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Complexes of Functional Phosphines. 23.[1] PPh_3 and β-Ketophosphine Complexes of Cobalt(II). Crystal and Molecular Structures of $CoCl_2[Ph_2PCH_2C(O)Ph]_2$ and $Co_2(CO)_6[Ph_2PCH_2C(O)Ph]_2$ and of the Trinuclear, Mixed-Metal Complex $[(Ph_3P)_2Ag(\mu\text{-}Cl)_2Co(\mu\text{-}Cl)_2Ag(PPh_3)_2]\cdot 0.5OEt_2$

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The solution chemistry of cobalt(II) ketophosphine complexes $CoX_2[Ph_2PCH_2C(O)Ph]_2$ (**1a**, X = Cl; **1b**, X = Br; **1c**, X = I) has been examined and compared to that of $[CoX_2(PPh_3)_2]$ (**2a**, X = Cl; **2b**, X = Br; **2c**, X = I). All the complexes undergo a tetrahedral–octahedral equilibrium in methanol. This is facilitated by solvent coordination rather than by the ligand's keto functions. Some degree of ligand displacement also occurs. The crystal structure of **1a** has been elucidated, showing a pseudotetrahedral cobalt(II) geometry. A long interligand hydrogen-bond, not present in powder samples, is observed between the methylene group of a $Ph_2PCH_2C(O)Ph$ ligand and the ketone function of the other $Ph_2PCH_2C(O)Ph$ ligand. **1a** reacts with $Na[Co(CO)_4]$ to afford the crystallographically characterized, metal–metal bonded centrosymmetric complex $Co_2(CO)_6[Ph_2PCH_2C(O)Ph]_2$ (**5**) (Co–Co = 2.666(1) Å). The reactivity of **1a** with $AgBF_4$ and $TlPF_6$ has also been examined and compared to that of **2a** where the latter is reacted in the presence and absence of excess phosphine. Notable reaction products include the square planar cobalt(II) complex $[Co\{Ph_2PCH_2C(O)Ph\}\{Ph_2PCH_2C(O)Ph\}Cl]PF_6$ (**6**), which slowly transforms in solution to the octahedral complex $[Co\{Ph_2PCH_2C(O)Ph\}_2\{Ph_2PCH_2C(O)Ph\}Cl]PF_6$ (**7**). Reaction with $AgBF_4$ under similar conditions affords the silver phosphine complex $Ag\{Ph_2PCH_2C(O)Ph\}_2Cl$ (**8**). **2a** reacts with $AgBF_4$ to give $[Ag(PPh_3)_2]BF_4$, but additionally in the presence of PPh_3 gives $(Ph_3P)_2Ag(\mu\text{-}Cl)_2Co(\mu\text{-}Cl)_2Ag(PPh_3)_2$ (**13**). The latter formulation involving a central $CoCl_4^{2-}$ core, and an almost linear Ag–Co–Ag arrangement has been confirmed by single-crystal X-ray diffraction. The solid state structures of **1a**, **5**, and **13**·$0.5OEt_2$ have been determined by single-crystal X-ray analysis. **1a** crystallizes in the monoclinic space group $P2_1/c$ with $Z = 4$ in a unit cell of dimensions $a = 10.985(2)$ Å, $b = 17.236(4)$ Å, $c = 19.547(4)$ Å, and $\beta = 104.87(2)°$. **5** crystallizes in the triclinic space group $P\bar{1}$ with $Z = 1$, $a = 8.916(2)$ Å, $b = 11.177(7)$ Å, $c = 12.009(4)$ Å, $\alpha = 81.15(5)°$, $\beta = 76.39(2)°$, and $\gamma = 67.47(3)°$. Complex **13**·$0.5OEt_2$, crystallizes in the monoclinic space group $P2_1/c$ with $Z = 8$, $a = 21.840(5)$ Å, $b = 17.664(6)$ Å, $c = 36.890(7)$ Å, and $\beta = 93.14(2)°$.

Introduction

Functional phosphine ligands which contain two types of inequivalent donors often lead to a more subtle control of the coordination sphere of the metal centers to which they are bound and to improved catalytic properties over their corresponding monodentate phosphines.[2] The more weakly bonded donor can temporarily occupy and protect a coordination site at the metal center, allowing intramolecular control of coordinative unsaturation. Complexes containing hemilabile oxygen functions, such as ketones, esters, or ethers, have proved to be of considerable utility, although the role of the labile function varies. Their activity as intramolecular solvent-like donors, which are readily displaced by coordinating substrates, has provided enhanced cobalt and rhodium carbonylation catalysts.[3–5] Coordination of the functional group can also enhance reactivity, such as oxidative addition[6] or ligand transformations,[7] while resulting conformational changes and phosphine-substrate hydrogen bonding may increase the stereospecificity of hydrogenation catalysts, as in the synthesis of L-dopa.[8,9]

However, despite the wide-spread application of functional phosphines, studies have almost exclusively concentrated on square planar and octahedral coordination geometries.[2,10] Tetrahedral cobalt(II) ether–phosphine complexes have been reported, although they primarily serve as precursors for cobalt(I) compounds.[11] Thus, we report here the synthesis and reactivity of cobalt(II) and cobalt(0) complexes with the ketophosphine ligand $Ph_2PCH_2C(O)Ph$.

Results

Reactivity of $Ph_2PCH_2C(O)Ph$ Complexes. The complexes $CoX_2[Ph_2PCH_2C(O)Ph]_2$ (**1a**, X = Cl; **1b**, X = Br; **1c**, X = I)

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(1) Part 22. Braunstein, P.; Kelly, D. G.; Tiripicchio, A.; Ugozzoli, F.; *Inorg. Chem.* **1993**, *32*, 4845.

(2) Bader, A.; Lindner, E. *Coord. Chem. Rev.* **1991**, *108*, 27 and references cited therein.

(3) Lindner, E.; Sickinger, A.; Wegner, P. *J. Organomet. Chem.* **1988**, *349*, 75.

(4) Lindner, E.; Glaser, P. *J. Organomet. Chem.* **1990**, *391*, C37.

(5) Wegman, R. W.; Abatjoglou, A. G.; Harrison, A. M. *J. Chem. Soc., Chem. Commun.* **1987**, 1891.

(6) Miller, E. M.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1974**, 480.

(7) Werner, H.; Stark, A.; Schulz, M.; Wolf, J. *Organometallics* **1992**, *11*, 1126.

(8) Knowles, W. S. *Acc. Chem. Res.* **1983**, *16*, 106.

(9) (a) Descotes, G.; Lafont, D.; Sinou, D.; Brown, J. M.; Chaloner, P. A. *Nouv. J. Chim.* **1981**, *5*, 167. (b) Brown, J. M.; Chaloner, P. A.; Nicholson, P. N. *J. Chem. Soc., Chem. Commun.* **1978**, 646.

(10) Klein, H.-F.; Karsch, H. H. *Inorg. Chem.* **1974**, *14*, 473.

(11) Lindner, E.; Schrober, U.; Glaser, E.; Norz, H.; Wegner, P. *Z. Naturforsch. B.* **1987**, *42*, 1527.

0020-1669/94/1333-0233$04.50/0

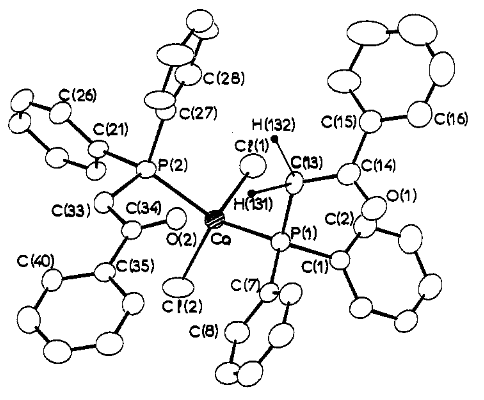


Figure 1. ORTEP plot of $CoCl_2[Ph_2PCH_2C(O)Ph]_2$ (**1a**) with the atomic numbering scheme.

Table I. Electronic Spectra for the Complexes $CoX_2[Ph_2PCH_2C(O)Ph]_2$ (**1a–c** and **2a–c**) and $CoX_2(PPh_3)_2$ (**3a–c** and **4a–c**) in Methanol and Dichloromethane

complex	electronic spectral data, nm[a]	ν(C=O), cm^{-1}
1a[b]	668 (275) 628 (290) 590 (225)	1674
1b[b]	685 (320) 655 (340) 610 sh	1674
1c[b]	760 (370) 721 (640) 687 (620) 643 (380)	1676
2a[b]	737 (500) 636 (745) 608 (710)	
2b[b]	753 (620) 665 (960) 640 sh	
2c[b]	794 (825) 725 (1125) 687 (735)	
3a[c]	520 (19)	1678
3b[c]	545 (21)	1678
3c[c]	558 (47)	1679
4a[c]	521 (15) 485 sh	
4b[c]	520 (9) 457 sh	
4c[c]	505 (12) 473 (11)	

[a] Extinction coefficients in parentheses, mol^{-1} cm^{-1} dm^3. [b] Recorded in dichloromethane. [c] Recorded in methanol.

were readily synthesized from anhydrous cobalt(II) chloride for **1a** or by anion exchange for **1b** and **1c**.[1] The compounds are blue, green and brown, respectively, in the solid state; colors which correspond to those of the extensively studied $CoX_2(PPh_3)_2$ analogues.[12] Magnetic susceptibility and infrared data suggest that the complexes are pseudotetrahedral and contain uncoordinated ketone functions, conclusions corroborated by the X-ray structure determination of **1a**, Figure 1. An additional feature of the crystalline compound, not observed in solution or for amorphous samples, is the presence of a single intramolecular $>C{=}O\cdots H{-}CH<$ hydrogen interaction between the two ketophosphine ligands (see Discussion). Complexes **1a** and **1b** dissolve in common solvents (ethanol, THF, or dichloromethane) to give blue or green solutions, respectively. **1c** appears green or brown depending on the solvent used, but is consistently recovered from solution as a brown solid. Electronic spectra were recorded for CH_2Cl_2 solutions and are essentially similar to those of the triphenylphosphine complexes, Table I, although considerably lower molar extinction coefficients were observed (see Discussion). However, there is no infrared evidence for P,O chelation in solutions of these complexes.

When **1a–c** are dissolved in methanol the intense colors of the complexes are replaced by pale pink or brown solutions. When heated, the original blue, green, and green/brown solutions are restored which again become pale on cooling. The electronic spectra of these solutions show none of the bands associated with **1a–c** in other solvents. Instead weak bands in the visible region, typical of octahedral cobalt(II), are recorded. Infrared spectra of these methanol solutions continue to exhibit stretches assignable to uncoordinated keto functional groups.

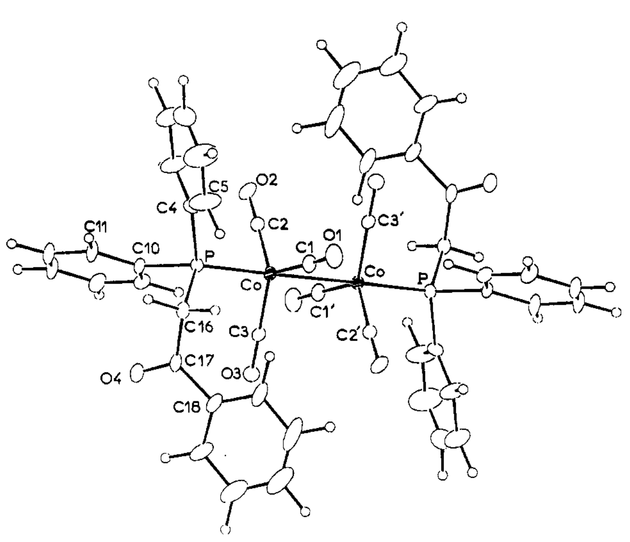
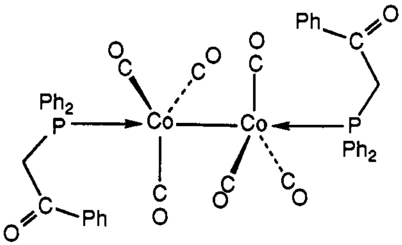


Figure 2. ORTEP plot of $Co_2(CO)_6[Ph_2PCH_2C(O)Ph]_2$ (**5**) with the atomic numbering scheme.

Attempts to generate organometallic derivatives of **1a** via reaction with $Na[Co(CO)_4]$ resulted in the isolation of the complex $Co_2(CO)_6[Ph_2PCH_2C(O)Ph]_2$ (**5**). Solution infrared spectra show a strong ν(CO) band at 1954 cm^{-1} which typifies axially substituted dicobalt hexacarbonyl complexes.[13] An axial substitution is confirmed for **5** in the solid state by an X-ray structure determination, Figure 2. Similar $[Co(CO)_4]^-$ oxidations to give the axial phosphine derivatives $Co_2(CO)_6(PR_3)_2$ have also been observed in reactions with Pt(II) complexes.[14] There is a continuing interest in the synthesis of such complexes[15] owing to their extensive use as hydroformylation and selective hydrogenation catalysts. Complex **5** is readily oxidized by iodine, and although the reaction yields a green cobalt(I) intermediate (IR(KBr): ν(C≡O) 1991 m, 1953 w, 1925 m, ν(C=O) 1675 s. $^{31}P\{^1H\}$ NMR (C_6D_6/THF): δ 50.5 s), it is accompanied by CO evolution; thus, further oxidation and total loss of CO appears unavoidable. Cobalt(I) compounds of general formula $CoI(CO)_3(PR_3)$ are well-known; however, further oxidation has been observed for other cobalt(I) carbonyl derivatives which leads to the formation of CoI_2.[16] The composition of the final paramagnetic complex formed here could not be fully determined, however, total CO loss and the presence of P-bound ketophosphine are apparent from the compound's IR spectrum. Thus the compound may be similar to the crystallographically characterized $[CoI(\mu\text{-}I)(PPh_3)]_2$.[17]



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The reaction of **1a** with 2 equiv of $TlPF_6$ might be expected to generate a dicationic complex by substitution of the chloride

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[12] Cotton, F. A.; Faut, O. D.; Goodgame, D. M. L.; Holm, R. H. *J. Am. Chem. Soc.* **1961**, *83*, 1780.

[13] (a) Vohler, O. *Chem. Ber.* **1958**, *91*, 1235; (b) Manning, A. R. *J. Chem. Soc. A* **1968**, 1135.

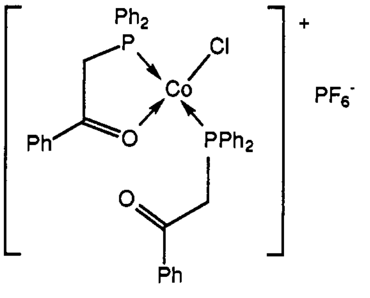
[14] (a) Braunstein, P.; Dehand, J.; Nennig, J.-F. *J. Organomet. Chem.* **1975**, *92*, 117. (b) Barbier, J.-P.; Braunstein, P.; Fischer, J.; Ricard, L. *Inorg. Chim. Acta* **1978**, *31*, L361.

[15] Paciello, R. A. *Organometallics*, **1993**, *12*, 565.

[16] Heck, R. F. *J. Am. Chem. Soc.* **1964**, *86*, 5138.

[17] (a) Pierrard, J.-C.; Rimbault, J.; Hugel, R. *J. Chem. Res., Synop.* **1984**, *10*, 316. (b) Gorter, S.; Hinrichs, W.; Reedijk, J.; Rimbault, J.; Pierrard, J.-C.; Hugel, R. *Inorg. Chim. Acta* **1985**, *105*, 181.

anions. In fact, a brown monocationic complex, **6**, is formed. Spectroscopic and magnetic data allow the formulation of a trans square planar structure. Attempts to fully abstract the available chloride anions by prolonged reaction times, heating, or the addition of excess $TlPF_6$ all failed.



6

Complex **6** is unstable in solution and rearranges over *ca.* 7 d to give the pale pink crystalline complex $\mathbf{7}\cdot CH_2Cl_2$. The nature of **7** can be derived with confidence on the basis of spectroscopic evidence and appears to result simply from the intermolecular transfer of a phosphine ligand to afford $[Co\{Ph_2PCH_2C(O)Ph\}_2\{Ph_2PCH_2C(O)Ph\}Cl]PF_6$. Unfortunately, the geometric arrangement around the octahedral cobalt(II) center cannot be assigned without crystallographic evidence.

Reaction of **1a** with 2 equiv of $AgBF_4$ results in the precipitation of a pale purple light sensitive solid. X-ray powder diffraction confirms the presence of AgCl in this precipitate, and BF_4^- is detected by its strong infra-red absorption. Characterization of the remaining soluble material indicates the presence of $Ag[Ph_2PCH_2C(O)Ph]_2Cl$ (**8**) as the unique solution product. The

$$CoCl_2[Ph_2PCH_2C(O)Ph]_2 + 2AgBF_4 \rightarrow \underset{\mathbf{8}}{Ag[Ph_2PCH_2C(O)Ph]_2Cl} + AgCl + Co(BF_4)_2 \quad (1)$$

^1H NMR spectrum of **8** exhibits a doublet at δ 4.08 [$^2J(PH)$ = 6.7 Hz] corresponding to the PCH_2 protons. Comparison with conventionally synthesized **8**, as well as $Ag[Ph_2PCH_2C(O)Ph]Cl$ (**9**), $Ag[Ph_2PCH_2C(O)Ph]BF_4$ (**10**), and $[Ag\{Ph_2PCH_2C(O)Ph\}_2]BF_4$ (**11**), indicates these PCH_2 resonances are unique to each complex of this series (see Experimental Section). $^{31}P\{^1H\}$ NMR spectra were also recorded for **8–11** and for silver(I) complexes of PPh_3 (see below). In all cases the complexes undergo rapid phosphine exchange at ambient temperature, and under these conditions silver(I)–phosphorus coupling is unresolved. Coupling is apparent in the low-temperature spectrum of **10** and has previously been reported for $[Ag(PPh_3)_2]^+$ (δ 15.3 ppm, $^1J(Ag\text{–}P)$ = 507 Hz at 193 K),[18] suggesting that the complexes do not exhibit anomalous behavior. However, since ^1H spectra yield unique PCH_2 resonances for **8–11** at ambient temperature these were used to identify the reaction products in preference to low-temperature $^{31}P\{^1H\}$ NMR. Thus, the reaction of **1a** with $AgBF_4$ gives **8** as the sole product with no anion scrambling or equilibrium between mono- and bis(phosphine) complexes. Attempts to stabilize a cobalt(II) complex in the presence of $AgBF_4$ by using the nominally octahedral methanol adduct **3a** resulted in the same reaction products as eq 1.

Reactivity of PPh_3 Complexes. In view of the interesting behavior of **1a–c** in methanol, the solution properties of the corresponding PPh_3 complexes, **2a–c**, were examined. The compounds exhibit the expected blue, green, and brown colors, respectively, in ethanol, THF, and dichloromethane; the electronic spectra of the compounds in the latter solvent are in agreement with those previously reported, Table I. However, thermally reversible pale pink compounds are formed in methanol, **4a–c**, and allylic alcohol. A series of equilibria appear to exist in these solvents. **4a–c** can be recovered from these solutions and can indeed by synthesized in methanol. However, some degree of ligand displacement must also occur, since free PPh_3 has also been recovered from a methanol solution of **4b**.

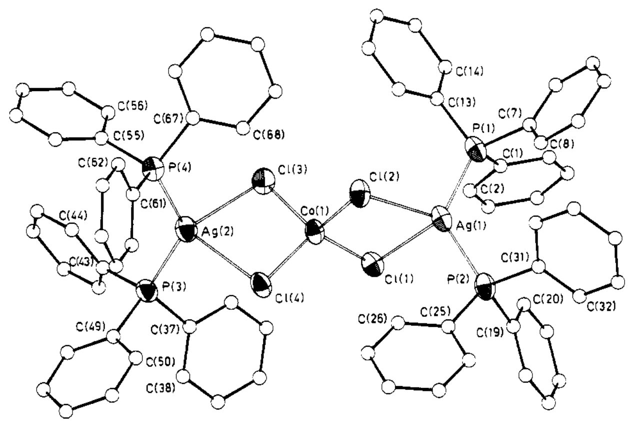


Figure 3. View of the structure of one of the two independent complexes $[(Ph_3P)_2Ag(\mu\text{-}Cl)_2Co(\mu\text{-}Cl)_2Ag(PPh_3)_2]$ in $\mathbf{13}\cdot 0.5OEt_2$ with the atomic numbering scheme.

To further elucidate the role of the keto function in the reactivity of **1a** with $TlPF_6$ and $AgBF_4$, control reactions were performed using **2a**. In addition reactions were carried out in the presence of 2 equiv of PPh_3 to provide comparisons with the stabilizing role of the keto ligand function of $Ph_2PCH_2C(O)Ph$. **2a** reacts with 2 equiv of $AgBF_4$ to yield the silver complex $[Ag(PPh_3)_2]BF_4$ (**12**) with the precipitation of AgCl. Thus the reactivity is similar to that of **1a**, but BF_4^- is the counteranion rather than Cl^-. **12** is also formed in the presence of excess PPh_3, along with a second complex, **13**. Separation of the compounds leads to the identification of **13** as the silver–cobalt complex $Ag_2(PPh_3)_4CoCl_4$. The latter was recrystallized from CH_2Cl_2/Et_2O to afford $\mathbf{13}\cdot 0.5\,OEt_2$ which was characterized by single-crystal X-ray diffraction (Figure 3).

The reaction of $TlPF_6$ with **2a** is influenced by the presence of moisture. Thus, partial hydrolysis of $TlPF_6$ results in the isolation of free phosphine (formed in ca. 33% yield) and a second solution product. The latter was identified as $[Ph_3PH]PF_6$ (**14**) and formed by the protonation of PPh_3 in the presence of the PF_6^- counterion. Under rigorously anhydrous conditions, the blue complex **2a** reacts (irrespective of the presence of excess ligand) to give an unstable emerald green product **15**. Complete characterization of the latter has proved difficult; however, a tentative formulation can be made on the basis of the following evidence. PF_6^- anions are clearly identified by $^{31}P\{^1H\}$ NMR, these cannot be derived from $TlPF_6$ since their intensity greatly exceeds that expected from the poorly soluble thallium salt. Replacement of Cl^- by PF_6^- at the cobalt(II) center must therefore occur. However, further $^{31}P\{^1H\}$ NMR studies indicate that **15** is unstable in solution, liberating free PPh_3 and regenerating the blue coloration of **2a**, and **2a** is indeed recovered from solution. Since Cl^- and PF_6^- must be present in **15** and since the complex liberates PPh_3 on rearrangement back to **2a**, we can tentatively suggest **15** is a complex of the form $[CoCl(PPh_3)_2]PF_6$. Moreover, as the latter would contain three-coordinate cobalt, stabilization via halide bridging may occur to give $[Co(\mu\text{-}Cl)(PPh_3)_2]_2(PF_6)_2$.

Description of the Crystal Structure of $CoCl_2[Ph_2PCH_2C(O)Ph]_2$ (1a). The molecular conformation, Figure 1, shows a tetrahedral $[CoCl_2P_2]$ cobalt centre with uncoordinated keto functions. Selected bond distances and angles are given in Table II. Bond lengths within the two ligands are identical but the two phosphines lie in different orientations relative to the metal center. The $-CH_2C(O)Ph$ functions are thus inversely positioned with respect to cobalt, with Co···O(1) = 5.354 Å, Co···C(13) = 3.373

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[18] Alyea, E. C.; Malito, J.; Nelson, J. H. *Inorg. Chem.* **1987**, *26*, 4294.

Table II. Selected Bond Distances (Å) and Angles (deg) in $CoCl_2[Ph_2PCH_2C(O)Ph]_2$ (**1a**)

Co–Cl(1)	2.216(2)	Co–Cl(2)	2.196(2)
Co–P(1)	2.397(2)	Co–P(2)	2.402(2)
P(1)–C(1)	1.815(6)	P(2)–C(21)	1.814(6)
P(1)–C(7)	1.808(7)	P(2)–C(27)	1.814(7)
P(1)–C(13)	1.833(7)	P(2)–C(33)	1.826(7)
C(13)–C(14)	1.51(1)	C(33)–C(34)	1.48(1)
C(14)–O(1)	1.195(8)	C(34)–O(2)	1.221(8)
C(14)–C(15)	1.49(1)	C(34)–C(35)	1.483(9)
Cl(1)–Co–Cl(2)	117.9(1)	P(1)–Co–Cl(2)	111.0(1)
P(1)–Co–Cl(1)	105.3(1)	P(2)–Co–Cl(1)	102.5(1)
P(2)–Co–Cl(2)	106.9(1)	P(1)–Co–P(2)	113.1(1)
Co–P(1)–C(1)	111.5(2)	Co–P(2)–C(21)	113.4(2)
Co–P(1)–C(7)	120.1(2)	Co–P(2)–C(27)	115.8(2)
Co–P(1)–C(13)	105.0(2)	Co–P(2)–C(33)	115.2(2)
C(1)–P(1)–C(13)	106.0(3)	C(21)–P(2)–C(33)	99.5(3)
C(7)–P(1)–C(13)	109.4(3)	C(27)–P(2)–C(33)	107.8(3)
C(1)–P(1)–C(7)	104.1(3)	C(21)–P(2)–C(27)	103.2(3)
P(1)–C(13)–C(14)	118.7(4)	P(2)–C(33)–C(34)	114.1(5)
C(13)–C(14)–O(1)	120.1(7)	C(33)–C(34)–O(2)	119.9(6)
C(13)–C(14)–C(15)	118.5(6)	C(33)–C(34)–C(35)	118.9(6)

Table III. Selected Bond Distances (Å) and Angles (deg) for $Co_2(CO)_6[Ph_2PCH_2C(O)Ph]_2$ (**5**)[a]

Co–Co	2.666(1)	P(1)–C(4)	1.830(5)
Co–C(1)	1.784(7)	P(1)–C(10)	1.801(7)
Co–C(2)	1.754(7)	P(1)–C(16)	1.827(6)
Co–C(3)	1.772(5)	Co–P(1)	2.171(2)
C(1)–O(1)	1.136(9)	C(16)–C(17)	1.509(7)
C(2)–O(2)	1.150(8)	C(17)–O(4)	1.202(9)
C(3)–O(3)	1.132(6)	C(17)–C(18)	1.483(9)
Co–Co–P(1)	177.60(8)	C(1)–Co–C(2)	119.4(3)
Co–Co–C(1)	86.8(2)	C(1)–Co–C(3)	119.4(3)
Co–Co–C(3)	83.4(2)	Co–Co–C(2)	84.8(2)
Co–P(1)–C(4)	113.5(2)	C(2)–Co–C(3)	118.9(3)
Co–P(1)–C(10)	116.5(2)	C(4)–P(1)–C(10)	103.3(3)
Co–P(1)–C(16)	116.4(2)	C(4)–P(1)–C(16)	101.6(3)
Co–C(1)–O(1)	178.2(5)	C(10)–P(1)–C(16)	103.7(3)
Co–C(2)–O(2)	177.8(5)	C(16)–C(17)–O(4)	119.0(5)
Co–C(3)–O(3)	178.6(6)	C(16)–C(17)–C(18)	121.4(6)
P(1)–Co–C(1)	95.3(2)	O(4)–C(17)–C(18)	119.5(5)
P(1)–Co–C(2)	93.2(2)	C(17)–C(18)–C(19)	116.1(7)
P(1)–Co–C(3)	96.5(2)	C(17)–C(18)–C(23)	123.3(5)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table IV. Selected Bond Distances (Å) and Angles (deg) for $[(Ph_3P)_2Ag(\mu\text{-}Cl)_2Co(\mu\text{-}Cl)_2Ag(PPh_3)_2]\cdot 0.5OEt_2$ (**13**·$0.5OEt_2$)

Ag(1A)–Cl(1A)	2.776(6)	Ag(1B)–Cl(1B)	2.718(7)
Ag(1A)–Cl(2A)	2.719(6)	Ag(1B)–Cl(2B)	2.687(6)
Ag(1A)–P(1A)	2.439(7)	Ag(1B)–P(1B)	2.419(10)
Ag(1A)–P(2A)	2.442(7)	Ag(1B)–P(2B)	2.440(7)
Ag(2A)–Cl(3A)	2.727(6)	Ag(2B)–Cl(3B)	2.728(6)
Ag(2A)–Cl(4A)	2.740(6)	Ag(2B)–Cl(4B)	2.749(6)
Ag(2A)–P(3A)	2.465(7)	Ag(2B)–P(3B)	2.455(6)
Ag(2A)–P(4A)	2.438(7)	Ag(2B)–P(4B)	2.462(6)
Co(1A)–Cl(1A)	2.271(6)	Co(1B)–Cl(1B)	2.277(7)
Co(1A)–Cl(2A)	2.278(7)	Co(1B)–Cl(2B)	2.273(6)
Co(1A)–Cl(3A)	2.274(7)	Co(1B)–Cl(3B)	2.269(6)
Co(1A)–Cl(4A)	2.283(6)	Co(1B)–Cl(4B)	2.268(6)
P(1A)–C(1A)	1.819(16)	P(1B)–C(1B)	1.873(21)
P(1A)–C(7A)	1.885(38)	P(1B)–C(7B)	1.708(24)
P(1A)–C(7C)	1.779(36)	P(1B)–C(13B)	1.912(34)
P(1A)–C(13A)	1.798(16)	P(2B)–C(19B)	1.795(17)
P(2A)–C(19A)	1.838(16)	P(2B)–C(25B)	1.776(18)
P(2A)–C(25A)	1.830(14)	P(2B)–C(31B)	1.828(18)
P(2A)–C(31A)	1.803(42)	P(3B)–C(37B)	1.820(13)
P(2A)–C(31C)	1.809(39)	P(3B)–C(43B)	1.799(12)
P(3A)–C(37A)	1.816(17)	P(3B)–C(49B)	1.838(13)
P(3A)–C(43A)	1.799(16)	P(4B)–C(55B)	1.803(15)
P(3A)–C(49A)	1.822(16)	P(4B)–C(61B)	1.798(15)
P(4A)–C(55A)	1.781(16)	P(4B)–C(67B)	1.815(15)
P(4A)–C(61A)	1.803(17)		
P(4A)–C(67A)	1.832(16)		
P(1A)–Ag(1A)–P(2A)	128.4(2)	P(1B)–Ag(1B)–P(2B)	126.7(3)
Cl(2A)–Ag(1A)–P(2A)	112.4(2)	Cl(2B)–Ag(1B)–P(2B)	113.4(3)
Cl(2A)–Ag(1A)–P(1A)	111.2(2)	Cl(2B)–Ag(1B)–P(1B)	99.6(3)
Cl(1A)–Ag(1A)–P(2A)	103.9(2)	Cl(1B)–Ag(1B)–P(2B)	101.2(2)
Cl(1A)–Ag(1A)–P(1A)	109.1(2)	Cl(1B)–Ag(1B)–P(1B)	123.9(3)
Cl(1A)–Ag(1A)–Cl(2A)	80.8(2)	Cl(1B)–Ag(1B)–Cl(2B)	83.5(2)
P(3A)–Ag(2A)–P(4A)	132.1(2)	P(3B)–Ag(2B)–P(4B)	132.9(2)
Cl(4A)–Ag(2A)–P(4A)	115.3(2)	Cl(4B)–Ag(2B)–P(4B)	108.6(2)
Cl(4A)–Ag(2A)–P(3A)	98.9(2)	Cl(4B)–Ag(2B)–P(3B)	106.6(2)
Cl(3A)–Ag(2A)–P(4A)	103.0(2)	Cl(3B)–Ag(2B)–P(4B)	106.2(2)
Cl(3A)–Ag(2A)–P(3A)	115.2(2)	Cl(3B)–Ag(2B)–P(3B)	109.5(2)
Cl(3A)–Ag(2A)–Cl(4A)	80.7(2)	Cl(3B)–Ag(2B)–Cl(4B)	80.8(2)
Cl(3A)–Co(1A)–Cl(4A)	101.9(3)	Cl(3B)–Co(1B)–Cl(4B)	102.9(3)
Cl(2A)–Co(1A)–Cl(4A)	109.5(3)	Cl(2B)–Co(1B)–Cl(4B)	115.2(3)
Cl(2A)–Co(1A)–Cl(3A)	113.8(3)	Cl(2B)–Co(1B)–Cl(3B)	110.8(3)
Cl(1A)–Co(1A)–Cl(4A)	117.1(3)	Cl(2B)–Co(1B)–Cl(3B)	110.8(3)
Cl(1A)–Co(1A)–Cl(3A)	111.9(3)	Cl(1B)–Co(1B)–Cl(3B)	111.6(3)
Cl(1A)–Co(1A)–Cl(2A)	103.1(3)	Cl(1B)–Co(1B)–Cl(2B)	104.6(3)
Ag(1A)–Cl(1A)–Co(1A)	87.3(2)	Ag(1B)–Cl(1B)–Co(1B)	85.4(2)
Ag(1A)–Cl(2A)–Co(1A)	88.6(2)	Ag(1B)–Cl(2B)–Co(1B)	86.3(2)
Ag(2A)–Cl(3A)–Co(1A)	88.8(2)	Ag(2B)–Cl(3B)–Co(1B)	88.4(2)
Ag(2A)–Cl(4A)–Co(1A)	88.3(2)	Ag(2B)–Cl(4B)–Co(1B)	87.9(2)

Å, Co···O(2) = 3.598 Å, and Co···C(33) = 5.458 Å. This conformation results in a weak interaction between H(131) of the $H_2C(13)$ group and O(2): the H-bonding distance is long, 2.57(6) Å, and therefore the strength of the interaction cannot be great [O(2)···C(13) = 3.333(8) Å, C(13)–H(131)–O(2) = 131(3)°, C(34)–O(2)–H(131) = 160(3)°].[19] However, this secondary ligand interaction is consistent with the infrared spectrum of crystalline **1a**. Two ν(CO) bands are observed at 1678 and 1660 cm^{-1}, compared with the free ligand value of 1670 cm^{-1}. Thus the H-bonding interaction significantly affects both ketone groups. In contrast, a single ν(CO) stretch, at *ca.* 1670 cm^{-1}, is recorded for both powder samples and solutions of **1a**. Therefore, in view of the relative long H-bond, and its absence from powder samples, it would be unwise to conclude that the interaction is more than a favorable crystal packing effect.

Description of the Crystal Structure of $Co_2(CO)_6[Ph_2PCH_2C(O)Ph]_2$ (5). The molecular structure is shown in Figure 2. Selected bond distances and angles are given in Table III. The molecule exhibits a center of symmetry at the middle of the metal–metal bond. The geometry about each Co atom is trigonal bipyramidal with three equatorial carbonyls and a phosphine ligand trans to the other Co atom (P–Co–Co = 177.60(8)°). The three carbonyl ligands are linear (Co–C–O > 177.8°), but the P–Co–C(carbonyl) angles (95.3, 93.2, 96.5) indicate a slight tripod-type bending toward the inside of the molecule. The centrosymmetry implies a perfectly staggered arrangement of the six carbonyl ligands which minimizes the steric repulsion. The metal–metal distance of 2.666(1) Å is essentially the same as those observed in the related complexes $Co_2(CO)_6(PMe_3)_2$ (2.669(1) Å)[20a] and $Co_2(CO)_6(PBu_3)_2$ (2.66(1) Å).[20b,c] There is no intramolecular interaction between the phosphine ligands and the $Co(CO)_3$ groups. Thus, the conformation of the phosphine ligands is probably controled by molecular packing.

Description of the Crystal Structure of $[(Ph_3P)_2Ag(\mu\text{-}Cl)_2Co(\mu\text{-}Cl)_2Ag(PPh_3)_2]\cdot 0.5OEt_2$ (13·0.5OEt₂). In the crystals of **13**·$0.5OEt_2$ two independent molecules (A and B) of the complex, slightly differing in the orientation of the phenyl groups of the PPh_3 ligands, and diethyl ether molecules of solvation are present. A view of molecule A is shown in Figure 3 together with the atom numbering scheme. Selected bond distances and angles in the two molecules are given in Table IV. Complex **13**·$0.5OEt_2$ contains a $CoCl_4^{2-}$ core, but each pair of Cl atoms bridges a Ag atom, such that in the almost linear Ag–Co–Ag metal arrangement a double Cl bridge links the Ag and Co atoms.

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(19) Taylor, R.; Kennard, O. *J. Am. Chem. Soc.* **1982**, *104*, 5063.

(20) (a) Jones, R. A.; Seeberger, M. H.; Stuart, A. L.; Whittlesey, B. R.; Wright, T. C. *Acta Crystallogr.* **1986**, *C42*, 399. (b) Bryan, R. F.; Manning, A. R. *J. Chem. Soc., Chem. Commun.* **1968**, 1316. (c) Ibers, J. A. *J. Organomet. Chem.* **1968**, *14*, 423.

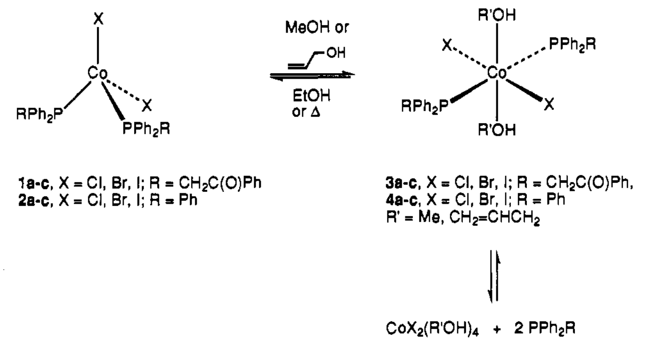
The values of the Ag···Co separations are 3.503(3) and 3.514(3) Å [3.405(3) and 3.499(3) Å] and that of the Ag–Co–Ag angle is 171.9(1)° [178.2(1)°]. Each Ag atom completes its tetrahedral coordination through two P atoms from the PPh$_3$ ligands. Two nearly rectangular AgCoCl$_2$ arrangements can be considered approximately orthogonal to one another, the dihedral angle between the two mean planes being 93.0(2)° [91.7(2)°]. The structure of **13**·0.5OEt$_2$ is comparable with that of [(Ph$_3$P)$_2$Ag(μ-Cl)$_2$OsCl$_2$(μ-Cl)$_2$Ag(PPh$_3$)$_2$], in which the central hexacoordinate Os atom replaces the tetracoordinate Co atom.[21] In the structure of [{(en)$_2$Co(SCH$_2$COO)}$_2$Ag]$^{3+}$, to our knowledge the only other available for a complex with bridged Ag and Co atoms (although the latter atoms are in the oxidation state +3 and show octahedral coordination), two sulfur atoms bridge the Ag and Co atoms.[22] The Co–Cl bond lengths are practically equal, ranging from 2.271(6) to 2.283(6) Å [2.268(6)–2.277(7) Å] and do not appear to be influenced by the bridging behavior (being only slightly longer than the mean value found for terminal Co–Cl bonds in several structures [2.251(26) Å].[23] The Cl–Co–Cl angles range from 101.9(2) to 117.1(2)° [102.9(2)–115.2(2)°]. The Ag–Cl bond lengths, 2.776(6) and 2.719(6) Å [2.718(7) and 2.687(6) Å], are comparable with those found in the complex [(Ph$_3$P)$_2$Ag(μ-Cl)$_2$OsCl$_2$(μ-Cl)$_2$Ag(PPh$_3$)$_2$], 2.678(2) and 2.807(3) Å.[21] The Ag–P bond lengths in **13**·0.5OEt$_2$, ranging from 2.438(7) to 2.465(7) Å [2.419(10)–2.462(7) Å] are comparable, even if at the upper quartile, with those found in silver complexes with PPh$_3$ [2.419(46) Å].[24]

Discussion

Solution Properties. The significance of the relatively low molar absorption coefficients of **1a–c** in dichloromethane, compared to those reported for **2a–c**, was explored. Ligand chelation and a resultant equilibrium between the comparatively strongly colored tetrahedral compounds and relatively pale octahedral P,O chelates is feasible. Should such an equilibrium occur, the octahedral complexes with their much weaker d–d transitions would effectively be masked by the stronger transitions of the tetrahedral complexes. However, uncoordinated ketone functions are readily distinguished from P,O-chelated systems by their distinctive infrared bands.[25] For **1a–c** only uncoordinated ketone could be observed in solution, effectively ruling out of T_d–O_h equilibrium. In fact, considerable variation in the position and intensity of the electronic transitions of the **2a–c** series has been reported in different solvent media.[12,26,27] Hence, variations observed between **1a–c** and **2a–c** may be accounted for by slight modifications in the cobalt-phosphine interactions and/or by dipolar interactions generated between the ketone functions and the solvent.

The behavior of **1a–c** in methanol cannot be accounted for by P,O chelation, since only uncoordinated ketone is observed. However, the visible spectra of **1a–c** in this solvent are typical of octahedral cobalt(II) geometries; thus a solvent interaction must be invoked. The behavior of **1a–c** and **2a–c** cannot be accounted for without invoking solvent coordination. In solvents such as THF, dichloromethane, or ethanol, all the complexes exhibit typically tetrahedral electronic spectra, but those in methanol are clearly of octahedral cobalt(II) species. Infrared spectra of **1a–c** indicate that the ketone ligand functions are not involved in coordination in any solvent, moreover complexes of PPh$_3$ do not offer additional intramolecular ligand donors. Thus it is reasonable to postulate the formation of solvated octahedral complexes **3a–c** and **4a–c** (Scheme I). The coordination of solvent would agree with the observed properties of the complexes in methanol: solvent loss on heating or drying in vacuo to regenerate tetrahedral complexes. However, there is evidence that ligand displacement must also occur since free PPh$_3$ has been isolated from **2b** in methanol. Such behavior is indicative of a second equilibrium step. The sensitivity of these solvent equilibria is notable. Tetrahedral species are not only regenerated on heating but also on dilution with other alcohols. Only methanol and allylic alcohol facilitate the formation of octahedral complexes, EtOH, *i*-PrOH, *n*-PrOH, *t*-BuOH, and *n*-BuOH do not appear to coordinate in the same manner.

Scheme I



Reactions with Noncoordinating Anions. The substitution of chloride for BF$_4^-$ or PF$_6^-$ in the presence of hemilabile functional phosphines is a common procedure for generating chelated ligands. Examples of P,O chelation have previously been observed for dicationic ketophosphine complexes of the series [M{Ph$_2$PCH$_2$C(O)R}$_2$]X$_2$ (M = Ni, Pd, Pt; X = BF$_4^-$, PF$_6^-$).[28-30] Here we have not only found differing reactivity between the cobalt(II) complexes and those of nickel, palladium, and platinum but also different behavior between the commonly used thallium and silver halide abstractors, TlPF$_6$ and AgBF$_4$.

It is surprising that only partial chloride substitution, to give **6**, can be achieved for **1a** in the presence of TlPF$_6$, since the analogy between **1a** and the Ni, Pd, and Pt complexes extends to a common donor set and coordination number. Moreover, although the precursor complexes of cobalt and Ni, Pd, and Pt differ in coordination geometry, **6** displays a magnetic moment commensurate with a single unpaired electron and therefore a square-planar electronic configuration. Square-planar cobalt(II) complexes are relatively uncommon and are generally formed only with chelating polydentate ligands which overcome the comparatively small ligand field stabilization energy provided by this geometry. Such chelation is clearly not produced by ketophosphines and more subtle effects must influence the geometry of **6**.

Distortion of dihedral angles can produce a continuous range of structures between true tetrahedral and square-planar geometries.[31] In contrast, electronic configurations are discontinuous. Such properties may provide the rationale for **6**: distortion of one dihedral angle toward 90° allows effective P,O chelation and results in the adoption of a low-spin electronic configuration. The geometry, however, remains grossly distorted toward tetrahedral with a large dihedral angle opposite the P,O chelate which inhibits the chelation of the second phosphine ligand.

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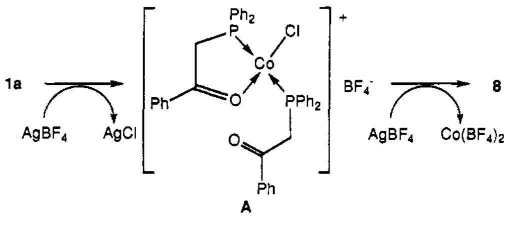
(21) Robinson, P. D.; Hinckley, C. C.; Matusz, M.; Kibala, P. A. *Polyhedron* **1987**, *6*, 1695.
(22) Heeg, M. J.; Elder, R. C.; Deutsch, E. *Inorg. Chem.* **1980**, *19*, 554.
(23) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.
(24) Heeg, M. J.; Elder, R. C.; Deutsch, E. *Inorg. Chem.* **1980**, *19*, 554.
(25) Braunstein, P.; Matt, D.; Dusausoy, Y. *Inorg. Chem.* **1983**, *22*, 2043.
(26) Pierrard, J.-C.; Rimbault, J.; Hugel, R. *Bull. Soc. Chim. Fr.* **1976**, 1711.
(27) Kato, H.; Akimoto, K. *J. Am. Chem. Soc.* **1974**, *96*, 1353.
(28) Bouaoud, S.-E.; Braunstein, P.; Grandjean, D.; Matt, D.; Nobel, D. *Inorg. Chem.* **1986**, *25*, 3765.
(29) Braunstein, P.; Matt, D.; Nobel, D.; Balegroune, F.; Bouaoud, S.-E.; Grandjean, D.; Fischer, J. *J. Chem. Soc., Dalton Trans.* **1988**, 353.
(30) Braunstein, P.; Matt, D.; Dusausoy, Y.; Fischer, J.; Mitschler, A.; Ricard, L. *J. Am. Chem. Soc.* **1981**, *103*, 5115.
(31) Sacconi, L.; Mani, F.; Bencini, A. In *Comprehensive Coordination Chemistry*, Wilkinson, G., Gillard, R. D., McCleverty, J. A. Eds.; Pergamon Press: Oxford, England, 1987; Vol. 5, pp 1–347.

Scheme II



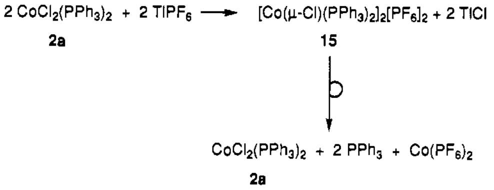
It is clear that P,O chelation is not the simple process which occurs for the Ni/Pd/Pt metals, and this may be due predominantly to the unfavorable nature of P,O chelation at a tetrahedral centre. It is clear that only one ketophosphine ligand is chelated in **6**. This appears to be a relatively energetically unfavorable compromise, and the metastable nature of **6** is illustrated by its slow rearrangement in solution to give the octahedral tris phosphine complex **7** by ligand transfer. Such a rearrangement still provides a chelation angle of *ca.* 90°, but also gives the energetically more favored octahedral d^7 electronic configuration.

Reaction of **1a** with $AgBF_4$ might also be expected to yield a dicationic P,O chelated cobalt(II) complex. In fact, the silver phosphine complex **8** is isolated in high yield as the only phosphine containing compound (Scheme II). In the analogous Ni, Pd, and Pt reactions there was no evidence for silver–phosphine competition products in equilibria with those of the group 8–10 metals, let alone the stoichiometric formation of such products. Moreover, since cobalt(II)–phosphorus bonds are not intrinsically significantly weaker than those of nickel(II), whilst those of silver(I) are not generally much stronger, other arguments must be invoked to explain the formation of **8**. Although no reaction intermediates could be fully characterized from the reaction of **1a** with $AgBF_4$, traces of a brown complex were observed in the crude reaction product, which may be the BF_4^- complex, **A** analogous to **6**. **A** is also suggested by the presence of infrared bands at 1591 and 1573 cm^{-1} during the reaction. The formation of such a complex again points to an initial abstraction of Cl^- to precipitate AgCl. However, unlike thallium which does not readily form phosphine coordination complexes, silver(I) does have significant affinity for phosphines. This accounts for the observation that a second equivalent of $AgBF_4$ is consumed to give **8** as a result of chloride and phosphine abstraction from **A**, leaving "naked" $Co(BF_4)_2$ to precipitate from the solution.

Additional reactions also lend weight to this scheme. **6** reacts with $AgBF_4$ to give a silver(I) phosphine complex, suggesting that these chelated intermediates are indeed susceptible to further reaction with silver. Furthermore, **2a** also reacts with 2 equiv of $AgBF_4$ to give phosphine abstraction from the cobalt center. However, in this case a BF_4^- counterion is present in this product, $Ag(PPh_3)_2BF_4{\cdot}0.5CH_2Cl_2$ (**12**$\cdot 0.5CH_2Cl_2$). Here chloride substitution is again likely as a first step since AgCl is once again present in the reaction precipitate. However, the absence of a stabilizing ketophosphine chelate is likely to result in the immediate precipitation of cobalt and the consequent coordination of free phosphine by the remaining $AgBF_4$.

Reactions with Noncoordinating Anions in the Presence of Excess Ligand. The reactivity of $TlPF_6$ with **2a** might be expected to promote total abstraction of Cl^- from **2a** to produce a coordinatively unsaturated complex resulting in the precipitation of TlCl and a cobalt(II) salt along with the liberation of free PPh_3. In fact, the reactivity of $TlPF_6$ with **2a** is more complex and is influenced by moisture. When water is present, PPh_3 is observed in solution along with $[Ph_3PH][PF_6]$ **14**, the proton source being likely to result from the hydrolysis of $TlPF_6$.

Under rigorously anhydrous conditions **2a** reacts with $TlPF_6$ (either in the presence or absence of excess ligand) to give a product which we have tentatively formulated as $[Co(\mu\text{-}Cl)(PPh_3)_2]_2[PF_6]_2$ (**15**). The partial abstraction of chloride anions by $TlPF_6$ has already been noted in the isolation of **6**. Here this behavior may result from the generation of a bridging chloride species which is less susceptible to reaction with $TlPF_6$. **15** could not be isolated in a pure form but the observation of PF_6^- resonances in the $^{31}P\{^1H\}$ NMR spectrum indicates the presence of this counter ion. Moreover, the rearrangement of **15** to reform **2a** suggests that at least one chloride anion must remain bound to the cobalt(II) center. The concurrent liberation of free PPh_3 along with **2a** adds weight to the following reaction scheme, although it must be stressed that the incomplete characterization of **15** renders the scheme purely tentative. The reactivity of **2a**



with $AgBF_4$ in the presence of excess ligand also affords notable products. In addition to the silver phosphine complex **12** characterized in the absence of free ligand, the silver-cobalt complex $Ag_2(PPh_3)_4CoCl_4$ is also formed. The visible spectrum of the complex is similar to that reported for the $CoCl_4^{2-}$ anion suggesting an ionic formulation $[Ag(PPh_3)_2]_2[CoCl_4]$.[32] However, far-IR studies indicate shifts for the typical ν_3 and ν_4 bands.[33] In addition, the complex appears non-conducting in dichloromethane, and no $^{31}P\{^1H\}$ NMR signal could be recorded, although such resonances are often observed when phosphines are not directly coordinated to the paramagnetic metal centre. Thus **13** contains a secondary chloride bridged interaction to give a $[(Ph_3P)_2Ag(\mu\text{-}Cl)_2Co(\mu\text{-}Cl)_2Ag(PPh_3)_2]$ species while maintaining the $CoCl_4^{2-}$ core. This was confirmed by a crystallographic study of **13**$\cdot 0.5CH_2Cl_2$, Figure 3, which does indeed indicate the presence of bridging chlorides.

Conclusion

The hemilabile properties of the ketophosphines appear significantly different for cobalt(II) when compared to the intensely studied Ni/Pd/Pt metals. Despite the accessibility of octahedral coordination to cobalt(II), the tetrahedral bis(phosphine) complexes show no propensity to become octahedral by P,O chelation. Such chelation appears particularly unfavorable in tetrahedral geometries, as evidenced by the formation of a square-planar complex on reaction with $TlPF_6$ and by breakdown of the cobalt(II) complex on reaction with $AgBF_4$. The latter reactions are of particular interest since tetrahedral intermediates have been proposed for both cobalt and rhodium catalyzed processes. Information which sheds light on the stability of such intermediates is clearly worth further study.

Experimental Section

A. Reagents and Physical Measurements. All reactions were performed in Schlenk-type flasks under nitrogen. Solvents were purified and dried under nitrogen. All reactions involving silver salts were carried out in the absence of light. Infrared spectra were performed in the 4000–400-cm^{-1} range on a Perkin-Elmer 398 spectrophotometer or Bruker IFS66 FT-IR, while far infrared spectra were recorded on a Bruker IFS88 FT-FIR machine as polyethene pellets. UV spectra were recorded on a Shimadzu UV260 spectrophotometer, and magnetic moments were obtained on a Johnson Matthey Faraday balance. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded at 200 and 81 MHz, respectively, on a FT Bruker WP-200SY instrument.

B. Syntheses. $Ph_2PCH_2C(O)Ph$ was prepared by the method previously described.[28] The complexes $CoX_2[Ph_2PCH_2C(O)Ph]_2$ (X = Cl, **1a**; X = Br, **1b**; X = I, **1c**) were prepared by previously published methods.[1] The corresponding triphenylphosphine complexes, CoX_2-

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(32) (a) Denning, R. G. *J. Chem. Phys.* **1966**, *45*, 1307. (b) Ferguson, J. *J. Chem. Phys.* **1963**, *39*, 116.

(33) Sabatini, A.; Sacconi, L. *J. Am. Chem. Soc.* **1964**, *87*, 17.

Table V. Crystallographic Data for $CoCl_2[Ph_2PCH_2C(O)Ph]_2$ (**1a**), $Co_2(CO)_6[Ph_2PCH_2C(O)Ph]_2$ (**5**), and $[(Ph_3P)_2Ag(\mu\text{-}Cl)_2Co(\mu\text{-}Cl)_2Ag(PPh_3)_2]\cdot 0.5OEt_2$ (**13**·$0.5Et_2O$)

	1a	**5**	**13**·$0.5Et_2O$
formula	$C_{40}H_{34}Cl_2CoO_2P_2$	$C_{46}H_{34}Co_2O_8P_2$	$[C_{72}H_{60}Ag_2Cl_4CoP_4]\cdot 0.5\ O(C_2H_5)_2$
fw	738.2	894.6	1502.71
cryst system	monoclinic	triclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a, Å	10.985(2)	8.916(2)	21.840(5)
b, Å	17.236(4)	11.177(7)	17.664(6)
c, Å	19.547(4)	12.009(4)	36.890(7)
α, deg		81.15(5)	
β, deg	104.87(2)	76.39(2)	93.14(2)
γ, deg		67.46(3)	
V, Å^3	3577(1)	1071.4(8)	14210(6)
D_c, g cm^{-3}	1.36	1.38	1.289
Z	4	1	8
T, °C	25	25	25
F(000)	1524	458	5616
cryst. dimens, mm	0.20 × 0.12 × 0.11	0.1 × 0.1 × 0.14	0.12 × 0.18 × 0.24
radiation[a]	graphite-filtered Mo Kα	graphite-filtered Mo Kα	niobium-filtered Mo Kα
μ, cm^{-1}	7.66	9.28	9.60
final R and R_w indices[b]	0.052, 0.048	0.049, 0.046	0.0778, 0.1017

[a] $\lambda = 0.710\,73$ Å. [b] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/w|F_o|^2]^{1/2}$.

Table VI. Positional Parameters and Their Estimated Standard Deviations for $CoCl_2[Ph_2PCH_2C(O)Ph]_2$ (**1a**)

atom	x	y	z	B,[a] Å^2	atom	x	y	z	B,[a] Å^2
Co	0.23656(8)	0.19356(5)	0.89224(4)	3.39(2)	C(20)	0.0207(9)	0.3767(6)	1.0621(5)	8.5(3)
Cl(1)	0.1778(2)	0.1290(1)	0.97645(9)	5.37(5)	P(2)	0.4301(2)	0.2531(1)	0.95608(8)	3.22(4)
Cl(2)	0.2789(2)	0.1265(1)	0.8056(1)	7.09(7)	C(21)	0.5527(6)	0.1837(4)	0.9946(3)	3.3(2)
P(1)	0.0716(2)	0.2856(1)	0.84784(9)	3.56(4)	C(22)	0.5422(6)	0.1065(4)	0.9740(3)	3.3(2)
C(1)	−0.0822(6)	0.2397(4)	0.8276(3)	3.6(2)	C(23)	0.6399(7)	0.0564(4)	0.9995(3)	3.9(2)
C(2)	−0.1219(7)	0.2014(5)	0.8808(4)	5.6(2)	C(24)	0.7475(7)	0.0793(4)	1.0460(4)	4.5(2)
C(3)	−0.2365(8)	0.1654(5)	0.8664(5)	6.6(3)	C(25)	0.7583(7)	0.1566(5)	1.0671(4)	5.3(2)
C(4)	−0.3120(7)	0.1630(5)	0.7996(5)	5.9(2)	C(26)	0.6640(6)	0.2076(4)	1.0426(4)	4.5(2)
C(5)	−0.2748(7)	0.1994(5)	0.7467(4)	5.8(2)	C(27)	0.4208(6)	0.3128(4)	1.0310(3)	3.3(2)
C(6)	−0.1602(7)	0.2363(5)	0.7610(4)	4.9(2)	C(28)	0.3885(7)	0.2776(4)	1.0869(4)	5.0(2)
C(7)	0.0702(6)	0.3417(4)	0.7696(3)	3.7(2)	C(29)	0.3791(7)	0.3203(5)	1.1456(4)	5.8(2)
C(8)	0.1196(7)	0.3070(4)	0.7181(4)	5.0(2)	C(30)	0.3991(7)	0.3970(5)	1.1477(4)	5.5(2)
C(9)	0.1169(8)	0.3449(6)	0.6558(4)	6.1(3)	C(31)	0.4355(9)	0.4320(5)	1.0943(4)	7.3(3)
C(10)	0.0689(8)	0.4177(6)	0.6456(4)	6.3(3)	C(32)	0.4437(8)	0.3907(4)	1.0357(4)	5.5(2)
C(11)	0.0192(7)	0.4537(5)	0.6942(4)	5.6(2)	C(33)	0.5118(6)	0.3090(4)	0.9021(3)	4.0(2)
C(12)	0.0204(7)	0.4146(5)	0.7573(4)	4.8(2)	C(34)	0.4311(6)	0.3666(4)	0.8550(3)	3.3(2)
C(13)	0.0760(6)	0.3514(4)	0.9221(3)	4.5(2)	O(2)	0.3337(4)	0.3888(3)	0.8677(2)	4.6(1)
C(14)	−0.0462(7)	0.3866(4)	0.9294(4)	4.5(2)	C(35)	0.4698(6)	0.3952(4)	0.7922(3)	3.4(2)
O(1)	−0.1252(5)	0.4057(4)	0.8780(3)	6.8(2)	C(36)	0.3857(6)	0.4374(4)	0.7420(4)	4.7(2)
C(15)	−0.0650(7)	0.3964(4)	1.0019(4)	4.6(2)	C(37)	0.4176(8)	0.4621(5)	0.6823(4)	5.9(2)
C(16)	−0.1739(8)	0.4296(5)	1.0074(5)	6.7(3)	C(38)	0.5340(9)	0.4469(5)	0.6734(4)	6.0(2)
C(17)	−0.200(1)	0.4415(7)	1.0699(7)	9.0(4)	C(39)	0.6195(7)	0.4079(5)	0.7238(4)	6.4(3)
C(18)	−0.119(1)	0.4193(6)	1.1286(7)	9.9(5)	C(40)	0.5881(6)	0.3807(4)	0.7832(4)	4.7(2)
C(19)	−0.006(1)	0.3887(7)	1.1287(5)	11.2(4)					

[a] Values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

$(PPh_3)_2$ (X = Cl, **2a**; X = Br, **2b**; X = I, **2c**) were synthesized by the method and Cotton *et al.*[12] Deep blue crystals of **1a** were formed on slow cooling of an ethanol solution from 60 to −20 °C.

$Co_2(CO)_6[Ph_2PCH_2C(O)Ph]_2$ (5). **1a** (0.199 g, 0.27 mmol) was slurried in 10 mL of toluene to which excess $Na[Co(CO)_4]$ was added to produce a red solution. After 0.5 h this was filtered and the solution evaporated to dryness. Complex **5** was recrystallized from toluene/pentane (0.080 g, 33%): mp 102 °C. IR (THF): $\nu(C{\equiv}O)$ 1954 vs, $\nu(C{=}O)$ 1673 m. IR (Nujol) $\nu(C{\equiv}O)$ 1965 m, 1943 s, 1926 s, $\nu(C{=}O)$ 1670 m. ^1H NMR ($CDCl_3$): δ 4.18 (m, 4H, $2PCH_2$), 7.19–7.96 (m, 30H, 6Ph). $^{31}P\{^1H\}$ ($CDCl_3/CH_2Cl_2$): δ 58.9 (s, 2P). Anal. Calcd for $C_{46}H_{34}Co_2O_8P_2$: C, 61.8; H, 3.8. Found: C, 61.7; H, 3.8 (M = 894.6).

$[\overline{\mathrm{CoCl\{Ph_2PCH_2C(O}}\mathrm{)Ph\}\{Ph_2PCH_2C(O)Ph\}](PF_6)}$ (6). $TlPF_6$ (0.259 g, 0.74 mmol) was added to a 10 mL dichloromethane solution of **1a** (0.547 g, 0.74 mmol). The initial blue solution was stirred for 1 d, turning first green and then brown. The solution was filtered and the remaining precipitate extracted with a further 20 mL of solvent. The solutions were combined and evaporated to dryness to afford **3** as a brown solid (0.62 g, 99%): mp 148–150 °C. IR (KBr): ν(CO) 1672 m, 1610 m, 1591 m, 1573 s, $\nu(PF_6)$ 840 s. IR (Nujol): ν(CO) 1670–1660 br m, 1605 m, 1590 m, 1567 s. Magnetic moment: $\mu_{eff} = 1.8\mu_B$. UV–vis (CH_2Cl_2): no bands between 800 and 400 nm. Conductivity ($MeNO_2$): Λ_M = 100–110 S cm^2 mol^{-1} for (4–6) × 10^{-3} M solutions. Anal. Calcd for $C_{40}H_{34}ClF_6CoO_2P_3$: C, 56.7; H, 4.0. Found: C, 56.5; H, 4.1 (M = 848.0).

$[\overline{\mathrm{CoCl\{Ph_2PCH_2C(O}}\mathrm{)Ph\}_2\{Ph_2PCH_2C(O)Ph\}](PF_6)\cdot CH_2Cl_2}$ (7·CH_2Cl_2). Complex **6** (0.046 g, 0.054 mmol) was dissolved in dichloromethane (10 mL). Et_2O (20 mL) was allowed to slowly diffuse into the solution over *ca.* 7 d. During this time the solution lost its brown coloration and precipitated pale-purple crystals of **7**·CH_2Cl_2, which were filtered from the solution and dried in air (0.040 g, 89% with respect to ligand): mp 162–163 °C. IR(KBr): ν(CO) 1670 s, 1635 m, 1627 m, 1577 s, $\nu(PF_6)$ 840 s. Anal. Calcd for $C_{60}H_{51}ClF_6CoO_3P_4\cdot CH_2Cl_2$: C, 59.2; H, 4.3. Found: C, 59.4; H, 4.1 (M = 1152.3 + 84.9).

$[Ag\{Ph_2PCH_2C(O)Ph\}_2]Cl$ (8). $AgBF_4$ (0.105 g, 0.54 mmol) was added to a solution of **1a** (0.197 g, 0.27 mmol) in CH_2Cl_2 (10 mL). The solution gradually lost its blue coloration over 4 h while precipitating a pale purple solid. Filtration and removal of solvent gave a pale brown solid which was redissolved in MeOH and filtered through Celite to afford **8** (0.190 g, 95%): mp 72 °C. IR(KBr): ν(CO) 1669 s. ^1H NMR ($CDCl_3$): δ 4.08 (d, 4H, $^2J(PH)$ = 7 Hz, PCH_2), 7.31–7.90 (m, 30H, 6Ph). $^{31}P\{^1H\}$ ($CDCl_3/CH_2Cl_2$): δ −5.9 (br,s). Anal. Calcd for $C_{40}H_{34}AgClO_2P_2$: C, 63.9; H, 4.6. Found: C, 64.4; H, 4.5 (M = 752.0).

Table VII. Positional Parameters and Their Estimated Standard Deviations for $Co_2(CO)_6[Ph_2PCH_2C(O)Ph]_2$ (**5**)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
Co	0.3755(1)	0.04390(9)	0.58785(8)	3.73(2)	C(11)	0.1168(7)	0.2400(6)	0.9336(5)	8.11(4)
P(1)	0.1784(2)	0.1197(2)	0.7329(1)	4.01(3)	C(12)	0.1658(8)	0.2725(7)	1.0233(6)	12.61(4)
C(1)	0.2441(6)	0.0303(5)	0.5028(5)	5.31(4)	C(13)	0.3244(8)	0.2390(6)	1.0256(6)	12.47(4)
O(1)	0.1596(5)	0.0249(5)	0.4477(4)	8.87(4)	C(14)	0.4434(7)	0.1697(6)	0.9432(6)	9.66(4)
C(2)	0.4305(6)	0.1817(5)	0.5655(5)	4.74(4)	C(15)	0.4006(7)	0.1336(5)	0.8528(5)	6.81(4)
O(2)	0.4648(5)	0.2726(4)	0.5546(4)	7.73(4)	C(16)	0.0670(6)	0.0133(5)	0.8055(5)	5.26(4)
C(3)	0.4932(6)	−0.0965(5)	0.6636(5)	4.52(4)	C(17)	0.1723(6)	−0.1077(6)	0.8658(5)	5.67(4)
O(3)	0.5701(5)	−0.1848(4)	0.7125(4)	6.54(4)	O(4)	0.2113(5)	−0.0984(4)	0.9524(4)	6.73(4)
C(4)	0.0094(6)	0.2653(5)	0.6944(5)	5.15(4)	C(18)	0.2230(7)	−0.2376(6)	0.8227(6)	7.77(4)
C(5)	−0.1241(7)	0.2605(7)	0.6658(7)	12.35(4)	C(19)	0.3063(7)	−0.3407(6)	0.8895(7)	10.35(4)
C(6)	−0.2473(8)	0.3699(7)	0.6364(8)	15.86(4)	C(20)	0.3535(8)	−0.4633(7)	0.8577(8)	16.01(4)
C(7)	−0.2370(8)	0.4796(7)	0.6342(7)	11.69(5)	C(21)	0.3122(8)	−0.4774(7)	0.7552(8)	19.54(4)
C(8)	−0.1127(8)	0.4953(7)	0.6630(7)	12.51(4)	C(22)	0.2419(8)	−0.3790(7)	0.6905(8)	20.92(4)
C(9)	0.0180(7)	0.3825(6)	0.6922(7)	10.14(4)	C(23)	0.1908(7)	−0.2562(6)	0.7235(6)	12.15(4)
C(10)	0.2352(6)	0.1681(5)	0.8483(5)	5.36(4)					

8 was also formed by the reaction of **2a** under similar conditions and on a similar scale (yield 68%). **8** was identified by spectroscopy and elemental analysis. **8** was also synthesized directly by the following procedure: $AgBF_4$ (0.104 g, 0.53 mmol) and L^1 (0.325 g, 1.07 mmol) were stirred in CH_2Cl_2 (10 mL) for 1 h, after which KCl (0.040 g, 0.54 mmol) was added and the reactants were stirred for a further 4 h. Filtration and removal of solvent in vacuo gave **8** as a white solid (0.206 g, 52%). Spectroscopic data are as above. Anal. Found: C, 64.1; H, 4.7.

Ag[Ph₂PCH₂C(O)Ph]Cl (9). $AgBF_4$ (0.315 g, 1.62 mmol) and L^1 (0.492 g, 1.62 mmol) were stirred in CH_2Cl_2 (10 mL) for 1 h, before KCl (0.125 g, 1.65 mmol) was added. After 4 h the colorless solution was filtered and concentrated to give **6**·$0.75CH_2Cl_2$ as an air and light sensitive solid which was dried in vacuo (0.643 g, 78%): mp 58 °C. IR (KBr): ν(CO) 1668 s, $\nu(BF_4)$ absent. ^1H NMR ($CDCl_3$): δ 4.27 (d, 2H, ^2J(PH) = 10.6 Hz, PCH_2), 7.43–7.95 (m, 15H, 3Ph). $^{31}P\{^1H\}$ NMR ($CDCl_3/CH_2Cl_2$): δ 0.4 (br, s). Anal. Calcd for $C_{20}H_{17}AgClOP{\cdot}C_{0.75}H_{1.5}Cl_{1.5}$: C, 48.7; H, 3.7. Found: C, 49.0; H, 4.0 (M = 447.7 + 63.7).

Ag[Ph₂PCH₂C(O)Ph]BF₄ (10). $AgBF_4$ (0.277 g, 1.42 mmol) and L^1 (0.433 g, 1.42 mmol) were stirred in CH_2Cl_2 (10 mL) for 1 h. Filtration and evaporation of solvent in vacuo yielded **10** as an air and light sensitive solid (0.627 g, 88%): mp 65–67 °C. IR (KBr): ν(CO) 1665–1650 s, br; $\nu(BF_4)$ 1100–1000 s, br. ^1H NMR ($CDCl_3$): δ 4.30 (d, 2H, ^2J(PH) = 9.8 Hz, PCH_2), 7.30–7.92 (m, 15H, 6Ph). $^{31}P\{^1H\}$($CDCl_3/CH_2Cl_2$): 296 K, δ 0.9 (br, s); 206 K, δ −2.5 (d, ^2J(AgP) = 670 Hz, $^{107/109}Ag$ satellites not resolved). Anal. Calcd for $C_{20}H_{17}AgBF_4OP$: C, 48.1; H, 3.4. Found: C, 48.4; H, 3.4 (M = 499.0).

[Ag{Ph₂PCH₂C(O)Ph}₂]BF₄ (11). $AgBF_4$ (0.097 g, 0.50 mmol) and L^1 (0.303 g, 1.00 mmol) were stirred in CH_2Cl_2 (10 mL) for 1 h. Filtration and evaporation of the solvent in vacuo yielded **11** (0.380 g, 95%): mp 83 °C. IR (KBr): ν(CO) 1668 s, br; $\nu(BF_4)$ 1100–1000 s, br. ^1H NMR ($CDCl_3$): δ 4.20 (s, 4H, PCH_2), 7.35–7.90 (m, 30H, 6Ph); $^{31}P\{^1H\}$ ($CDCl_3/CH_2Cl_2$ (296 K): δ −2.0. Anal. Calcd for $C_{40}H_{34}AgBF_4O_2P_2$: C, 59.8; H, 5.0. Found: C, 59.9; H, 5.0 (M = 803.3).

[Ag(PPh₃)₂]BF₄·0.5CH₂Cl₂ (12·0.5CH₂Cl₂). $AgBF_4$ (0.242 g, 1.24 mmol) was added to a 25 mL CH_2Cl_2 solution of **2a** (0.407 g, 0.62 mmol). The solution gradually lost its blue coloration over 4 h while precipitating a green solid. Filtration and removal of solvent gave a pale white solid which was recrystallized from CH_2Cl_2/Et_2O to give **12**·$0.5CH_2Cl_2$ after drying in vacuo (0.362 g, 77%): mp 230–232 °C. IR (KBr): ν(BF) 1100–1000 br. ^1H NMR ($CDCl_3$): δ 7.47–7.24 (m, 30H, 6Ph). $^{31}P\{^1H\}$ NMR ($CDCl_3/CH_2Cl_2$): δ 12.6 (br, s). Anal. Calcd for $C_{36}H_{30}AgBF_4P_2{\cdot}0.5CH_2Cl_2$: C, 57.6; H, 4.1. Found: C, 57.5; H, 4.3 (M = 719.3 + 42.5).

[(Ph₃P)₂Ag(μ-Cl)₂Co(μ-Cl)₂Ag(PPh₃)₂] (13). **2a** (0.984 g, 1.50 mmol) and PPh_3 (0.788 g, 3.00 mmol) were stirred in dichloromethane (50 mL) to give a deep blue solution. $AgBF_4$ (0.586 g, 3.01 mmol) was added and the reactants stirred for 1 d to give an off-white precipitate and a pale blue solution. Solvent was removed under reduced pressure, and the resultant solid was extracted with THF (50 mL) and then CH_2Cl_2 (50 mL), leaving a pale purple residue. **13** was recrystallized from THF on cooling to −20 °C. **12**·$0.5CH_2Cl_2$ was recovered from the CH_2Cl_2 extract on concentration and addition of pentane. **13** was identified by elemental analysis and spectroscopic data: (yield 0.753 g, 68% with respect to Cl); mp 228 °C. Far-IR (polyethene): $\nu(CoCl_4{}^{2-})$ ν_3 311 s, 290 s, ν_4 137 m. Magnetic moment: $\mu_{eff} = 4.8\mu_B$. UV–vis (CH_2Cl_2): 694 (ϵ 520), 666 (455) 613 (310) nm. Conductivity (CH_2Cl_2): Λ_M = 7 S cm^2 mol^{-1}. Anal. Calcd for $C_{72}H_{60}Ag_2Cl_4CoP_4$: C, 59.0; H, 4.1; Cl, 9.7. Found: C, 59.3; H, 4.0; Cl, 9.7 (M = 1465.7).

[Ph₃PH][PF₆] (14). **2a** (0.222 g, 0.34 mmol) was dissolved in CH_2Cl_2 (10 mL), and $TlPF_6$ (impure) (0.249 g, 0.71 mmol) was added. The solution gradually lost its blue coloration over 2 h while precipitating a purple solid (IR contains bands due to $PF_6{}^-$). Filtration and removal of solvent gave a white solid which was extracted with 50:50 mixture of hexane/toluene (20 mL). Concentration of the extract gave PPh_3 (0.059 g, 33%) identified by its melting point and ^{31}P NMR spectrum. The remaining solid was dried in vacuo and recrystallized from CH_2Cl_2/Et_2O to afford **14** (0.070 g, 25%): mp 142 °C. IR(KBr): $\nu(PF_6)$ 830 s. ^1H NMR ($CDCl_3$): δ 7.38–7.89 (m, 15H, Ph); $^{31}P\{^1H\}$ NMR ($CDCl_3/CH_2Cl_2$): δ 6.4 (s, 1P), −144.0 (1P, sept., ^1J(PF) = 716 Hz). Anal. Calcd for $C_{18}H_{16}F_6P_2$: C, 53.0, H, 4.0. Found: C, 53.0; H, 4.0 (M = 408.3).

[Co(μ-Cl)(PPh₃)₂](PF₆)₂ (15). **2a** (0.300 g, 0.46 mmol) and PPh_3 (0.240 g, 0.92 mmol) were dissolved in dichloromethane (10 mL) to give a deep blue solution. $TlPF_6$ (0.321 g, 0.92 mmol) was added, and the solution progressively turned emerald green. After 6 h, the solution was filtered and concentrated. Addition of toluene gave a green precipitate of **15** (0.310 g, 91%): mp 118–120 °C. IR(KBr): ν(PC) 1090 s, 1096 s, $\nu(PF_6)$ 843 s, 838 s. $^{31}P\{^1H\}$ NMR ($CDCl_3/CH_2Cl_2$): δ −143.2 (sept., ^1J(PF) = 711 Hz).

Evolution of 15 to give CoCl₂(PPh₃)₂ (2a). **15** (0.125 g, 0.12 mmol) was redissolved in dichloromethane (10 mL) to give a green solution. Over ca. 1 h this solution became blue and free PPh_3 was detected by $^{31}P\{^1H\}$ NMR. Slow Et_2O diffusion into this solution precipitated over ca. 2 d blue crystalline **2a** (0.035 g; 44%): mp 232 °C. IR(KBr): ν(PC) 1090s, 1096s, $\nu(PF_6)$ absent. Magnetic moment: $\mu_{eff} = 4.6\ \mu_B$. Anal. Calcd for $C_{36}H_{30}Cl_2CoP_2$: C, 66.0 H, 4.6. Found: C, 65.7; H, 4.7 (M = 654.4).

C. X-ray Data Collection and Structural Determinations of [CoCl₂{Ph₂PCH₂C(O)Ph}₂] (1a), Co₂(CO)₆[Ph₂PCH₂C(O)Ph]₂ (5), and [(Ph₃P)₂Ag(μ-Cl)₂Co(μ-Cl)₂Ag(PPh₃)₂]·0.5OEt₂ (13·0.5OEt₂). The crystallographic data for these compounds are summarized in Table V. Data were collected at room temperature on a Enraf-Nonius CAD4 four-circle (**1a** and **5**) and a Siemens AED (**13**·$0.5OEt_2$) single-crystal diffractometer using niobium-filtered Mo Kα radiation. All reflections with θ in the range 1–27 (**1a**), 1–20 (**5**), and 3–23° (**13**·0.5 OEt_2) were measured; of 8597 (**1a**), 3799 (**5**), and 19910 (**13**·$0.5OEt_2$) independent reflections, 2849 (**1a**), and 2915 (**5**) having $I > 6\sigma(I)$, and 5872 (**13**·$0.5OEt_2$), having $I > 2\sigma(I)$, were considered observed and used in the structure solution and refinement. For **1a** and **5** intensities were corrected for Lorentz–polarization effects, and an empirical absorption correction was made after isotropic convergence.[34,35] No correction for the absorption effect was applied for **13**·$0.5OEt_2$.

The structure of **1a** was solved by direct methods and successive Fourier difference syntheses and Fourier syntheses, and refined by full-matrix least-squares methods with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were refined and assigned isotropic

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(34) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A*, **1983**, *39*, 158.

(35) SDP Structure Determination Package. Enraf Nonius, Delft, The Netherlands, 1977.

Table VIII. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^4) for the Non-Hydrogen Atoms of Complex **13**·0.5OEt$_2$

atom	*x/a*	*y/b*	*z/c*	*U*	atom	*x/a*	*y/b*	*z/c*	*U*
Molecule A									
Ag(1A)	1162(1)	2206(1)	−4(1)	729(8)^a	C(32A)	−975(16)	1769(27)	−311(11)	590(112)
Ag(2A)	3284(1)	2344(1)	1486(1)	740(8)^a	C(33A)	−1323(16)	1258(27)	−525(11)	944(175)
Co(1A)	2173(1)	2393(2)	761(1)	591(12)^a	C(34A)	−1061(16)	582(27)	−636(11)	2564(755)
Cl(1A)	1641(3)	3323(3)	458(2)	674(23)^a	C(35A)	−452(16)	416(27)	−533(11)	1414(258)
Cl(2A)	1840(3)	1321(3)	468(2)	715(24)^a	C(36A)	−104(16)	927(27)	−319(11)	1665(307)
Cl(3A)	3203(3)	2575(4)	754(2)	754(25)^a	C(31C)	−420(15)	1548(24)	−153(12)	524(224)
Cl(4A)	2036(3)	2277(4)	1367(1)	713(24)^a	C(32C)	−742(15)	1752(24)	−475(12)	1212(237)
P(1A)	1635(3)	2302(4)	−586(2)	734(27)^a	C(33C)	−1092(15)	1214(24)	−670(12)	1672(304)
P(2A)	72(3)	2187(4)	112(2)	683(26)^a	C(34C)	−1120(15)	471(24)	−543(12)	1026(153)
P(3A)	3353(3)	3503(4)	1859(2)	689(26)^a	C(35C)	−798(15)	267(24)	−221(12)	1778(292)
P(4A)	3801(3)	1122(4)	1545(2)	673(26)^a	C(36C)	−448(15)	805(24)	−26(12)	1213(199)
C(1A)	1553(8)	3242(7)	−785(5)	736(69)	C(37A)	2857(7)	4259(9)	1685(5)	706(68)
C(2A)	1756(8)	3860(7)	−576(5)	831(77)	C(38A)	2558(7)	4757(9)	1910(5)	1089(97)
C(3A)	1670(8)	4594(7)	−710(5)	904(81)	C(39A)	2178(7)	5322(9)	1758(5)	1273(111)
C(4A)	1381(8)	4708(7)	−1053(5)	1140(99)	C(40A)	2097(7)	5389(9)	1382(5)	1088(94)
C(5A)	1179(8)	4089(7)	−1261(5)	2017(177)	C(41A)	2396(7)	4891(9)	1157(5)	1252(104)
C(6A)	1265(8)	3356(7)	−1127(5)	1325(118)	C(42A)	2776(7)	4327(9)	1309(5)	1091(97)
C(7A)	1221(18)	1652(21)	−922(10)	389(182)	C(43A)	4107(6)	3911(11)	1920(4)	723(71)
C(8A)	773(18)	1151(21)	−812(10)	1088(230)	C(44A)	4611(6)	3429(11)	1970(4)	933(82)
C(9A)	510(18)	629(21)	−1059(10)	1256(210)	C(45A)	5199(6)	3731(11)	2024(4)	1181(106)
C(10A)	695(18)	608(21)	−1415(10)	1876(450)	C(46A)	5283(6)	4514(11)	2029(4)	1246(111)
C(11A)	1143(18)	1109(21)	−1524(10)	1275(238)	C(47A)	4779(6)	4995(11)	1980(4)	1240(108)
C(12A)	1405(18)	1631(21)	−1278(10)	1605(269)	C(48A)	4191(6)	4694(11)	1925(4)	1228(109)
C(7C)	1357(18)	1628(22)	−914(9)	803(238)	C(49A)	3111(8)	3342(10)	2317(4)	685(66)
C(8C)	718(18)	1616(22)	−949(9)	857(163)	C(50A)	2567(8)	2950(10)	2365(4)	760(73)
C(9C)	421(18)	1203(22)	−1229(9)	976(175)	C(51A)	2353(8)	2865(10)	2712(4)	1030(94)
C(10C)	764(18)	803(22)	−1474(9)	488(87)	C(52A)	2682(8)	3173(10)	3011(4)	983(85)
C(11C)	1403(18)	815(22)	−1438(9)	1451(295)	C(53A)	3226(8)	3566(10)	2963(4)	1407(119)
C(12C)	1700(18)	1228(22)	−1158(9)	1321(254)	C(54A)	3441(8)	3650(10)	2616(4)	1125(98)
C(13A)	2445(6)	2141(10)	−608(5)	741(72)	C(55A)	4600(7)	1217(11)	1659(6)	739(73)
C(14A)	2804(6)	2450(10)	−872(5)	1043(94)	C(56A)	4942(7)	1636(11)	1421(6)	1163(101)
C(15A)	3419(6)	2244(10)	−885(5)	1219(109)	C(57A)	5566(7)	1757(11)	1500(6)	1547(134)
C(16A)	3675(6)	1729(10)	−633(5)	1509(129)	C(58A)	5848(7)	1460(11)	1818(6)	1733(156)
C(17A)	3317(6)	1420(10)	−369(5)	1387(120)	C(59A)	5506(7)	1041(11)	2055(6)	1603(138)
C(18A)	2702(6)	1626(10)	−356(5)	1028(93)	C(60A)	4882(7)	920(11)	1976(6)	1143(100)
C(19A)	−280(8)	3116(8)	17(4)	653(64)	C(61A)	3511(7)	518(10)	1890(4)	652(65)
C(20A)	5(8)	3574(8)	−232(4)	912(86)	C(62A)	3702(7)	−232(10)	1932(4)	957(87)
C(21A)	−245(8)	4277(8)	−328(4)	1039(92)	C(63A)	3469(7)	−680(10)	2204(4)	1096(96)
C(22A)	−781(8)	4522(8)	−176(4)	1086(97)	C(64A)	3045(7)	−378(10)	2434(4)	1008(90)
C(23A)	−1067(8)	4064(8)	73(4)	1274(114)	C(65A)	2855(7)	372(10)	2392(4)	1170(102)
C(24A)	−817(8)	3361(8)	169(4)	1193(104)	C(66A)	3088(7)	820(10)	2120(4)	1025(93)
C(25A)	−114(8)	1936(9)	575(3)	675(67)	C(67A)	3798(8)	512(9)	1143(4)	689(67)
C(26A)	364(8)	1956(9)	842(3)	568(61)	C(68A)	3282(8)	558(9)	904(4)	830(78)
C(27A)	251(8)	1782(9)	1201(3)	698(66)	C(69A)	3233(8)	89(9)	599(4)	1328(111)
C(28A)	−340(8)	1587(9)	1293(3)	928(84)	C(70A)	3699(8)	−425(9)	534(4)	1265(111)
C(29A)	−817(8)	1567(9)	1026(3)	1252(109)	C(71A)	4215(8)	−471(9)	774(4)	1303(114)
C(30A)	−704(8)	1741(9)	667(3)	1219(103)	C(72A)	4264(8)	−3(9)	1078(4)	985(88)
C(31A)	−366(16)	1603(27)	−208(11)	1540(387)					
Molecule B									
Ag(1B)	6827.0(9)	3316.4(12)	921.2(5)	895(9)^a	C(17B)	6782(19)	2668(16)	−620(8)	3346(269)
Ag(2B)	8985.3(8)	3250.1(10)	2359.7(4)	590(6)^a	C(18B)	6608(19)	2414(16)	−283(8)	3210(266)
Co(1B)	7909.1(14)	3284.9(17)	1621.4(8)	611(11)^a	C(19B)	6442(9)	5242(9)	1216(4)	778(74)
Cl(1B)	6878(3)	3142(4)	1654(2)	916(29)^a	C(20B)	7036(9)	5320(9)	1371(4)	997(89)
Cl(2B)	8055(3)	3375(4)	1018(2)	748(24)^a	C(21B)	7156(9)	5847(9)	1647(4)	1252(110)
Cl(3B)	8430(3)	2282(3)	1868(2)	670(23)^a	C(22B)	6683(9)	6296(9)	1769(4)	1227(104)
Cl(4B)	8275(3)	4271(3)	1963(2)	662(23)^a	C(23B)	6090(9)	6217(9)	1614(4)	1262(107)
P(1B)	6729(4)	2276(5)	496(3)	1377(48)^a	C(24B)	5969(9)	5690(9)	1337(4)	1075(95)
P(2B)	6348(3)	4561(4)	856(2)	747(27)^a	C(25B)	5544(7)	4419(13)	792(7)	1066(94)
P(3B)	10049(3)	3468(3)	2203(1)	475(21)^a	C(26B)	5267(7)	3960(13)	1044(7)	1132(98)
P(4B)	8509(3)	3019(3)	2939(2)	584(23)^a	C(27B)	4637(7)	3828(13)	1010(7)	1220(107)
C(1B)	5930(8)	1889(15)	454(5)	1196(101)	C(28B)	4284(7)	4154(13)	724(7)	1744(159)
C(2B)	5832(8)	1115(15)	404(5)	1314(110)	C(29B)	4561(7)	4613(13)	473(7)	2243(201)
C(3B)	5236(8)	838(15)	343(5)	1518(126)	C(30B)	5192(7)	4746(13)	507(7)	1766(156)
C(4B)	4740(8)	1336(15)	333(5)	1423(124)	C(31B)	6595(8)	5077(11)	460(4)	814(74)
C(5B)	4839(8)	2110(15)	383(5)	1492(129)	C(32B)	6519(8)	5853(11)	405(4)	1229(106)
C(6B)	5434(8)	2387(15)	444(5)	1617(139)	C(33B)	6745(8)	6196(11)	99(4)	1092(96)
C(7B)	7199(10)	1507(12)	546(10)	1305(114)	C(34B)	7045(8)	5762(11)	−153(4)	1078(92)
C(8B)	7494(10)	1070(12)	293(10)	1981(164)	C(35B)	7121(8)	4985(11)	−98(4)	1230(107)
C(9B)	7848(10)	449(12)	408(10)	1937(163)	C(36B)	6895(8)	4643(11)	209(4)	1290(110)
C(10B)	7909(10)	266(12)	776(10)	2276(190)	C(37B)	10438(6)	4250(7)	2440(4)	453(54)
C(11B)	7615(10)	703(12)	1029(10)	3551(296)	C(38B)	11071(6)	4277(7)	2514(4)	606(62)
C(12B)	7260(10)	1323(12)	914(10)	2159(173)	C(39B)	11341(6)	4923(7)	2671(4)	763(72)
C(13B)	7003(19)	2504(16)	24(8)	1645(138)	C(40B)	10978(6)	5542(7)	2754(4)	740(71)
C(14B)	7573(19)	2849(16)	−6(8)	2175(177)	C(41B)	10345(6)	5515(7)	2680(4)	810(75)
C(15B)	7747(19)	3103(16)	−343(8)	1942(161)	C(42B)	10075(6)	4869(7)	2523(4)	653(63)
C(16B)	7352(19)	3013(16)	−650(8)	2826(236)	C(43B)	10176(7)	3642(8)	1733(3)	500(54)

Table VIII (Continued)

atom	x/a	y/b	z/c	U	atom	x/a	y/b	z/c	U
				Molecule B (Continued)					
C(44B)	9671(7)	3588(8)	1485(3)	598(60)	C(61B)	7754(6)	2614(9)	2928(5)	568(59)
C(45B)	9740(7)	3733(8)	1118(3)	694(68)	C(62B)	7398(6)	2610(9)	2602(5)	880(79)
C(46B)	10313(7)	3931(8)	998(3)	670(67)	C(63B)	6804(6)	2319(9)	2591(5)	1051(92)
C(47B)	10817(7)	3985(8)	1245(3)	777(74)	C(64B)	6565(6)	2031(9)	2906(5)	1343(117)
C(48B)	10749(7)	3841(8)	1613(3)	756(72)	C(65B)	6920(6)	2035(9)	3232(5)	1523(135)
C(49B)	10528(6)	2655(7)	2346(4)	518(56)	C(66B)	7515(6)	2326(9)	3243(5)	1453(128)
C(50B)	10458(6)	2395(7)	2698(4)	556(57)	C(67B)	8920(6)	2350(8)	3236(4)	590(60)
C(51B)	10781(6)	1760(7)	2826(4)	904(79)	C(68B)	9092(6)	1663(8)	3085(4)	755(68)
C(52B)	11175(6)	1384(7)	2602(4)	949(85)	C(69B)	9406(6)	1124(8)	3300(4)	906(83)
C(53B)	11246(6)	1643(7)	2249(4)	910(80)	C(70B)	9547(6)	1271(8)	3667(4)	1163(102)
C(54B)	10922(6)	2279(7)	2121(4)	670(64)	C(71B)	9374(6)	1957(8)	3818(4)	1484(130)
C(55B)	8481(9)	3889(7)	3193(4)	758(74)	C(72B)	9061(6)	2497(8)	3603(4)	936(83)
C(56B)	9019(9)	4314(7)	3200(4)	793(75)	O(1D)	5117(16)	1966(22)	8403(11)	3809(148)
C(57B)	9048(9)	5012(7)	3378(4)	1203(104)	C(1D)	5228(23)	2693(29)	9031(15)	3880(220)
C(58B)	8537(9)	5285(7)	3548(4)	942(83)	C(2D)	5312(24)	2764(33)	8650(16)	3742(222)
C(59B)	7998(9)	4860(7)	3540(4)	1011(90)	C(3D)	5011(25)	1872(35)	8054(18)	3338(241)
C(60B)	7970(9)	4162(7)	3363(4)	1142(101)	C(4D)	4921(23)	2561(33)	7844(15)	3939(235)

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

B_{eq} thermal parameters of the bonded carbons.[36] The final difference map showed no residual peaks. A weighting scheme $w = 1.7374[\sigma^2(F_0) + 0.00051F_0^2]^{-1}$ was used in the last cycles of refinement. Final R and R_w values were 0.052 and 0.048 respectively. Atomic coordinates with estimated standard deviations are given in Table VI.

The structure of **5** was solved by Patterson methods (Co, P) and successive Fourier difference syntheses (O, C) and refined by full-matrix least-squares method with anisotropic thermal parameters for all non-hydrogen atoms. The positional parameters of hydrogen atoms were calculated, then refined and were assigned isotropic thermal parameters B_{eq} of the bonded carbon atom.[36] Final R and R_w values were 0.049 and 0.046, respectively. Atomic coordinates with estimated standard deviations are given in Table VII.

The structure of **13**·0.5OEt$_2$ was solved by Patterson and Fourier methods. In the crystals two independent molecules (A and B), differing only in the orientation of the phenyl rings, and an ethyl ether molecule of solvation are present. Two phenyl rings of the molecule A were found disordered and distributed in two positions with equal occupancy factors. The refinement was carried out by blocked full-matrix least-squares methods, first with isotropic and then with anisotropic thermal parameters only for the Ag, Co, Cl, and P atoms. All phenyl rings were treated as rigid groups (C–C = 1.395 Å). The hydrogen atoms, at their geometrically calculated positions, could not be introduced in the final structure factor calculation because of the limits in the atom number of the program used. A weighting scheme $w = K[\sigma^2(F_0) + gF_0^2]^{-1}$ was used in the last cycles of refinement; at convergence the K and g values were 0.679 and 0.0066 respectively. Final R and R_w values were 0.0778 and 0.1017 respectively. The final atomic coordinates for the non-hydrogen atoms of **13**·0.5OEt$_2$ are given in Table VIII. For all three structures, neutral atomic scattering factors, corrected for the real and imaginary parts of anomalous dispersion, were obtained from standard sources.[37] Calculations for **13**·0.5OEt$_2$ were carried out on the GOULD POWERNODE 6040 and ENCORE 91 of the Centro di Studio per la Strutturistica Diffrattometrica del CNR, Parma, Italy, using the SHELX-76 and SHELXS-86 systems of crystallographic computer programs.[36]

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Supplementary Material Available: Coordinates for hydrogen atoms, thermal parameters for the non-hydrogen atoms, complete bond distances and angles, and experimental data for the X-ray diffraction study of **1a** (Tables S-I–S-IV), coordinates for hydrogen atoms, thermal parameters for the non-hydrogen atoms, complete bond distances and angles, and experimental data for the X-ray diffraction study of **5** (Tables S-V–S-VIII); thermal parameters for the non-hydrogen atoms, complete bond distances and angles, and experimental data for the X-ray diffraction study of **13**·0.5OEt$_2$ (Tables S-IX–S-XI) (30 pages). Ordering information is given on any current masthead page.

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(36) Sheldrick, G. M. SHELX-76. Program for crystal structure determination. University of Cambridge, England, 1976. SHELXS-86. Program for the solution of crystal structures. University of Göttingen, 1986.

(37) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol IV.