

X-ray structure⁵⁵ reveals coordination of the Ca(II) ion by a single carboxylate group from Asp-49, plus three peptide carbonyl groups and two water molecules. The charge prediction from our laser measurements (1.1-) is in excellent agreement with that expected on the basis of the known Ca(II) structure.

X-ray structural data is not available for the remaining proteins for which we have $^7F_0 \rightarrow ^5D_0$ excitation spectra (Table III). In the case of calmodulin,⁵⁶ where separate peaks for Eu(III) in the four distinct sites (I-IV) are not resolved, a charge of 2.7- is predicted from the center of the observed band. This finding is consistent with the results obtained on parvalbumin, with which calmodulin is highly homologous. From the primary sequence⁵² it appears that either three or four carboxylates are available in each of the binding sites. The constitution of the metal ion binding sites in prothrombin, human factor Xa, and transferrin are not precisely known from X-ray or primary sequence data, and the predictions presented here (Table III) represent a tentative guide.

While the correlation presented in this paper does not allow us to determine the metal ion coordinating groups in proteins with exact certainty, it does provide a useful guide and, in cases where

changes are observed as a function of various biochemical parameters (pH, ionic strength, inhibitor concentration, etc.), should allow a choice to be made between alternative possibilities. The utility of the present method is by no means limited to macromolecular systems but is proving useful in elucidating the solution coordination chemistry of complexes of smaller molecules such as the crown ethers.⁵⁷

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Registry No. Na₃[Eu(DPA)₃], 94903-36-3; Eu(IMDA)(DCTA)³⁻, 94820-49-2; Eu(DPA)₃³⁻, 38721-36-7; Na₃[Eu(ODA)₃], 94902-09-7; Eu(IMDA)₃³⁻, 33848-98-5; Eu(B)₂⁶⁻ (B = chelidamate), 94820-50-5; Eu(ODA)₃³⁻, 43030-81-5; Eu(DTPA)²⁻, 12302-13-5; Eu(DOTA)⁻, 80927-24-8; Eu(DPA)₂⁻, 94820-51-6; Eu(B)₂⁻ (B = chelidamate), 94820-52-7; Na[Eu(EDTA)(H₂O)₃], 41742-73-8; Eu(IMDA)₂⁻, 15697-13-9; Eu(ODA)₂⁻, 94820-53-8; Eu(EDA)₂⁻, 94820-54-9; Eu(HEDTA), 77461-02-0; [Eu(dbm)₃(H₂O)], 12121-06-1; Eu(NO₃)₃, 10138-01-9; [Eu(nic)₃(H₂O)₂], 94820-55-0; [Eu(acac)₃(H₂O)₂], 52081-76-2; [Eu(NTA)(H₂O)₂], 33772-73-5; [Eu(H₂O)₆Cl₂]Cl, 87510-96-1; Eu(DPA)⁺, 94820-56-1; [Eu(S-ODA)(H₂O)₄]Cl, 94820-57-2; Eu(B) (B = chelidamate), 94820-58-3; Eu(ODA)⁺, 37209-87-3; Eu(IMDA)⁺, 15697-12-8; Eu(EDA)⁺, 72926-87-5; [Eu(dtd)₂](BF₄)₃, 87050-40-6.

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Comparison of the Self-Reactivity of [CpCo(P[~]P)I]⁺ Complexes, P[~]P = Ph₂P(CH₂)_nPPh₂ (n = 1-4), Leading to Bridged and Oxidized "Dangling" P[~]P Reactions and Spectral Studies and the Structures of [CpCo(dppm)I]I·CHCl₃, CpCo[dppm(O)]I₂, and Cp₂Co₂I₄(μ-dpppent)

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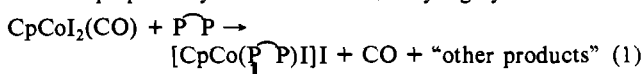
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The intrinsic stability of bis(tertiary phosphine) chelate complexes of the type [CpCo(P[~]P)I]I, where P[~]P = Ph₂P(CH₂)_nPPh₂ (n = 1-4), was investigated in CH₂Cl₂ and CDCl₃ solution by ¹H and ³¹P{¹H} NMR spectroscopy and product isolation. Depending on P[~]P, the complexes range from indefinitely stable (n = 2, 3, ≥90 h) to reactive (n = 4, <2 h). The organometallic products of these rearrangements were identified as CpCo[P[~]P(O)]I₂, containing an oxidized "dangling" phosphine, and Cp₂Co₂I₄(μ-P[~]P), containing a bridged phosphine. The stability (n = 4 ≪ 1 < 2, 3) originates in the chelate ring strain, which in turn controls the ease of formation of the neutral complex, CpCoI₂(P[~]P), containing monodentate P[~]P. The importance of this species in the stability of the chelate salts of interest, [CpCo(P[~]P)I]I, is evidenced by the fact that these salts are destabilized by the presence of excess I⁻. Moreover, the BF₄⁻ and PF₆⁻ salts of [CpCo(P[~]P)I]⁺ are stable in situations where the I⁻ salt is not. Dissociation constants, K_D, are in the range of (2-7) × 10⁻⁴ M for the ion pairs [CpCo(P[~]P)I]X, X = I⁻, BF₄⁻, PF₆⁻. These relatively small values along with evidence from the ¹H NMR spectra of various contact ion pairs suggest that the [CpCo(P[~]P)I] contact ion pair is responsible for the formation of CpCoI₂(P[~]P). The formation of CpCo[P[~]P(O)]I₂ requires the presence of light and at least adventitious O₂/H₂O. These observations, although not conclusive, are most consistent with oxidation initiated by photolysis of the Co-I bond. H₂O₂ oxidizes [CpCo(P[~]P)I]I to CpCo[P[~]P(O)]I₂ to a greater extent in complexes where the chelate ring is strained. X-ray crystal structure determinations were conducted on [CpCo(dppm)I]I·CHCl₃ (*I*₄, a = 18.271 (6) Å, c = 25.496 (8) Å, Z = 8), CpCo[dppm(O)]I₂ (*P*₂/n, a = 8.383 (4) Å, b = 10.388 (3) Å, c = 33.16 (1) Å, β = 91.43 (3)°, Z = 4), and Cp₂Co₂I₄(μ-dpppent) (*P*₂/c, a = 14.978 (5) Å, b = 18.556 (5) Å, c = 15.011 (5) Å, β = 103.03 (2)°, Z = 4).

Introduction

The synthesis of metal-halide complexes in which bis(tertiary phosphine) ligands are present in the coordination sphere has been important to us for parameterizing the steric and electronic factors that bias the Michaelis-Arbuzov transformations involving these complexes.¹⁻³ In most instances, the desired complexes, [CpCo(P[~]P)I]I, where P[~]P is a bis(tertiary phosphine) ligand,⁴

could be prepared by reaction 1 in relatively high yield with clean



product separation.² However, **1** may undergo further chemistry, and variables such as reactant stoichiometry, time, solvent, and temperature decidedly influence the products obtained from reaction 1. To the extent that these reactions and other products might intervene in the Arbuzov transformation of **1**, we felt obliged to characterize them.

The present study contributes to the understanding of factors that affect the modes of bonding of bis(tertiary phosphine) ligands in transition-metal chemistry. Chelated, bridged, and monodentate or "dangling" bis(tertiary phosphine) ligands have been isolated

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(4) Abbreviations: η⁵-C₅H₅, Cp; bis(diphenylphosphino)methane, dppm; 1,2-bis(diphenylphosphino)ethane, dppe; 1,3-bis(diphenylphosphino)propane, dppp; 1,4-bis(diphenylphosphino)butane, dppb; 1,5-bis(diphenylphosphino)pentane, dpppent.

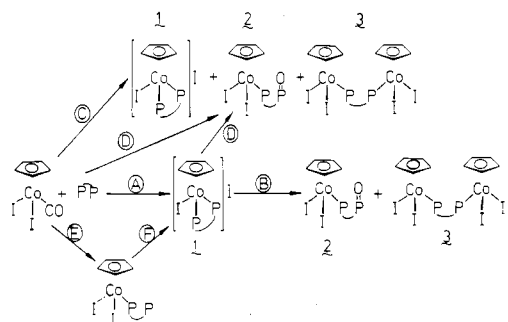


Figure 1. Reaction scheme. Reactions A–F are described in the Results along with details of the conditions.

Table I. Percent Yield of the Products 1–3 Shown in Figure 1 for Reactions A–D

product	reactn ^a	chelate			
		dppm	dpepe	dppp	dppb
1	A	90	94	92	94
2	B	10	(5) ^b	0	50
3	B	10		0	50
1	C	40	90	90	18
2	C	25	0	(2) ^b	10
3	C	25	10	(8) ^b	50
1	D	73	95	80	10
2	D	25	(2) ^b	16	65
3	D	2	(0) ^b	0	15

^a See text for details of these reactions. ^b Yields of 2 and 3 less than 10% can be difficult to separate. The yields are often best established by integration of the ¹H NMR spectra.

before with the same metal center.⁵ However, it was intriguing to discover that the “dangling” mode in the products here involves a phosphoryl rather than phosphine terminus. One of the central features that controls the nature of the products of reaction 1 is the strain in the chelate ring of **1**. This is apparent in the stability and further reactions of **1**, which markedly depend on P^{P} . In addition to characterizations by the product formulation, yield, and ³¹P and ¹H NMR spectra, crystal structure determinations of the chelate complex, $[\text{CpCo}(\text{dppm})\text{I}]\text{I}\cdot\text{CHCl}_3$, the oxidized dangler complex, $\text{CpCo}[\text{dppm}(\text{O})]\text{I}_2$, and the phosphine-bridged complex, $\text{Cp}_2\text{Co}_2\text{I}_4(\mu\text{-dppent})$, have been determined in order to substantiate the findings.

Results

An understanding of reaction 1 evolves from a systematic study of its course under a variety of conditions. To this end, the reaction sequences shown in Figure 1 are described in this section. ¹H and ³¹P NMR spectroscopy, conductivity, IR spectroscopy, elemental analyses, and X-ray crystallography underpin the results. Key interpretations are correlated insofar as possible in the Discussion.

Reaction A. The stoichiometric reaction of P^{P} (dppm, dpepe, dppp, dppb) and $\text{CpCoI}_2(\text{CO})$ in CH_2Cl_2 at room temperature results in a momentary color change from violet to brown. The product, if harvested within 3 h, is $[\text{Cp}(\text{Co}(\text{P}^{\text{P}})\text{I})\text{I}]$ (**1**) in almost quantitative yield (Table I). These complexes were characterized elsewhere for $\text{P}^{\text{P}} = \text{dpepe}$, dppp, and dppb.^{2,6} $[\text{CpCo}(\text{dppm})\text{I}]\text{I}$ has not been previously reported. The same reaction with dppent fails to produce **1** but instead gives $\text{Cp}_2\text{Co}_2\text{I}_4(\mu\text{-dppent})$ and perhaps $\text{Co}(\text{dppent})_2\text{I}$, which are described below.

The ¹H and ³¹P NMR spectra of these products (Table II) agree with their formulation as phosphine-chelated complexes. $\delta(^1\text{H})$ of Cp (5.2–5.7) is characteristic of monocations of this type.² When BF_4^- or PF_6^- replaces I^- as the counterion, small but resolvable shifts in the Cp signal arise from the different contact ion pairs. As the P^{P} chelate in **1** becomes larger, both the cyclopentadienyl and methylene protons become increasingly

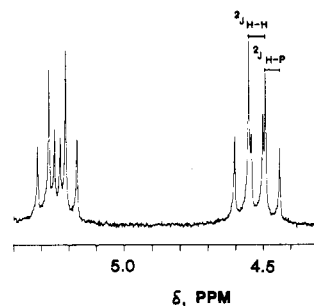


Figure 2. ¹H NMR spectrum of the CH_2 region of $[\text{CpCo}(\text{dppm})\text{I}]\text{I}$ in CD_3CN .

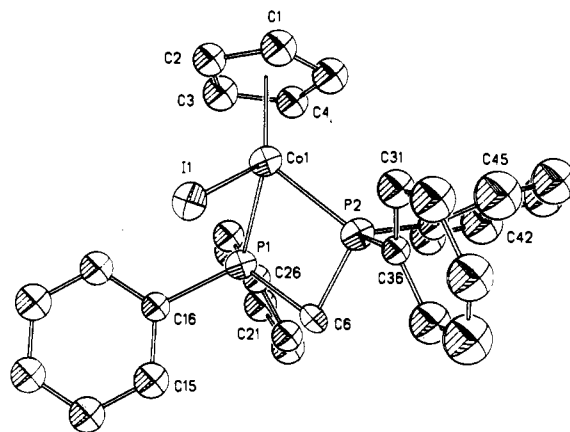


Figure 3. Molecular structure of $[\text{CpCo}(\text{dppm})\text{I}]^+$ depicting the 40% probability thermal ellipsoids of all atoms except those of the cyclopentadienyl and phenyl rings.

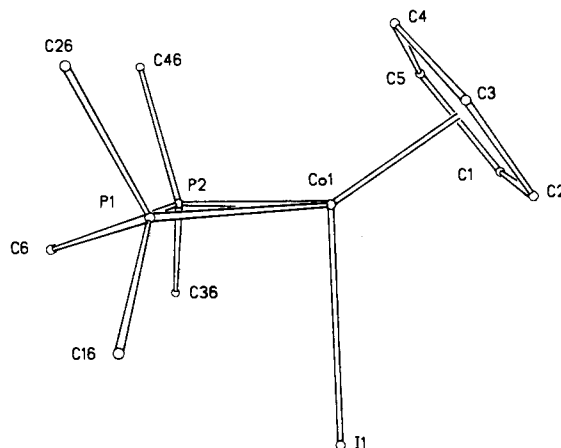


Figure 4. Near-neighbor environment of the Co atom in $[\text{CpCo}(\text{dppm})\text{I}]^+$ showing the puckering of the dppm chelate ring.

shielded. The CH_2 signals of $[\text{CpCo}(\text{dppm})\text{I}]\text{I}$ are shown in Figure 2. We find, in general, that the methylene proton signals in these complexes are strongly solvent sensitive.⁷ The phenyl region was not analyzed because of its complexity and the minimal information it affords here. The ³¹P/¹H chemical shifts follow the pattern characteristic of chelated bis(tertiary phosphine) alkanes of ring size 4–7.⁸

The molecular structure of $[\text{CpCo}(\text{dppm})\text{I}]\text{I}\cdot\text{CHCl}_3$ was determined in part to establish the characteristics of this product and in part because the structure of a $\text{Co}(\text{III})\text{-dppm}$ complex has not been reported. Tables III and IV list the atomic coordinates and selected bond lengths and angles, respectively. Figure 3 depicts the molecular structure and labeling scheme. The strain within

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Table II. ^1H (0–7 ppm) and ^{31}P [^1H] Chemical Shifts and Coupling Constants (Hz) in CDCl_3 ^{a,b}

complex	$\delta(^1\text{H})$		$\delta(^{31}\text{P})$
	$\eta^5\text{-C}_5\text{H}_5$	$-\text{CH}_2-$	
[CpCo(dppm)I]I	5.72 5.78 ^c	4.53 ($^2J_{\text{HH}} = 15.0$, $^2J_{\text{HP}} = 13.0$) 5.30, 4.55 ($^2J_{\text{HH}} = 15.2$, $^2J_{\text{HP}} = 12.9$) ^c	0.20 0.81
[CpCo(dppe)I]I	5.57	3.27–3.35 (b d) ($^2J_{\text{HP}} = 9.7$)	80.91
[CpCo(dppp)I]I	5.46	2.97 (b m)	28.30
[CpCo(dppb)I]I	5.28	3.50 (b), 2.62 (b), 1.86 (b)	34.87
[CpCo(dppp)I]BF ₄	5.43	2.97 (b m)	
[CpCo(dppb)I]BF ₄	5.19	3.47 (b), 2.60 (b), 1.90 (b)	
[CpCo(dppb)I]PF ₆	5.14	3.49 (b), 2.60 (b), 1.90 (b)	
Cp ₂ Co ₂ I ₄ (μ -dppm)	4.91	4.05 (b)	33.66
Cp ₂ Co ₂ I ₄ (μ -dppe)	4.95	2.70 (s)	35.36
Cp ₂ Co ₂ I ₄ (μ -dppp)	4.90	2.65 (m), 1.26	30.11
Cp ₂ Co ₂ I ₄ (μ -dppb)	4.94	2.4 (b), 1.26 (b), 1.12 (b)	31.39
Cp ₂ Co ₂ I ₄ (μ -dpppent)	4.95 4.97	2.52 (b), 1.59, 1.08 (b)	31.78
CpCo[dppm(O)]I ₂	5.01	3.98 (t) ($^2J_{\text{HP}} = 9.9$)	29.70 (b) 27.16 (d, $^2J_{\text{PP}} = 31.8$)
CpCo[dppe(O)]I ₂	4.97	3.08 (b), 2.21 (b)	33.01 30.97
CpCo[dppp(O)]I ₂	4.95		
CpCo[dppb(O)]I ₂	4.98	2.65 (b), 2.06 (b), 1.47 (b), 1.30 (b)	31.51 30.92

^a Phenyl region not shown. ^b Abbreviations: b = broad, m = multiplet, d = doublet, t = triplet. ^c CD₃CN.

the four-membered chelate ring is evident in the bond distances and angles. The P–Co–P angle of 75.1 (3)^o is characteristic of chelated dppm.^{9,10} The Co–P–C and P–C–P angles likewise are strained, being 13–18^o less than tetrahedral. While the Co–P bond lengths are the same as those for monodentate dppm (vide infra) and chelated dppe,^{11,12} the P–C bond distances lengthen by 0.03–0.1 Å to reduce the strain. The P–P interatomic distance of 2.690 (8) Å, although it is short and is in the range of weak P–P bonding,¹³ cannot arise from a bonding interaction. Figure 4 shows the puckering of the chelate ring which is common with dppm.⁹

The large distinction in the ^1H NMR spectrum between the axial and equatorial methylene protons of dppm (Figure 2) could be caused by the magnetic anisotropy of the Γ^- and C_5H_5^- ligands. However, as noted above, the solvent also plays a role. The compactness of the coordination sphere is evident by the fact that the Cp ring is forced to tip away from the iodide ligand.

The chelate complexes, **1**, are starting points for numerous reactions, several of which complicate the substitution chemistry of the iodide ligand. The most problematical property of **1** is its tenuous stability in solution.

Reaction B. [CpCo(P⁺P)I]I (**1**) was allowed to remain in CDCl_3 or CH_2Cl_2 solution at room temperature and in contact with the atmosphere for about 90 h. Two new metal-containing products form in yields that strongly depend on the bis(tertiary phosphine) ligand. When P⁺P = dppb, evidence of changes in **1** appears within 1 h. On the other hand, less than 3% conversion occurs after 90 h when P⁺P = dppe and dppp. The products were identified as the neutral complex **2**, containing a dangling oxidized phosphine ligand, and **3**, the phosphine-bridged complex. The percentages of **1**, **2**, and **3** after 90 h are given in Table I. Reducing the temperature to –78 °C had little effect on the product distribution although the reaction rate diminished. Reaction B as shown in Figure 1 is not stoichiometric. One-third of an equivalent of P⁺P is unaccounted for. From IR and NMR spectroscopy it appears that this residual phosphine is oxidized to P⁺P(O) and (O)P⁺P(O).

While [CpCo(dppb)I]I is by far the least stable in CH_2Cl_2 , having decomposed entirely after 90 h, it is noteworthy that the

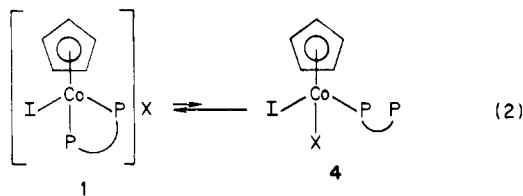
Table III. Atomic Coordinates ($\times 10^4$) and Temperature Factors ($\text{Å}^2 \times 10^3$) for [CpCo(dppm)I]I- CHCl_3 ^a

atom	x	y	z	U_{iso}
I(1)	8814 (1)	5084 (1)	1916 (1)	59 (1)*
I(2)	5000	0	509 (1)	93 (1)*
I(3)	5000	5000	1566 (1)	84 (1)*
Co(1)	8474 (2)	4042 (2)	1290 (1)	52 (1)*
P(1)	7745 (4)	4803 (4)	860 (3)	50 (2)*
P(2)	7395 (4)	3926 (4)	1671 (3)	56 (3)*
C(1)	9287 (11)	3292 (11)	1537 (6)	72 (9)
C(2)	9603 (11)	3791 (11)	1175 (6)	61 (8)
C(3)	9204 (11)	3746 (11)	698 (6)	75 (9)
C(4)	8640 (11)	3219 (11)	765 (6)	59 (8)
C(5)	8692 (11)	2938 (11)	1284 (6)	80 (10)
C(6)	6959 (14)	4742 (12)	1346 (9)	41 (9)*
C(11)	8644 (9)	5900 (9)	498 (8)	72 (9)
C(12)	8789 (9)	6609 (9)	323 (8)	89 (10)
C(13)	8264 (9)	7157 (9)	384 (8)	81 (10)
C(14)	7595 (9)	6997 (9)	622 (8)	76 (9)
C(15)	7450 (9)	6288 (9)	798 (8)	69 (8)
C(16)	7975 (9)	5740 (9)	736 (8)	48 (6)
C(21)	6591 (9)	4725 (11)	138 (7)	67 (9)
C(22)	6308 (9)	4667 (11)	–369 (7)	83 (10)
C(23)	6766 (9)	4477 (11)	–785 (7)	81 (9)
C(24)	7508 (9)	4346 (11)	–695 (7)	90 (11)
C(25)	7791 (9)	4405 (11)	–188 (7)	74 (9)
C(26)	7333 (9)	4594 (11)	229 (7)	56 (8)
C(31)	7785 (8)	3763 (9)	2703 (8)	66 (8)
C(32)	7657 (8)	3794 (9)	3243 (8)	108 (13)
C(33)	6992 (8)	4059 (9)	3432 (8)	103 (12)
C(34)	6453 (8)	4293 (9)	3082 (8)	117 (13)
C(35)	6581 (8)	4262 (9)	2542 (8)	83 (10)
C(36)	7246 (8)	3997 (9)	2352 (8)	44 (6)
C(41)	6609 (12)	3071 (11)	951 (8)	80 (10)
C(42)	6253 (12)	2428 (11)	803 (8)	121 (15)
C(43)	6134 (12)	1876 (11)	1172 (8)	119 (15)
C(44)	6372 (12)	1966 (11)	1688 (8)	130 (15)
C(45)	6728 (12)	2609 (11)	1836 (8)	145 (17)
C(46)	6847 (12)	3161 (11)	1468 (8)	58 (8)

^a Values marked with an asterisk denote equivalent isotropic U values defined as one-third of the trace of the orthogonalized U_{ij} tensor.

BF₄[–] and PF₆[–] salts of [CpCo(dppb)I]⁺ are indefinitely stable. The coordinating tendency of the counterion has a role in cleaving the chelate ring. Reaction 2 occurs when X = Γ^- , but not when X = BF₄[–] and PF₆[–]. The addition of 1 equiv of excess Γ^- in the form of [(*n*-Pr)₄N]⁺I[–] initiates reaction 2 when X = BF₄[–] and PF₆[–] and enhances it when X = Γ^- , according to the yield data in Table

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V, which were established after 12 h. In an attempt to explain this observation, the dissociation constants, K_D , for the contact ion pairs $[\text{CpCo}(\text{dppb})\text{I}]\text{X}$ ($\text{X} = \text{I}^-, \text{BF}_4^-, \text{PF}_6^-$) and $[(n\text{-Pr})_4\text{N}]\text{I}$ were measured in CH_2Cl_2 . K_D was found to be essentially the same for all three organometallic salts (Table V) but larger by 1 order of magnitude than that of $[(n\text{-Pr})_4\text{N}]\text{I}$. Note that K_D for **1** is unaffected by whether dppp or dppb is the chelate ligand. K_D reveals that the concentration of free solvated ions is small compared to the concentration of ion pairs in these solutions. Therefore, even when excess $[(n\text{-Pr})_4\text{N}]\text{I}$ is present, the ion pair needed for reaction 2, $[\text{CpCo}(\text{dppb})\text{I}]\text{I}$, only partially forms. This conclusion is substantiated by the ^1H NMR spectrum of the reaction mixture, in which Cp signals for the various ion pairs of **1** are clearly evident. These experiments also suggest that the iodide anion of the $[\text{CpCo}(\text{dppb})\text{I}]\text{I}$ contact ion pair, rather than the free iodide ion in the solution, is responsible for reaction 2.

Reaction 2 is also solvent dependent. A solvent of low dielectric constant (CH_2Cl_2 , CDCl_3) confers less stability on **1** than does one of high dielectric constant (MeOH) because of the different ability of these solvents to support ionic charge. The equilibrium constant in reaction 2 leading to instability of the chelate complex is larger in CH_2Cl_2 or CDCl_3 than in MeOH.

The formation of the phosphine-bridged complex **3**, directly from the species in reaction 2, is imaginable. However, without O_2 and at least traces of H_2O , **2** does not appear. A 50-psi atmosphere of O_2 was found to have little effect on the yield or rate of formation of **2**. Reaction B also occurs to a greater extent in the room light than in the dark under the same conditions.

^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy was valuable, but not in every case definitive, for establishing the nature of the products from this reaction. Figure 5 shows the ^1H NMR spectrum of the methylene protons and the $^{31}\text{P}\{^1\text{H}\}$ spectrum of $\text{CpCo}[\text{dppm}(\text{O})]\text{I}_2$. The proton spectrum suggests that both phosphorus nuclei are magnetically equivalent while the ^{31}P spectrum reveals that they are not. This discrepancy does not exist with any other complex. The molecular structure of $\text{CpCo}[\text{dppm}(\text{O})]\text{I}_2$ (vide infra) establishes the composition of this complex so that it can only be a fortuitous coincidence of chemical shift and ^{31}P coupling in the methylene protons that occasions the 1:2:1 triplet in Figure 5. $\delta(^1\text{H})$ for Cp of the neutral complexes **2** and **3** is 4.9–5.0, which, owing to the charge effect, is more shielded than that of the monocation series **1**. The Cp chemical shift difference is small among compounds of type **2** and **3** compared to that of **1** because the coordination sphere of Co has essentially invariant geometry in the former while the angles differ in the latter. The ^{31}P chemical shifts of coordinated P(III) and dangling P(V) in **2** are similar, as Figure 5 illustrates. This likeness makes their assignment tentative, although the line width of the terminal phosphorus atom might be expected to be narrower than that of the coordinated phosphorus atom.

The conflicting ^1H and ^{31}P NMR spectra of $\text{CpCo}[\text{dppm}(\text{O})]\text{I}_2$ prompted us to establish its identity by X-ray crystallography. Table VI gives the atomic coordinates and Table IV selected bond lengths and angles for this complex. Figure 6 shows the atomic arrangement. The position of the $\text{P}=\text{O}$ bond vector relative to the cobalt coordination sphere is determined by the iodine atoms, which force the phenyl rings on the coordinated phosphorus atom trans to the iodide atoms. The orientation of these phenyl rings is passed along by steric demands to the P(V) center, forcing its phenyl rings and the phosphoryl oxygen atom into the position shown. Opening the dppm chelate ring when forming **2** fails to shorten the Co–P bond but instead permits expansion of the Co–P–C angle from about 95 to 113° and the P–C–P angles from 91 to 119.5° . The relaxation of strain in these angles is accom-

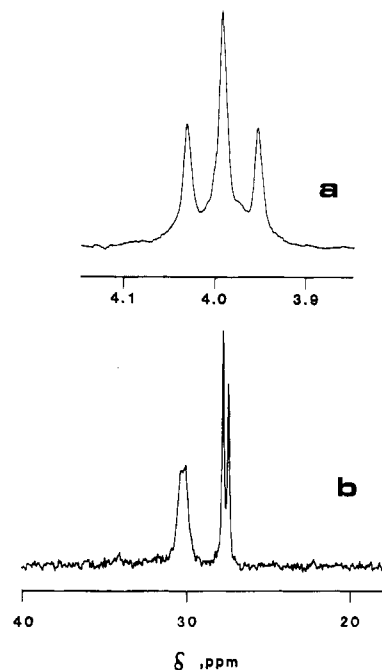


Figure 5. ^1H (a) and $^{31}\text{P}\{^1\text{H}\}$ (b) NMR spectra of the CH_2 region of $\text{CpCo}[\text{dppm}(\text{O})]\text{I}_2$ in CDCl_3 . The simple triplet in (a) suggests the phosphorus nuclei are equivalent while the $^{31}\text{P}\{^1\text{H}\}$ spectrum reveals they are not.

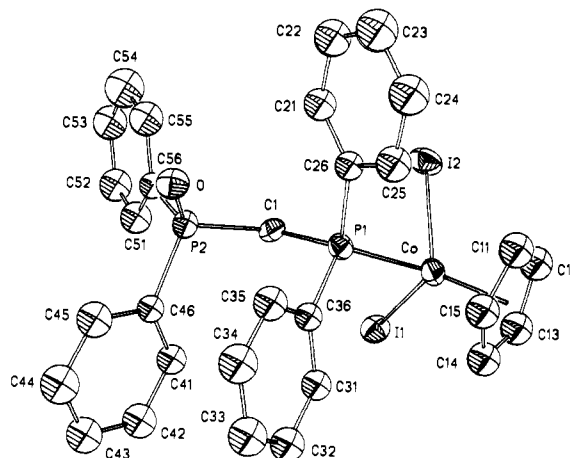
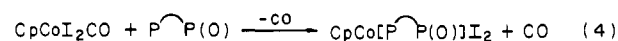
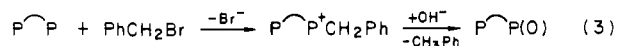


Figure 6. Molecular structure of $\text{CpCo}[\text{dppm}(\text{O})]\text{I}_2$ showing the 40% probability thermal ellipsoids of all atoms except those of the cyclopentadienyl and phenyl rings.

panied by shortening of the P–C bonds from 1.85 (2) and 1.92 (2) Å in **1** to 1.825 (9) and 1.836 (9) Å in **2**. Thus the Co–P distance seems unaffected by whether the phosphorus atom is part of a chelate ring or is terminal, whereas the other distances and angles are sensitive to this difference. As with **1**, the Cp ring of **2** appears to tip away from the I atoms to avoid crowding. The Co–I bond lengths in the neutral complex **2** slightly exceed that in the cationic complex **1**, probably in response to the difference in the residual charge.

2 can also be synthesized in good yield by reactions 3 and 4 in acetone. The organometallic product of reaction 4 is the same



2

as that from reaction B. Recall that **2** is not produced by reaction B, except in inconsequential yield, when $\widehat{\text{P}}\text{P} = \text{dppe}$ and dppp . If desired, it is available from reactions 3 and 4.

Table IV. Selected Bond Distances and Angles

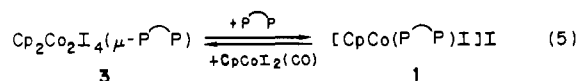
	[CpCo(dppm)I]I-CHCl ₃	CpCo[dppm(O)]I ₂	(μ-dpppent)Cp ₂ Co ₂ I ₄
(a) Bond Distances (Å)			
Co(1)-I(1)	2.556 (4)	2.598 (1)	2.576 (3)
Co(1)-I(2)		2.572 (1)	2.600 (3)
Co(2)-I(3)			2.591 (3)
Co(2)-I(4)			2.581 (3)
Co(1)-P(1)	2.216 (8)	2.229 (3)	2.231 (5)
Co(1)-P(2)	2.203 (8)		
Co(2)-P(2)			2.240 (5)
Co(1)-CNT(1) ^a	1.691 (10)	1.704 (7)	1.692 (7)
Co(2)-CNT(2)			1.707 (7)
P(1)-C(1)		1.825 (9)	1.849 (15)
P(2)-C(1)		1.836 (9)	
P(1)-C(6)	1.924 (23)		
P(2)-C(6)	1.845 (23)		
P(2)-C(5)			1.837 (16)
P(2)-O		1.477 (6)	
P(1)⋯P(2)	2.690 (9)		
(b) Bond Angles (deg)			
I(1)-Co(1)-P(1)	89.4 (2)	96.7 (1)	92.1 (1)
I(1)-Co(1)-P(2)	91.0 (2)		
I(2)-Co(1)-P(1)	89.0 (1)	89.0 (1)	93.3 (1)
I(1)-Co(1)-I(2)		94.5 (0)	94.7 (1)
I(3)-Co(2)-I(4)			93.9 (1)
I(3)-Co(2)-P(2)			91.8 (1)
I(4)-Co(2)-P(2)			95.1 (1)
P(1)-Co(1)-P(2)	75.1 (3)		
CNT(1)-Co(1)-I(1)	122.3 (3)	120.1 (2)	119.6 (2)
CNT(1)-Co(1)-I(2)		121.7 (2)	122.1 (2)
CNT(1)-Co(1)-P(1)	133.7 (4)	126.5 (2)	126.7 (3)
CNT(1)-Co(1)-P(2)	130.3 (4)		
CNT(2)-Co(2)-I(3)			121.2 (2)
CNT(2)-Co(2)-I(4)			121.7 (2)
CNT(2)-Co(2)-P(2)			125.2 (4)
Co(1)-P(1)-C(6)	94.1 (7)		
Co(1)-P(2)-C(6)	96.8 (8)		
Co(1)-P(1)-C(1)		112.7 (3)	115.2 (6)
Co(2)-P(2)-C(5)			113.8 (6)
P(1)-C(6)-P(2)	91.2 (10)		
P(1)-C(1)-P(2)		119.5 (5)	
C(16)-P(1)-C(26)	98.0 (9)		
C(36)-P(1)-C(46)	104.4 (9)		103.6 (5)
C(26)-P(1)-C(36)		106.0 (3)	
C(26)-P(1)-C(1)		105.1 (3)	
C(36)-P(1)-C(1)		105.2 (4)	105.3 (7)
C(46)-P(1)-C(1)			103.7 (7)
C(46)-P(2)-C(56)		107.8 (3)	
C(56)-P(2)-C(66)			105.0 (6)
C(6)-P(1)-C(16)		111.8 (9)	
C(6)-P(1)-C(26)		105.3 (9)	
C(6)-P(2)-C(36)		107.2 (9)	
C(6)-P(2)-C(46)		105.9 (10)	
C(5)-P(2)-C(56)			107.2 (7)
C(5)-P(2)-C(66)			104.0 (7)
C(1)-P(2)-O		114.3 (4)	
C(46)-P(2)-O		112.7 (3)	
C(56)-P(2)-O		112.2 (4)	

^a CNT = centroid of Cp ring.Table V. Conversion Percentages from Excess I⁻ Experiment in Reaction B,^a along with the Limiting Equivalent Conductance Values of the Complex and the Dissociation Constant

complex	% conversion to 2 and 3	Λ ₀ , Ω ⁻¹ cm ⁻¹	10 ⁴ K _D , M
[CpCo(dppm)I]I	5-10		
[CpCo(dppe)I]I	0		
[CpCo(dppp)I]I	0	79.5	3.1
[CpCo(dppp)I]BF ₄	0	91.5	2.6
[CpCo(dppb)I]I	82	66.0	7.0
[CpCo(dppb)I]BF ₄	25	95.0	2.4
[CpCo(dppb)I]PF ₆	23	83.1	3.4
[(i-Pr) ₄ N]I		128.4	0.22

^a After 12 h with a sixfold excess of [(i-Pr)₄N]I.

Reaction C. In a reaction similar to A, CpCoI₂(CO) and P[~]P were combined in CH₂Cl₂ or CDCl₃ at room temperature for 3-5 h while exposed to the atmosphere in 2/1 stoichiometry instead of 1/1. Excess CpCoI₂(CO) should enhance the formation of the dimer 3 and possibly the oxidized dangler 2. Indeed, under these conditions with P[~]P = dppm, a mixture of 1, 2, and 3 is formed. 3 predominates over 1 when P[~]P = dpbb, while 1 strongly predominates over 3 with P[~]P = dppe and dppp. For P[~]P = dpbb and dppm, 3 and 1 are interconverted within seconds by reaction 5. The formation of 2, however, requires considerably more time



and is not interconvertible with 1 or 3 by any of these reactions.

Table VI. Atomic Coordinates ($\times 10^4$) and Temperature Factors ($\text{Å}^2 \times 10^3$) for $\text{CpCo}[\text{dppm}(\text{O})]\text{I}_2^a$

atom	x	y	z	U_{iso}
I(1)	-800 (1)	6793 (1)	346 (1)	49 (1)*
I(2)	1176 (1)	9906 (1)	692 (1)	57 (1)*
Co	2051 (2)	7776 (1)	370 (1)	37 (1)*
P(1)	2751 (3)	7053 (2)	982 (1)	33 (1)*
P(2)	1298 (3)	6143 (3)	1805 (1)	36 (1)*
O	2840 (7)	6358 (6)	2020 (2)	44 (2)*
C(1)	1081 (10)	7007 (9)	1324 (3)	35 (3)*
C(11)	4123 (8)	8459 (7)	121 (2)	61 (3)
C(12)	2808 (8)	8839 (7)	-129 (2)	59 (3)
C(13)	2022 (8)	7707 (7)	-270 (2)	60 (3)
C(14)	2850 (8)	6628 (7)	-106 (2)	58 (3)
C(15)	4148 (8)	7093 (7)	136 (2)	57 (3)
C(21)	3831 (6)	8905 (7)	1543 (2)	52 (3)
C(22)	4951 (6)	9766 (7)	1705 (2)	64 (3)
C(23)	6498 (6)	9788 (7)	1560 (2)	77 (4)
C(24)	6925 (6)	8948 (7)	1253 (2)	69 (3)
C(25)	5805 (6)	8087 (7)	1090 (2)	56 (3)
C(26)	4258 (6)	8066 (7)	1236 (2)	39 (2)
C(31)	2886 (7)	4519 (6)	720 (2)	43 (2)
C(32)	3390 (7)	3239 (6)	730 (2)	54 (3)
C(33)	4575 (7)	2854 (6)	1008 (2)	64 (3)
C(34)	5257 (7)	3749 (6)	1274 (2)	63 (3)
C(35)	4753 (7)	5029 (6)	1263 (2)	51 (3)
C(36)	3568 (7)	5414 (6)	986 (2)	36 (2)
C(41)	-161 (7)	3070 (6)	1422 (2)	48 (3)
C(42)	-422 (7)	2646 (6)	1396 (2)	63 (3)
C(43)	367 (7)	1813 (6)	1664 (2)	66 (3)
C(44)	1417 (7)	2305 (6)	1959 (2)	73 (4)
C(45)	1678 (7)	3629 (6)	1985 (2)	62 (3)
C(46)	889 (7)	4461 (6)	1717 (2)	38 (2)
C(51)	-1922 (8)	6378 (6)	2035 (2)	60 (3)
C(52)	-3119 (8)	6989 (6)	2248 (2)	68 (3)
C(53)	-2741 (8)	8026 (6)	2500 (2)	75 (4)
C(54)	-1167 (8)	8452 (6)	2539 (2)	95 (5)
C(55)	30 (8)	7841 (6)	2325 (2)	66 (3)
C(56)	-347 (8)	6804 (6)	2073 (2)	38 (2)

^a Values marked with an asterisk denote equivalent isotropic U values defined as one-third of the trace of the orthogonalized U_{ij} tensor.

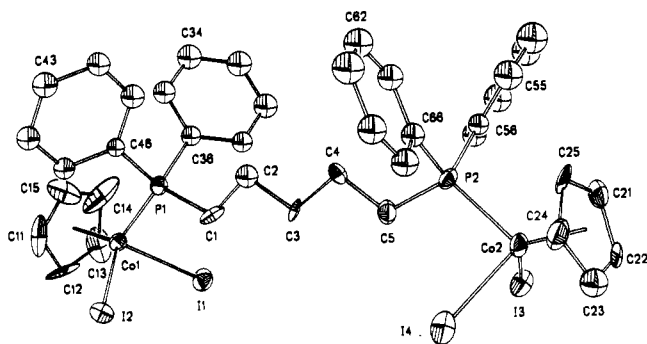


Figure 7. Molecular structure of $\text{Cp}_2\text{Co}_2\text{I}_4(\mu\text{-dppent})$ showing the 40% probability thermal ellipsoids of all atoms except the phenyl rings. Approximate twofold symmetry exists at C(3).

The reaction of $\text{CpCoI}_2(\text{CO})$ with dppent produces $\text{Cp}_2\text{Co}_2\text{I}_4(\mu\text{-dppent})$ and perhaps $\text{Co}(\text{dppent})_2\text{I}$.¹³ We have been unable to synthesize **1** with dppent , but presumably **2** can be prepared if desired by reactions 3 and 4. The crystal structure of $\text{Cp}_2\text{Co}_2\text{I}_4(\mu\text{-dppent})$ was determined because structural information on this phosphine ligand is rare. Table VII lists the atomic coordinates, and Table IV provides selected bond lengths and angles. As shown in Figure 7, the complex exists in the cis configuration in the solid state with approximately twofold symmetry at C(3). Co-P and Co-I bond lengths are similar to those in $\text{CpCo}[\text{dppm}(\text{O})]\text{I}_2$. Comparable tilting of the Cp ring occurs to avoid the I atoms. The ^1H NMR spectrum of a CDCl_3 solution of this complex at room temperature reveals two closely spaced lines in the Cp signal in a ratio of about 4/1 that may be caused by two conformers. Splitting of the Cp signal is not observed for

Table VII. Atomic Coordinates ($\times 10^4$) and Temperature Factors ($\text{Å}^2 \times 10^3$) for $\text{Cp}_2\text{Co}_2\text{I}_4(\mu\text{-dppent})^a$

atom	x	y	z	U_{iso}
I(1)	738 (1)	6236 (1)	7819 (1)	52 (1)*
I(2)	1119 (1)	3693 (1)	820 (1)	46 (1)*
I(3)	4412 (1)	2779 (1)	7141 (1)	50 (1)*
I(4)	6120 (1)	2240 (1)	633 (1)	55 (1)*
Co(1)	10795 (2)	1895 (1)	7288 (2)	34 (1)*
Co(2)	4860 (2)	3084 (1)	956 (2)	35 (1)*
P(1)	98 (3)	2151 (3)	1532 (3)	31 (2)*
P(2)	5800 (3)	3710 (3)	2058 (3)	32 (2)*
C(1)	9235 (12)	2639 (9)	5474 (10)	42 (7)*
C(2)	8696 (12)	3259 (10)	4953 (11)	45 (5)
C(3)	7975 (10)	2947 (9)	4139 (10)	35 (7)*
C(4)	7334 (10)	3510 (9)	3634 (10)	31 (6)*
C(5)	6631 (11)	3148 (10)	2847 (12)	43 (7)*
C(11)	12189 (13)	1934 (15)	7892 (14)	92 (12)*
C(12)	11792 (16)	1296 (11)	8160 (14)	90 (11)*
C(13)	11125 (15)	1523 (15)	8620 (12)	101 (13)*
C(14)	11076 (20)	2284 (16)	8618 (14)	113 (14)*
C(15)	11742 (17)	2483 (14)	8163 (13)	85 (11)*
C(21)	3691 (11)	3717 (11)	649 (13)	51 (8)*
C(22)	3458 (12)	3046 (10)	229 (11)	53 (8)*
C(23)	4035 (11)	2925 (11)	-388 (13)	55 (6)
C(24)	4646 (12)	3532 (11)	-321 (12)	59 (8)*
C(25)	4408 (11)	4026 (11)	293 (11)	53 (8)*
C(31)	8558 (7)	3245 (6)	7164 (7)	43 (5)
C(32)	8074 (7)	3649 (6)	7683 (7)	61 (6)
C(33)	8521 (7)	4184 (6)	8271 (7)	67 (6)
C(34)	9452 (7)	4315 (6)	8340 (7)	63 (6)
C(35)	9935 (7)	3911 (6)	7821 (7)	52 (5)
C(36)	9488 (7)	3376 (6)	7233 (7)	39 (5)
C(41)	10562 (6)	4229 (6)	6001 (7)	50 (5)
C(42)	11130 (6)	4734 (6)	5716 (7)	46 (5)
C(43)	11987 (6)	4525 (6)	5588 (7)	53 (5)
C(44)	12276 (6)	3813 (6)	5744 (7)	47 (5)
C(45)	11708 (6)	3308 (6)	6029 (7)	40 (5)
C(46)	10851 (6)	3517 (6)	6157 (7)	30 (4)
C(51)	4998 (8)	8911 (5)	11452 (8)	50 (5)
C(52)	5529 (8)	9272 (5)	10942 (8)	69 (7)
C(53)	5911 (8)	9941 (5)	11234 (8)	72 (7)
C(54)	5761 (8)	10248 (5)	12036 (8)	79 (7)
C(55)	5229 (8)	9886 (5)	12546 (8)	67 (6)
C(56)	4847 (8)	9218 (5)	12254 (8)	34 (4)
C(61)	3198 (8)	10002 (7)	12844 (7)	49 (5)
C(62)	2619 (8)	10486 (7)	13147 (6)	59 (6)
C(63)	2333 (8)	10348 (7)	13953 (6)	67 (6)
C(64)	2627 (8)	9726 (7)	14456 (6)	53 (6)
C(65)	3207 (8)	9242 (7)	14152 (6)	51 (5)
C(66)	3492 (8)	9380 (7)	13346 (6)	40 (5)

^a Values marked with an asterisk denote equivalent isotropic U values defined as one-third of the trace of the orthogonalized U_{ij} tensor.

3 with any of the other bis(tertiary phosphine) ligands. It may be that the cis-trans motion of the metal centers becomes faster as the $-\text{CH}_2-$ bridge becomes shorter or that this motion does not occur at all as the bridge is shortened.

Reaction D. In an effort to enhance the yield of the oxidized dangler **2**, we investigated methods of oxidation stronger than merely exposing the solution to atmospheric $\text{O}_2/\text{H}_2\text{O}$. In reaction D, 30% H_2O_2 was added to either **1** or a solution of $\text{CpCoI}_2(\text{CO})$ and $\widehat{\text{P}}\text{P}$. The mixture was stirred in CH_2Cl_2 at 0–25 °C for 6–12 h. Coordinated phosphine ligands have been oxidized in this manner elsewhere.^{14,15} **2** is produced in all cases, but the yield depends markedly on the bis(tertiary phosphine). Dppm and dppb complexes of **1** afford **2** in substantial quantity, while **1** with dppe and dppp does so to a lesser extent. The data in Table I give the yields in each case after 6 h. **2** continues to form with time. The oxidation of $[\text{CpCo}(\text{dppb})\text{I}]\text{I}$ is further accentuated when the reaction is conducted in MeOH because the competing bridged product, **3**, appears not to form. An approximately equal yield

(14) Siegl, W. L.; Lapporte, S. J.; Collman, J. P. *Inorg. Chem.* **1971**, *10*, 2158.

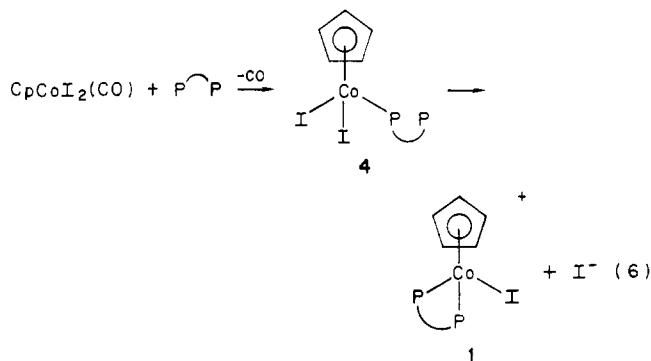
(15) Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1982**, 581.

of **1** and **2** is obtained after 6 h.

Reactions E and F. When reaction A is conducted in C_6H_6 rather than CH_2Cl_2 , evidence for the course of formation of **1** is obtained. C_6H_6 fails to support ionic charge to the same extent as CH_2Cl_2 , favoring neutral species over charged ones. Upon adding dppm, the violet solution containing $CpCoI_2(CO)$ initially turns green with liberation of CO. (In CH_2Cl_2 , **1** forms rapidly and the green species cannot be detected.) The green is characteristic of neutral complexes of the type $CpCoI_2L$, $L = PR_3$, AsR_3 ,¹⁶ as well as $CpCo[dppm(O)]I_2$ and $Cp_2Co_2I_4(\mu-dppm)$, suggesting that $CpCoI_2(P^+P^-)$ (**4**) is the first product formed. After several minutes, this green fades to brown and is accompanied by precipitation of **1**. No bridged complex **3** or oxidized dangler **2** is able to form under these conditions. The first step of the reaction of $CpCoI_2(CO)$ with P^+P^- appears, therefore, to be the liberation of CO and coordination of one end of the bis(tertiary phosphine) ligand. The chelation step is slow in C_6H_6 because charge separation is required.

Discussion

The results above imply that **1** forms stepwise by sequence 6.



Although **4** is visible only in C_6H_6 solution, where ionic charge is expected to be weakly supported, the evidence implicates **4** as the important species in further reactions of **1**. In other metal complexes, species similar to **4** are found to be short lived compared to **1**.¹⁷ The most important factor in forming **4** from **1** appears to be the chelate ring strain. However, the chelate effect and the desirability of reducing the ionic strength in the non-aqueous solvents, CH_2Cl_2 or $CDCl_3$, are countervailing forces and are separately testable. The stability of the chelate in **1** is controlled mostly by its intrinsic strain, and indeed the spontaneous conversion of **1** to **2** and **3** follows the trend expected on the basis of this strain: $dppb \gg dppm > dppe, dppp$. The desirability of reducing the ionic charge is manifested in the reduction of the stability of **1** upon the addition of excess I^- . **2** and **3** form, probably via **4**, in the order that again parallels the ring strain: $dppb > dppm > dppe, dppp$. That the equilibrium in sequence 6 is key to the longevity of **1** is further supported by the observation that **1** is indefinitely stable in a solvent, such as $MeOH$, which is effective at supporting ionic charge. Moreover, BF_4^- and PF_6^- salts of $[CpCo(dppb)I]^+$ are stable in any solvent in the absence of a coordinating ligand, such as added I^- .

The interconversion of **3** and **1** is relatively rapid by reaction 5, but the extent of the reaction continues to depend on the strain in the chelate ring. However, reaction 5 is not necessarily representative of the more intriguing and much slower transformation of **1** to **2** and **3** by reaction B. Unfortunately, how **2** and **3** form is difficult to assess. The slow rate of reaction B at room temperature attests to processes of complexity and/or low probability. **3** could form via **4** with the loss of P^+P^- , but no free P^+P^- is found in any of these reactions. It is more probable that **1** and **2** are involved in producing **3** because the reaction residue after removal of the organometallic components contains $P^+P(O)^-$ and $(O)-P^+P(O)$ on the basis of the IR and NMR spectra.¹⁸ The oxidation

of the P^+P^- ligand is interesting because, although the phosphine to phosphine oxide transformation is widely studied in transition-metal chemistry,¹⁹⁻²¹ the spontaneous oxidation of a bis(tertiary phosphine) as in **1** \rightarrow **2** is not common.²²⁻²⁴ We are mindful that the objective of this study was to delineate reaction **1**, rather than to determine the mechanism affording **2**, and are cautious about the mechanistic truth in the oxidation of substrates and ligands by metal complexes because conclusions are sometimes confounded by the low concentration and/or short life of vital intermediates. The discussion of oxidation will be directed at noting several conditions that seem important in forming **2**.

(1) The metal complex is required in reaction B for the oxidation of P^+P^- . Without it, P^+P^- is stable under the same conditions. In most metal-mediated oxidation reactions, a metal- O_2 complex is believed to be involved,^{25,26} and many dioxygen complexes of cobalt are known.^{27,28} The metal is assigned a higher formal oxidation state with concomitant reduction of O_2 . It is hard to imagine how the Co(III) center in **1** or **4** might add O_2 in this manner, but Cp ring slippage from η^5 to η^3 with accompanying coordination of O_2 to the metal is a possibility.²⁹ Despite efforts to use analytically pure metal complexes, it is possible that a trace impurity might also be responsible. For instance, $Co(PC=CP)_2^{2+}$ adds dioxygen.³⁰ Oxidation of a coordinated P(III) atom to $P^V=O$ by insertion of oxygen into the $M-P$ bond has also been proposed.^{31,32}

(2) Reaction B occurs to a lesser extent in the dark than in room light or UV illumination. Oxidation by 1O_2 is thus a possibility, but UV photolysis of the reaction in the presence of methylene blue as a 1O_2 generator did not affect the extent or rate of the formation of **2**. Alternatively, photolysis of the Co-I bond leading to I^- and a Co(II) center could occur.³³ I^- would be expected to attack and oxidize a momentarily dangling phosphine ligand. O_2 and/or H_2O could then supply an oxygen atom, leading to the highly stable phosphoryl group. Controlled experiments indicate that both O_2 and H_2O are influential in forming **2**. However, a 50-psi pressure of O_2 does not measurably affect the rate at which **2** forms, suggesting that, whatever the mechanism, O_2 , at least, is not involved in the rate-limiting step. To us, the photolytic $I^- \rightarrow$ Co(III) charge-transfer route seems most plausible, but we can only safely conclude that, whatever the agent or agents responsible for the spontaneous oxidation of **1**, they are not highly active and/or are present in low concentration. Multiple and competitive processes could be involved.

As with the spontaneous oxidation in reaction B leading to **2**, the more efficient oxidation of **1** by the addition of H_2O_2 yields **2** in amounts that nonetheless depend on the chelate ring strain: $dppb > dppm > dppe, dppp$. The initial step of H_2O_2 oxidation probably still requires the formation of **4** but then takes a different path.

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Experimental Section

All solvents were reagent grade or better and, except for the controlled-atmosphere experiments where the solvents were carefully dried and sparged with dry N_2 , were used as received. $\text{CpCo}(\text{CO})_2$ (Strem) and all bis(tertiary phosphine) ligands were used without further purification. $\text{CpCoI}_2(\text{CO})$ was prepared as before.³⁴ All reactions were carried out at 22–25 °C unless otherwise indicated. The ^1H NMR spectra ($\delta(\text{Me}_4\text{Si}) = 0.00$) were recorded on a Bruker WA250 spectrometer. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were obtained with a Bruker WM250 spectrometer with $\text{CH}_2\text{Cl}_2/\text{CDCl}_3$ (8/2, v/v) as the solvent. They are referenced to external 85% H_3PO_4 with downfield shifts being positive. IR spectra of compounds containing $\text{P}=\text{O}$ were recorded in a KBr matrix. Modes characteristic of the $\text{P}=\text{O}$ linkage appeared at about 1125 and 1188 cm^{-1} in all phosphoryl-containing compounds. Elemental analyses were performed by Microanalysis, Wilmington, DE, and are satisfactory on all new compounds. Experiments requiring an inert atmosphere were conducted in a Vacuum Atmospheres MO 40-1 drybox.

Reaction A. The synthesis and characterization of $[\text{CpCo}(\text{dppe})\text{I}]$, $[\text{CpCo}(\text{dppp})\text{I}]$, and $[\text{CpCo}(\text{dppb})\text{I}]$ are reported elsewhere.² $[\text{CpCo}(\text{dppm})\text{I}]$ was prepared as follows: dppm (0.458 g, 1.19 mmol) was added to a dark purple solution of $\text{CpCoI}_2(\text{CO})$ (0.484 g, 1.19 mmol) in 60 mL of CH_2Cl_2 . Gas (presumably CO) evolved immediately upon mixing with concomitant color change to dark brown. After the mixture was stirred for 3 h, the solvent was removed under reduced pressure. The brown residue was dissolved in CHCl_3 and separated on a silica gel column. The major band (brown) was further eluted by $\text{CHCl}_3/\text{MeOH}$ (8/2, v/v). Evaporation of the solvent yielded brown crystals (0.79 g, 90%, mp 147–148 °C). The crystal lattice entrained 1 equiv of CHCl_3 . In 3 out of 10 reactions a minor dark green band initially eluted with CHCl_3 and yielded about 0.05 g (5%) of $\text{CpCo}[\text{dppm}(\text{O})\text{I}_2]$ described below.

The reaction with dppent produced an anomalous result. The addition of dppent (0.426 g, 0.97 mmol) in CH_2Cl_2 to $\text{CpCoI}_2(\text{CO})$ (0.393 g, 0.97 mmol) produced a muddy blue solution. On a silica gel column, a large green-blue band could be eluted with CHCl_3 , which contained blue-green crystals (0.212 g, 27%) of $\text{Cp}_2\text{Co}_2\text{I}_4(\mu\text{-dppent})$. Further elution with MeOH gave a brown band containing a brown solid (0.64 g). The complex possessed no Cp signal but did contain complexed dppent with equivalent phosphorus atoms ($\delta = 38.03$) and was neutral by conductivity. A plausible formula is $\text{Co}(\text{dppent})_2\text{I}$. dppb is able to strip Cp from $\text{CpRh}(\text{CO})_2$.³⁵

$[\text{CpCo}(\text{dppb})\text{I}]^+$ salts of BF_4^- and PF_6^- were prepared in $\geq 90\%$ yield by the addition of a stoichiometric amount of AgBF_4 or AgPF_6 to $[\text{CpCo}(\text{dppb})\text{I}]$ in CH_3CN . After they were stirred for 1 h, the solutions were filtered through Celite to give the desired salts: $[\text{CpCo}(\text{dppb})\text{I}]\text{BF}_4$ (mp 169–170 °C), $[\text{CpCo}(\text{dppb})\text{I}]\text{PF}_6$ (mp 165–166 °C), and $[\text{CpCo}(\text{dppb})\text{I}]\text{BF}_4$ (mp 151–151 °C).

Reaction B. $[\text{CpCo}(\text{dppm})\text{I}]$ (20 mg) was dissolved in 1 mL of CDCl_3 and the solution monitored by ^1H NMR. The Cp signal of the chelate complex gradually diminished in intensity with growth of signals for $\text{CpCo}[\text{dppm}(\text{O})\text{I}_2]$ and $\text{Cp}_2\text{Co}_2\text{I}_4(\mu\text{-dppm})$. Integration of the peaks revealed that 20% of the chelate complex was transformed after 90 h. A similar experiment with $[\text{CpCo}(\text{dppb})\text{I}]$ resulted in a much more rapid change. Within a few hours two new Cp signals appeared, attributable to the oxidized dangler 2 and bridged complex 3. The color changed gradually from brown to blue-green. After 90 h, no chelate complex, 1, remained. When the reaction was conducted on a larger scale with 1 g of 1, the products were separated by elution with CHCl_3 on silica gel. A first dark green band contained dark green crystals of $\text{CpCo}[\text{dppb}(\text{O})\text{I}_2]$ (0.50 g, mp 150–151 °C). A slower moving blue band gave a gray-blue solid identified as $\text{Cp}_2\text{Co}_2\text{I}_4(\mu\text{-dppb})$ (0.36 g, mp 199–201 °C). This bridged complex is far less soluble in CHCl_3 than the oxidized dangler complex and, unlike the dangler, it is insoluble in acetone. This difference can also be used to separate the original reaction mixture. Washing the initial residue with acetone until the wash is colorless, followed by solvent removal, gave 2. Dissolution of the remaining residue in CH_2Cl_2 gave a blue solution containing 3 and some $\text{dppb}(\text{O})/\text{dppb}(\text{O}_2)$ as evidenced by the ^1H and ^{31}P NMR spectra and the IR spectrum.

$[\text{CpCo}(\text{dppe})\text{I}]$ and $[\text{CpCo}(\text{dppp})\text{I}]$ were unchanged after 90 h in CDCl_3 according to the ^1H NMR spectra. Likewise, $[\text{CpCo}(\text{dppb})\text{I}]\text{BF}_4$ and $[\text{CpCo}(\text{dppb})\text{I}]\text{PF}_6$ are stable in CDCl_3 .

The addition of 5 equiv of $[(n\text{-Pr})_4\text{N}]\text{I}$ to $[\text{CpCo}(\text{dppm})\text{I}]$ in CH_2Cl_2 resulted in a 5–10% conversion to 2 and 3 within 12 h. A similar reaction with $[\text{CpCo}(\text{dppb})\text{I}]$ resulted in an 82% conversion to 2 and 3. $[\text{CpCo}(\text{dppe})\text{I}]$ and $[\text{CpCo}(\text{dppp})\text{I}]$ are stable in the presence of excess

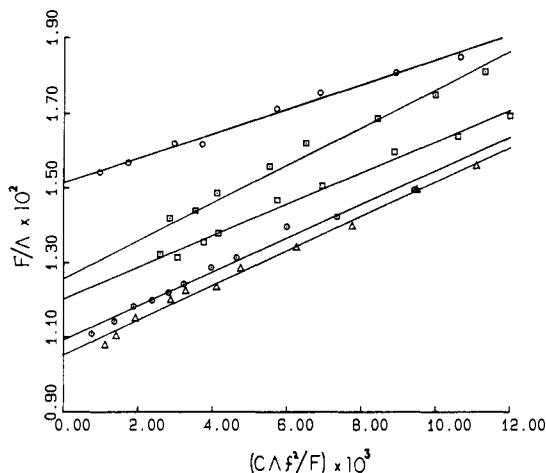


Figure 8. Fuoss plot in the concentration range of $(0.15\text{--}5.0) \times 10^{-4}$ M for $[\text{CpCo}(\text{dppb})\text{I}]$ (○), $[\text{CpCo}(\text{dppp})\text{I}]$ (□), $[\text{CpCo}(\text{dppb})\text{I}]\text{PF}_6$ (□), $[\text{CpCo}(\text{dppp})\text{I}]\text{BF}_4$ (◇), and $[\text{CpCo}(\text{dppb})\text{I}]\text{BF}_4$ (Δ).

Γ . Likewise, $[\text{CpCo}(\text{dppb})\text{I}]\text{X}$, $\text{X} = \text{BF}_4^-, \text{PF}_6^-$, is stable in CH_2Cl_2 solution until excess Γ^- (6 equiv of $[(n\text{-Pr})_4\text{N}]\text{I}$) was added, whereupon the ^1H NMR spectrum revealed a gradual conversion to 2 and 3. However, after 12 h only about 25% of the chelate complex converted, which compares with 82% when the initial complex was $[\text{CpCo}(\text{dppb})\text{I}]$.

Reaction C. A reaction otherwise the same as A, but with a 2/1 stoichiometric ratio of $\text{CpCoI}_2(\text{CO})$ to $\widehat{\text{P}}\text{P}$, resulted in a more complex product distribution. Product separation and identifications were accomplished as described for reaction B. In this reaction, however, some unreacted purple $\text{CpCoI}_2(\text{CO})$ was first eluted from the silica gel column with CHCl_3 .

In variations on reaction B, the chelate complex 1 was reacted with 1 equiv of $\text{CpCoI}_2(\text{CO})$, or $\text{Cp}_2\text{Co}_2\text{I}_4(\mu\text{-P}^*\text{P})$ was reacted with 1 equiv of $\widehat{\text{P}}\text{P}$. When $\widehat{\text{P}}\text{P} = \text{dppm}$ or dppb , 1 and 3 can be rapidly interconverted in CDCl_3 solution as evidenced by the ^1H NMR spectra. Complex 1 involving dppe or dppp is stable toward this treatment.

Reaction D. Five drops of 30% H_2O_2 were stirred in 40 mL of CH_2Cl_2 with 0.1 g of 1 for 6 h. After removal of the solvent, the residue was dissolved in CDCl_3 and the product distribution determined by ^1H NMR spectroscopy.

Reactions E and F. dppm (0.254 g, 0.66 mmol) was dissolved in 25 mL of C_6H_6 at 20 °C. $\text{CpCoI}_2(\text{CO})$ (0.268 g, 0.66 mmol) was added. Gas evolved as the violet solution became first blue and then brown within 1 min. Finally a brown precipitate identified as 1 formed.

$\text{CpCo}[\text{dppe}(\text{O})\text{I}_2]$, $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2(\text{O})$ (0.096 g, 0.23 mmol), prepared by the method of Quagliano et al.,³⁶ was dissolved in 10 mL of CH_2Cl_2 and added to $\text{CpCoI}_2(\text{CO})$ (0.094 g, 0.23 mmol) in 15 mL of CH_2Cl_2 . After it was stirred for 1.5 h, the green reaction mixture was chromatographed on silica gel. Elution with CHCl_3 produced a purple band of unreacted $\text{CpCoI}_2(\text{CO})$ followed by 0.06 g of dark green $\text{CpCo}[\text{dppe}(\text{O})\text{I}_2]$ (mp 175–176 °C). In a like manner, $\text{CpCo}[\text{dppb}(\text{O})\text{I}_2]$ was prepared to check the correspondence of this product with that of reaction B.

Determination of K_D . The dissociation constants in Table V were determined by conductance. CH_2Cl_2 was purified by distillation under an N_2 atmosphere over P_2O_5 , resulting in $\Lambda = 4.0 \times 10^{-7} \Omega^{-1} \text{cm}^{-1}$, which is negligible for these studies. Resistivities of the solution were measured at 20.0 ± 0.1 °C on a Leeds and Northrup potentiometer bridge with a range of $(0.1\text{--}2.4) \times 10^5 \Omega$. The cell used was a Yellow Springs Instrument Co. Model 2402 with a constant of 0.1163 cm^{-1} measured from the conductivity of a 0.0200 demal KCl solution.³⁷ The measurement for $[\text{CpCo}(\text{dppb})\text{I}]$ was completed within 2.5 h in order to minimize the effects of decomposition. That decomposition does not interfere is evident by the fact that the stable complex, $[\text{CpCo}(\text{dppp})\text{I}]$, has similar conductivity over this time.

The equivalent conductances were measured in the concentration range of $(0.15\text{--}5.0) \times 10^{-4}$ M. For equilibria involving ion pairs and free ions³⁸

$$F/\Delta = 1/\Lambda_0 + C\Delta^2/K_D\Lambda_0^2F \quad (7)$$

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Table VIII. Structural, Acquisition, and Refinement Details of X-ray Crystallographic Studies

	[CpCo(dppm)]I	CpCo[dppm(O)]I ₂	Cp ₂ Co ₂ I ₄ (μ-dppent)
formula	C ₃₀ H ₂₇ CoI ₂ P ₂ ·CHCl ₃	C ₃₀ H ₂₇ CoI ₂ P ₂ O	C ₃₉ H ₄₀ Co ₂ I ₄ P ₂
cryst syst	tetragonal	monoclinic	monoclinic
space group	I $\bar{4}$ (No. 82)	P2 ₁ /n (No. 14)	P2 ₁ /c (No. 14)
a, Å	18.271 (6)	8.383 (4)	14.978 (5)
b, Å		10.388 (3)	18.556 (5)
c, Å	25.496 (8)	33.16 (1)	15.011 (5)
β, deg		91.43 (3)	103.03 (2)
V, Å ³	8498.4 (61)	2887.2 (18)	4064.5 (23)
Z	8	4	4
ρ(calcd)	1.40	1.79	1.95
temp, °C	23	23	24
cryst dimens, mm	0.22 × 0.26 × 0.29	0.25 × 0.31 × 0.36	0.16 × 0.22 × 0.25
radiation		Mo Kα (λ = 0.710 73 Å)	
diffractometer		Nicolet P3	
monochromator		highly oriented graphite	
abs coeff, cm ⁻¹	45.3	28.4	39.3
transmission (max, min)	0.454, 0.366	0.213, 0.167	0.230, 0.170
scan speed, deg min ⁻¹	fixed, 5	var, 5–20	fixed, 10
2θ scan range, deg	4 ≤ 2θ ≤ 43	4 ≤ 2θ ≤ 45	4 ≤ 2θ ≤ 45
scan technique	ω	Wyckoff	2θ/θ
data collected	h, k, l	±h, k, l	±h, k, l
unique data	2219 (2417 collected)	3769 (4102 collected)	4962 (5375 collected)
unique data, F _o ≥ nσ(F _o)	1951 (n = 3)	3099 (n = 2.5)	2947 (n = 3)
std reflns	3/197 (no decay)	3/197 (4% decay)	3/197 (no decay)
R (av rednt), %	2.01	3.51	2.86
R _F , R _{wF} , %	7.21, 7.10	4.85, 5.32	6.09, 5.91
GOF	1.726	1.344	1.083
wt factor	0.001	0.001	0.001
highest pk (fdm), e Å ⁻³	0.86	0.89	0.80
mean shift/esd max	0.076	0.006	0.020

F and f_j respectively, are functions that correct for thermal motion of the ions and the activity coefficient given by eq 8. In the calculation of F ,

$$f^2 = \exp[-(8.405 \times 10^6)C^{1/2}A^{1/2}F^{1/2}/D^{3/2}T^{3/2}\Omega_0^{1/2}] \quad (8)$$

a viscosity of 4.414×10^{-3} P and a dielectric constant, D , of 9.14 D for CH₂Cl₂ at 20 °C were used.^{39,40} The dissociation constant, K_D , and the limiting equivalent conductance, Λ_0 , were obtained by plotting F/Δ vs. $CA/\Delta^2/F$ as shown in Figure 8. The resulting values of K_D and Λ_0 are given in Table V. Although the four most concentrated solutions used exceed the critical concentration limit, defined as $C_0 = (3.2 \times 10^{-7})D^3$, these few points still lie on the straight line formed by the lower concentration data and were therefore included. The error in Λ_0 and K_D is $\pm 10\%$.⁴¹

X-ray Structural Determination. In all structural determinations the computer programs used throughout were the P3 and SHELXTL (Version 4.1) packages distributed by Nicolet Corp. (Madison, WI) and were executed on the University of Delaware Data General Nova 4 computer. All specimen crystals selected for data collection were mounted on fine glass fibers with urethane varnish, which was also used to create a barrier to the atmosphere. In all cases the reflection data were corrected for Lp effects as well as for absorption by an empirical (ψ -scan) procedure (XEMP). Except for CpCo[dppm(O)]I₂, reflection profile fitting procedures were used to improve the precision in the measurement of weak reflections. Unit cell parameters were derived from the angular settings of 25 well-centered reflections ($22^\circ \leq 2\theta \leq 28^\circ$). All experimental details are summarized in Table VIII.

(i) [CpCo(dppm)]I·CHCl₃. Crystals of this complex diffracted weakly and displayed very large mosaic spread. The best of seven specimens screened showed reflection line widths at half-height of greater than 1°.

Initial photographic work and intensity data symmetry indicated 4/ m Laue symmetry, and systematic absences indicated only I centering. The allowed tetragonal space groups were $I4$, $I\bar{4}$, and $I4/m$. Statistics based upon E values strongly supported the two noncentrosymmetric alternatives, $I\bar{4}$ and $I4$. The choice of the former space group was supported ultimately by the solution and chemically reasonable refinement of the structure in $I\bar{4}$.

The direct-methods routine SOLV provided an E map with the positions of the I and Co atoms. Subsequent difference Fourier syntheses located the remaining non-hydrogen atoms, including a highly disordered mole-

cule of CHCl₃ for each Co complex ion. At least two partially occupied CHCl₃ sites were evident. Despite various attempts to model the disorder, it became apparent that a multitude of unresolvable orientations exists at each site. Occupancies of the CHCl₃ sites were constrained to one full CHCl₃ molecule.

In the final blocked-cascade refinement cycles, the model used was as follows: all non-hydrogen atoms anisotropic except for the carbon atoms in the Cp and benzene rings and in the CHCl₃ molecule; the Cp and benzene rings constrained to rigid, planar bodies; all hydrogen atoms placed in idealized and updated positions ($d(C-H) = 0.96$ Å). Enantiomorphic inversion produced significantly larger residuals ($R_F = 7.38$, $R_{wF} = 7.26\%$).

(ii) CpCo[dppm(O)]I₂. Systematic absences in the intensity data uniquely defined the space group as $P2_1/n$. Solution and refinement procedures were the same as used for [CpCo(dppm)]I·CHCl₃.

(iii) Cp₂Co₂I₄(μ-dppent). Systematic absences in the intensity data uniquely defined the space group as $P2_1/c$. Solution and refinement procedures were the same as used for [CpCo(dppm)]I·CHCl₃, except that the Cp rings were refined anisotropically. During the final stages of refinement, two carbon atoms, C(2) and C(23), became nonpositive definite and were refined isotropically.

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Registry No. [CpCo(dppm)]I, 94890-27-4; [CpCo(dppm)]I·CHCl₃, 94890-28-5; [CpCo(dppe)]I, 32842-39-0; [CpCo(dppp)]I, 89463-02-5; [CpCo(dppp)]I·BF₄, 94890-30-9; [CpCo(dppb)]I, 89463-03-6; [CpCo(dppb)]I·BF₄, 94904-34-4; [CpCo(dppb)]I·PF₆, 94890-32-1; CpCo[dppm(O)]I₂, 94890-33-2; CpCo[dppe(O)]I₂, 94890-34-3; CpCo[dppp(O)]I₂, 94890-35-4; CpCo[dppb(O)]I₂, 94904-35-5; Cp₂Co₂I₄(μ-dppm), 94890-36-5; Cp₂Co₂I₄(μ-dppe), 94890-37-6; Cp₂Co₂I₄(μ-dppp), 94890-38-7; Cp₂Co₂I₄(μ-dppb), 94890-39-8; Cp₂Co₂I₄(μ-dppent), 94890-40-1; [CpCo(dppm)]I⁺, 94890-41-2; [CpCo(dppe)]I⁺, 47752-10-3; [CpCo(dppp)]I⁺, 94890-29-6; [CpCo(dppb)]I⁺, 94890-31-0; Co(dppent)₂I, 94890-42-3; CpCo₂(CO), 12012-77-0; dppe(O), 984-43-0; dppb(O), 85686-00-6; dppm, 2071-20-7; dppe, 1663-45-2; dppp, 6737-42-4; dppb, 7688-25-7; dppent, 27721-02-4; [(n-Pr)₄N]I, 631-40-3; [(n-Pr)₄N]⁺, 13010-31-6.

Supplementary Material Available: Listings for each of the three crystal structures of bond angles, anisotropic temperature factors, hydrogen atom coordinates, and observed and calculated structure factors (59 pages). Ordering information is given on any current masthead page.

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