from the recrystallization solvent was somewhat disordered. The two C–C bonds of $(CH_3)_2CO$ refined to 1.45(2) and 1.33(2) Å, C–O = 1.20(1) Å. Large thermal parameters are also associated with the solvent molecule.

Atomic scattering factors are from Cromer and Waber [21a], and anomalous dispersion corrections are from Cromer [21b].

### *Crystal Structures*

The crystal structures of $\{CpCo(dppe)[P(OMe)_3]\}(PF_6)_2 \cdot Me_2CO$, **1**, and $\{CpCo(dppe)[P(O)(OMe)_2]\}HgI_3$, **2**, were determined. In addition, the structure of $\{CpCo(dppe)[P(OMe)_3]\}(BF_4)_2$ was solved, but excessive disorder of the $BF_4^-$ ions precluded a fully satisfactory refinement ($R = 0.11$)*.

The cation of $\{CpCo(dppe)[P(OMe)_3]\}(PF_6)_2 \cdot Me_2CO$ is shown in Fig. 1. Atomic coordinates, selected bond lengths and selected bond angles are given in Tables II and III, respectively. The Cp ring is regular and normal. The P–Co–P bond angles fall in the range of 86.7–97.3°, the most acute $CoP_2$ angle involving the puckered dppe chelate ring. These same features are present in the $BF_4^-$ salt of **1**. The $PF_6^-$ ions exhibit some disorder as is evident in the thermal parameters of the F atoms. The acetone molecule, likewise, is partially disordered.

The cation of $\{CpCo(dppe)[P(O)(OMe)_2]\}HgI_3$ is shown in Fig. 2, while Tables IV and III give the atomic coordinates and selected bond distances and angles, respectively. The angles in the $CoP_3$ portion of **2** more closely approximate the pseudooctahedral coordination of Co (87.5–91.6°) than in **1**. The most acute $CoP_2$ angle is again contained in the puckered

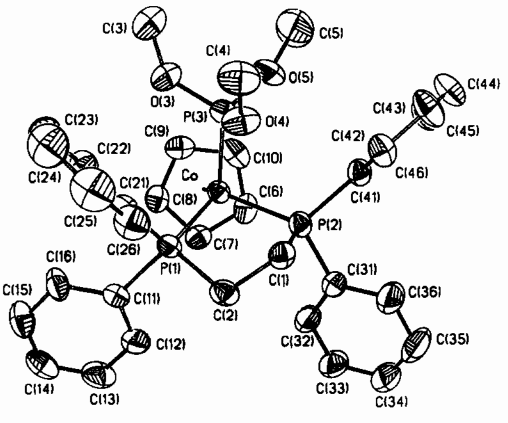

Fig. 1. The molecular structure of $\{CpCo(dppe)[P(OMe)_3]\}^{2+}$ crystallized as the $PF_6^-$ salt showing 40% probability thermal ellipsoids.

TABLE II. The Fraction Atomic Coordinates ($\times 10^4$) and Temperature Factors ($Å^2 \times 10^3$) for $\{CpCo(dppe)[P(OMe)_3]\}(PF_6)_2 \cdot Me_2CO$

| Atom | $x$ | $y$ | $z$ | $U_{iso}$[a] |
|---|---|---|---|---|
| Co | 2234.3(6) | 1093.7(5) | 1241.6(4) | 41(1) |
| P(1) | 970(1) | 1764(1) | 1584(1) | 46(1) |
| P(2) | 3125(1) | 950(1) | 2262(1) | 48(1) |
| P(3) | 3174(1) | 2200(1) | 1147(1) | 51(1) |
| P(4) | 4450(1) | 3668(1) | 4020(1) | 60(1) |
| P(5) | 225(2) | 7551(1) | 1201(1) | 77(1) |
| O(3) | 2689(4) | 2746(3) | 557(2) | 88(2) |
| O(4) | 3320(4) | 2791(3) | 1727(2) | 73(2) |
| O(5) | 4293(3) | 1959(4) | 1114(3) | 110(3) |
| F(1) | 3564(4) | 3766(3) | 4383(2) | 103(2) |
| F(2) | 5330(4) | 3554(3) | 4647(2) | 139(3) |
| F(3) | 4625(3) | 4654(2) | 4046(2) | 101(2) |
| F(4) | 5294(4) | 3583(3) | 3627(3) | 125(3) |
| F(5) | 4256(3) | 2688(2) | 3976(2) | 96(2) |
| F(6) | 3569(4) | 3776(3) | 3375(2) | 130(2) |
| F(11) | 597(4) | 7069(4) | 1844(3) | 152(3) |
| F(12) | 22(5) | 8355(4) | 1562(3) | 185(4) |
| F(13) | −152(6) | 8033(4) | 572(3) | 173(4) |
| F(14) | 486(7) | 6794(4) | 850(3) | 208(5) |
| F(15) | 1383(4) | 7891(4) | 1311(3) | 158(3) |
| F(16) | −920(4) | 7276(6) | 1161(3) | 220(4) |
| C(1) | 2537(4) | 1707(4) | 2695(3) | 54(2) |
| C(2) | 1329(4) | 1619(4) | 2435(3) | 56(3) |
| C(3) | 3003(7) | 3074(6) | 70(4) | 118(5) |
| C(4) | 3693(6) | 3633(4) | 1809(4) | 88(4) |
| C(5) | 5159(7) | 2120(9) | 1048(5) | 210(8) |
| C(6) | 2433(5) | −177(4) | 1031(3) | 58(3) |
| C(7) | 1352(5) | 11(4) | 896(3) | 53(3) |
| C(8) | 1142(4) | 653(4) | 427(3) | 52(2) |
| C(9) | 2082(5) | 854(4) | 281(3) | 56(3) |
| C(10) | 2911(5) | 343(4) | 663(3) | 63(3) |
| C(11) | −388(4) | 1358(4) | 1295(3) | 51(2) |
| C(12) | −664(5) | 606(5) | 1528(3) | 75(3) |
| C(13) | −1670(5) | 268(5) | 1299(3) | 83(3) |
| C(14) | −2409(5) | 662(4) | 829(3) | 77(3) |
| C(15) | −2126(5) | 1393(4) | 586(4) | 84(3) |
| C(16) | −1141(4) | 1746(4) | 812(3) | 70(3) |
| C(21) | 820(4) | 2884(4) | 1447(3) | 52(2) |
| C(22) | 640(4) | 3186(4) | 841(3) | 62(3) |
| C(23) | 478(6) | 4035(4) | 709(4) | 87(3) |
| C(24) | 520(6) | 4587(5) | 1203(4) | 107(4) |
| C(25) | 720(6) | 4306(5) | 1804(4) | 101(4) |
| C(26) | 855(5) | 3448(4) | 1931(4) | 76(3) |
| C(31) | 2987(5) | −7(4) | 2681(3) | 57(2) |
| C(32) | 2184(5) | −583(4) | 2489(3) | 72(3) |
| C(33) | 2061(6) | −1257(5) | 2867(3) | 85(3) |
| C(34) | 2730(6) | −1348(5) | 3447(4) | 108(4) |
| C(35) | 3553(7) | −771(6) | 3664(4) | 129(5) |
| C(36) | 3689(6) | −125(5) | 3277(3) | 94(4) |
| C(41) | 4552(4) | 1117(4) | 2462(3) | 50(2) |
| C(42) | 5178(5) | 336(4) | 2251(3) | 60(3) |
| C(43) | 6259(5) | 643(4) | 2381(3) | 76(3) |
| C(44) | 6744(5) | 1346(5) | 2718(4) | 82(3) |
| C(45) | 6127(5) | 1916(5) | 2929(3) | 83(3) |
| C(46) | 5040(5) | 1803(4) | 2798(3) | 63(3) |
| O(1) | 3896(8) | 5104(7) | 587(5) | 229(6) |
| C(51) | 3895(17) | 6461(9) | 363(6) | 297(12) |

*(continued overleaf)*

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* $\{CpCo(dppe)[P(OMe)_3]\}(BF_4)_2$: $P2_1/c$, $a = 12.602(3)$, $b = 15.483(4)$, $c = 20.861(6)$ Å, $\beta = 102.50(2)°$, $Z = 4$.

TABLE II *(continued)*

| Atom | $x$ | $y$ | $z$ | $U_{iso}$[a] |
|---|---|---|---|---|
| C(52) | 3409(9) | 5739(7) | 411(5) | 153(6) |
| C(53) | 2260(12) | 5624(16) | 241(11) | 335(16) |

[a] Equivalent isotropic $U$ defined as one third of the trace of the orthogonalised $U_{ij}$ tensor.

TABLE III. Selected Bond Distances (Å) and Angles (°) for 1 and 2

| | 1 | 2 |
|---|---|---|
| Bond distances | | |
| Co–P(1) | 2.251(2) | 2.198(4) |
| Co–P(2) | 2.238(2) | 2.205(3) |
| Co–P(3) | 2.184(2) | 2.217(3) |
| P(3)–O(3) | 1.545(5) | 1.606(10) |
| P(3)–O(4) | 1.553(5) | 1.480(7) (P=O) |
| P(3)–O(5) | 1.525(5) | 1.600(7) |
| P(1)–C(2) | 1.813(6) | 1.859(9) |
| C(2)–C(1) | 1.527(8) | 1.503(16) |
| P(2)–C(1) | 1.826(6) | 1.828(9) |
| Hg–I(1) | | 2.723(1) |
| Hg–I(2) | | 2.674(1) |
| Hg–I(3) | | 2.673(1) |
| Bond angles | | |
| P(1)–Co–P(2) | 86.7(1) | 87.5(1) |
| P(1)–Co–P(3) | 97.3(1) | 89.6(1) |
| P(2)–Co–P(3) | 91.4(1) | 91.6(1) |
| P(1)–C(2)–C(1) | 109.2(4) | 114.7(7) |
| C(2)–C(1)–P(2) | 106.1(4) | 113.8(6) |
| Co–P(2)–C(1) | 106.1(2) | 108.0(3) |
| Co–P(1)–C(2) | 105.9(2) | 108.5(4) |
| Co–P(3)–O(3) | 114.8(2) | 105.0(3) |
| Co–P(3)–O(4) | 111.0(2) | 118.7(4) |
| Co–P(3)–O(5) | 111.6(2) | 107.0(3) |
| I(1)–Hg–I(2) | | 119.2(0) |
| I(1)–Hg–I(3) | | 113.1(0) |
| I(2)–Hg–I(3) | | 127.5(0) |

chelate ring. The $HgI_3^-$ ions exhibit a pattern of long and short Hg–I distances in addition to angular distortions. Such behavior is observed in other $HgI_3^-$ salts in which intermolecular Hg•••I interactions occur [22, 23]. In the absence of these interactions, the $HgI_3^-$ anion is symmetrical [24]. An unusual feature of {CpCo(dppe)[P(O)(OMe)$_2$]}$HgI_3$ is the distortion of the $HgI_3^-$ ion in the absence of any significant intermolecular interactions. As shown in Fig. 3, the anions and cations pack in respective columns with no important intermolecular contacts. Within the $HgI_3^-$ columns the nearest intermolecular Hg•••I contact is 5.86 Å, which exceeds the sum of the van der Waals radii of these elements by at least 2 Å [25].

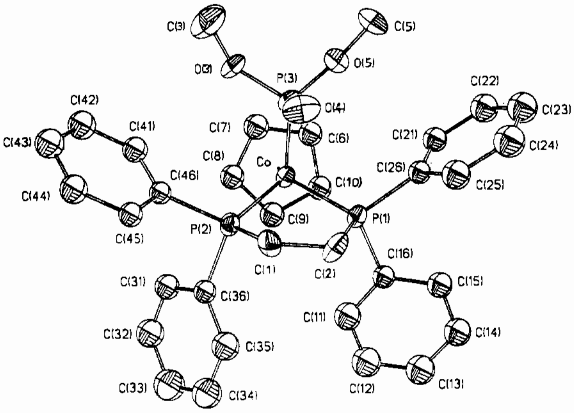

Fig. 2. The molecular structure of {CpCo(dppe)[P(O)(OMe)$_2$]}$^+$ crystallized as the $HgI_3^-$ salt. 40% probability thermal ellipsoids are shown for all atoms except the phenyl rings and $C_5H_5$.

TABLE IV. The Fractional Atomic Coordinates (×10$^4$) and Temperature Factors (Å$^2$ × 10$^3$) for {CpCo(dppe)[P(O)(OMe)$_2$]}$HgI_3$

| Atom | $x$ | $y$ | $z$ | $U_{iso}$ |
|---|---|---|---|---|
| Hg | 2377.7(5) | 2144.9(4) | 2349.1(4) | 64(1)[a] |
| I(1) | 3567(1) | 2290(1) | 986(1) | 64(1)[a] |
| I(2) | 3842(1) | 1287(1) | 3717(1) | 70(1)[a] |
| I(3) | −197(1) | 3042(1) | 2209(1) | 96(1)[a] |
| Co | 812(1) | 6976(1) | 2186(1) | 31(1)[a] |
| P(1) | 946(3) | 8597(2) | 2474(2) | 33(1)[a] |
| P(2) | 2600(3) | 6875(2) | 3311(2) | 35(1)[a] |
| P(3) | −466(3) | 7650(2) | 3391(2) | 40(1)[a] |
| O(3) | −562(7) | 6637(6) | 3581(5) | 58(4)[a] |
| O(5) | −1931(7) | 8021(5) | 2874(5) | 50(4)[a] |
| O(4) | −124(7) | 8514(6) | 4354(5) | 61(4)[a] |
| C(3) | −923(14) | 6736(11) | 4505(10) | 96(10)[a] |
| C(5) | −2855(11) | 8938(9) | 3459(9) | 70(7)[a] |
| C(1) | 2697(10) | 8233(7) | 4176(7) | 42(5)[a] |
| C(2) | 2036(11) | 9062(8) | 3702(7) | 48(6)[a] |
| C(10) | 312(7) | 6632(5) | 609(5) | 48(3) |
| C(6) | −697(7) | 6519(5) | 992(5) | 49(3) |
| C(7) | −144(7) | 5716(5) | 1421(5) | 53(3) |
| C(8) | 1206(7) | 5331(5) | 1302(5) | 50(3) |
| C(9) | 1488(7) | 5897(5) | 800(5) | 51(3) |
| C(11) | 2887(7) | 7977(5) | 1261(5) | 58(3) |
| C(12) | 3561(7) | 8093(5) | 627(5) | 73(4) |
| C(13) | 3060(7) | 8937(5) | 276(5) | 71(4) |
| C(14) | 1885(7) | 9665(5) | 558(5) | 59(3) |
| C(15) | 1211(7) | 9549(5) | 1191(5) | 49(3) |
| C(16) | 1712(7) | 8705(5) | 1543(5) | 39(3) |
| C(21) | −1639(7) | 9377(4) | 1772(4) | 44(3) |
| C(22) | −2790(7) | 10168(4) | 1754(4) | 60(3) |
| C(23) | −2868(7) | 11199(4) | 2484(4) | 64(3) |
| C(24) | −1795(7) | 11438(4) | 3232(4) | 66(4) |
| C(25) | −644(7) | 10648(4) | 3251(4) | 55(3) |
| C(26) | −566(7) | 9617(4) | 2521(4) | 37(3) |
| C(31) | 4435(6) | 5144(5) | 2270(5) | 48(3) |
| C(32) | 5576(6) | 4630(5) | 1815(5) | 63(3) |
| C(33) | 6431(6) | 5220(5) | 1871(5) | 77(4) |

*(Continued on facing page)*

TABLE IV *(continued)*

| Atom | $x$ | $y$ | $z$ | $U_{iso}$ |
|---|---|---|---|---|
| C(34) | 6145(6) | 6325(5) | 2382(5) | 68(4) |
| C(35) | 5004(6) | 6840(5) | 2836(5) | 56(3) |
| C(36) | 4149(6) | 6249(5) | 2780(5) | 38(3) |
| C(41) | 2181(6) | 5344(5) | 3887(4) | 46(3) |
| C(42) | 2366(6) | 4815(5) | 4553(4) | 56(3) |
| C(43) | 3201(6) | 5092(5) | 5478(4) | 55(3) |
| C(44) | 3850(6) | 5899(5) | 5737(4) | 49(3) |
| C(45) | 3664(6) | 6429(5) | 5072(4) | 37(3) |
| C(46) | 2829(6) | 6151(5) | 4147(4) | 33(2) |

[a]Equivalent isotropic $U$ defined as one third of the trace of the orthogonalised $U_{ij}$ tensor.

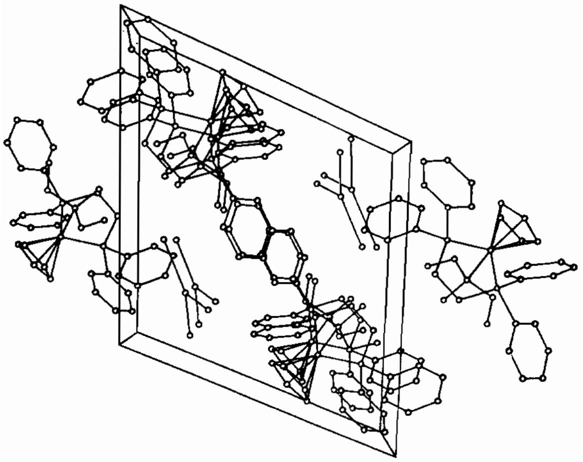

Fig. 3. The packing diagram of $\{CpCo(dppe)[P(O)(OMe)_2]\}$-$HgI_3$ viewed along the $a$ axis. The anions and cations pack in respective columns as shown.

Several structural differences stand out in the cations, **1** and **2**. The Co–$P(OMe)_3$ bond length is shorter than the Co–$P(O)(OMe)_2$ bond (2.184(2) *vs.* 2.217(3) Å), as also occurs in $CpCo[P(OMe)_3][P(O)(OMe)_2]_2$ [19] and $CpCr[P(OMe)_3]_2[P(O)(OMe)_2]$ [26]. This trend probably originates from the greater ionicity of the Co–P(V) bond than the Co–P(III) bond. The Co–P bonds involving the chelate ring apparently compensate for the difference in the electron density on cobalt by adjusting their distances accordingly, *viz.*, 2.20–2.21 Å in **2** but 2.24–2.25 Å in **1**. Similar bond length and angle compensations take place in the phosphite and phosphonate ligands. The P–O bond lengths of the $P(OMe)_3$ ligand of **1** are 1.53–1.55 Å. Upon dealkylation and formation of the phosphoryl group, the P=O distance shortens to 1.48 Å while the P–OC bond lengthens to 1.61–1.62 Å. The P=O unit forces the OMe groups away, resulting in a compression of the O(3)–P(3)–O(4) angle by about 5° compared to that of $P(OMe)_3$ of **1**.

Since the phosphoryl group is situated on the side of the molecule opposite the Cp ring, it is reasonable to assume that attack by the nucleophile in reaction (3) resulting in the conversion of **1** to **2** must have occurred from this direction, perhaps because it is the least sterically hindered region with Me exposure.

### *Possible Complexation Reactions of* 2

The position of P=O in **2** suggests that it might be able to coordinate Lewis acids. The reaction of **2** as the $I^-$ salt with $HgX_2$ (X = Cl, Br, I), $ZnX_2$ (X = Cl, Br) and $AlCl_3$ was tested by combining stoichiometric amounts of each in a MeOH solution (dry $CHCl_3$ in the case of $AlCl_3$). Color changes were noted with the $HgX_2$ salts. The products isolated by evaporation of the MeOH solution had melting points differing from $\{CpCo(dppe)[P(O)(OMe)_2]\}I$ (169 °C). However, the IR spectrum of the product was little changed in the P=O stretching frequency region, and the $^1H$ and $^{31}P\{^1H\}$ NMR spectra showed shifts characteristic only of different ion pairs of **2** [27]. We were further informed by the fact that the $BF_4^-$ salt of **2** did not react with $HgI_2$. Characterization of these products, including the crystal structure of $\{CpCo(dppe)[P(O)(OMe)_2]\}HgI_3$ reported in this paper, indicated that the iodide ion, rather than the cation, **2**, had complexed $HgX_2$ to form the $HgX_2I^-$ anion. This explains why the $BF_4^-$ salt of **2** fails to react with $HgX_2$.

$ZnX_2$ and $AlCl_3$ gave no evidence of complexation. The reactants were isolated in each case upon evaporation of the reaction mixture.

The tendency of **2** not to complex these Lewis acids possibly originates from the limited space available at the P=O site owing to the phenyl rings of dppe as shown in the crystal structure of $\{CpCo(dppe)[P(O)(OMe)_2]\}HgI_3$; Steric constraints should not, however, affect the basicity of P=O toward $H^+$.

A determination of the basicity of **2** toward $H^+$ was undertaken by potentiometrically titrating **2** in MeOH with various concentrations of HCl. The resulting titration curves contain no evidence of protonation. A plausible explanation for this finding is based on electrostatics. **2** already possesses unit positive charge so that protonation by acids of the concentration used here to produce the dipositive ion could be unfavorable.

We conclude from these experiments that, unlike many other phosphate-containing complexes [8–20], **2** exhibits little tendency toward secondary coordination. Steric hindrance and the positive charge on the complex mitigate against such reactions.

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