carbon atoms of a pyrrolyl ring bonded to Na(2) of a second unit. The coordination around chromium is distorted square-planar, the dihedral angle between the N(30)–Cr–N(10) and N(20)–Cr–N(40) planes being 23.4 (2)°. The chromium atom is σ-bonded to the four pyrrolyl groups and is coplanar with each ring. The Cr–N bonding distances are normal [Cr–N ranging between 2.074 (5) and 2.086 (5) Å] and compare well with those observed in **2**, **5**, and **7**. In contrast to the previous cases, the pyrrolyl rings are severely tilted in respect to each other [tilt angle = 86.9 (3), 84.9 (3)°] probably to minimize the steric interaction between the ortho methyl groups. However, it cannot be excluded that optimization of the coordination geometry around the Na atoms might be also responsible for this arrangement. The high asymmetry of the monomeric unit is mainly determined by the coordination around the two unequivalent Na atoms. Na(1) is bonded to the [N(20)–C(24)] ring in a rather symmetric η^5-fashion, the Na–C distances ranging between 2.667 and 2.957 Å. Conversely, the interaction of Na(1) with the second pyrrolyl ring (N(40)–C(44)) is limited to only one bond [Na(1)–C(44) = 2.783 (5) Å], the other distances (including from nitrogen) being larger than 3 Å. The bonding of Na(2) with the two rings is quite curious. Each ring is η^3-bonded (allylic-like) to Na(2), the shortest contacts being with C(34) and C(11) [Na(2)–C(34) = 2.680 (6) Å, Na(2)–C(11) = 2.631 (6) Å]. Furthermore, three carbon atoms of the two pyrrolyl rings bonded to Na(2) are engaged in a η^3-bonding with Na(1) of a second molecular unit. The shortest distance [Na(1)–C(13) = 2.685 (6) Å] compares with all the other short intramolecular Na–C contacts. This additional intermolecular interaction is responsible for the probably weak polymeric aggregation and the remarkably large thermal effect. In fact, at room temperature, no X-ray diffraction was observed. However, a standard data set was obtained at 130 K from the same crystal that decreased in size by 30% upon cooling.

The magnetic properties of this one dimensional polymer are very close to those of the monomeric square planar complex **5**. The value of the magnetic moment ($\mu_{\text{eff}} = 4.59\ \mu_B$) is consistent with a high-spin d^4 electronic configuration of chromium(II), suggesting that the polymeric aggregation of **6** affects only slightly the magnetic behavior of the central Cr^{2+} ion.

Sodium can be easily abstracted from the molecular core of **3** and **6** by simple treatment with strong coordinating agents (pyridine, crown-ethers), leading to the formation of monomeric **2** and **5**, respectively (Scheme I). This suggests furthermore that the coordination of Na to the pyrrolyl groups is quite labile [sharply in contrast to the case of $(Et_2N)_4CrLi_2(THF)_2$[16d] where the Li cation cannot be abstracted] and that the solid-state structure is probably not preserved in solution.

Acknowledgment. We are indebted to a reviewer for constructive suggestions. Part of the crystallographic work (A.L.S. and W.J.J.S.) has been supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO). X-ray data for **6** and **7** were kindly collected by A. J. M. Duisenberg. We thank Dr. J. L. de Boer and H. Betlehem for making available a CAD4-series 1 diffractometer for a preliminary room-temperature collection of the data set of **7** through the network.

Supplementary Material Available: For each complex, tables of crystal data, thermal parameters, hydrogen atom positional parameters, and extensive lists of bond angles and distances (27 pages); lists of observed and calculated structure factors (64 pages). Ordering information is given on any current masthead page.

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Crystal Structure and Reactivity of $[Cu(dmpe)_2][Cu(Co(CO)_4)_2]$ (dmpe = 1,2-Bis(dimethylphosphino)ethane): Staggered and Eclipsed Conformations of $[(CO)_4CoCuCo(CO)_4]^-$ Anions

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The reaction of $NaCo(CO)_4$ with 1,2-bis(dimethylphosphino)ethane (dmpe) and CuCl in dichloromethane solution gave pale yellow, air-sensitive $[Cu(dmpe)_2][Cu(Co(CO)_4)_2]$, which has been characterized by X-ray crystallography at room temperature. The crystals are monoclinic, space group $C2/c$, with unit cell dimensions a = 18.437 (5) Å, b = 9.880 (2) Å, c = 38.109 (9) Å, β = 102.07 (2)°, V = 6788 (3) Å^3, Z = 8, and R_{wF} = 6.02%. The anions $[(CO)_4CoCuCo(CO)_4]^-$ are monomers with staggered and eclipsed forms existing simultaneously in the unit cell. The staggered form adopts a linear conformation around copper, whereas in the eclipsed form the Co–Cu–Co bond angle is slightly less than 180°. Reaction of 2 equiv of the ligand dppe (1,2-bis(diphenylphosphino)ethane) with $[Cu(Co(CO)_4)_2]^-$ at −78 °C instantly affords the $Co(CO)_4^-$ anion and $Cu(dppe)_2^+$, indicative of a highly labile Cu–Co bond.

Introduction

Recently, much attention has been focused on synthetic[1-3] and theoretical[4] studies of heterobimetallic compounds containing copper. It has been reported that the reaction of L_2CuCl with the $Co(CO)_4^-$ anion leads to the formation of a binuclear Cu–Co complex (eq 1).[3] A single-crystal structural analysis of

$$L_2CuCl + NaCo(CO)_4 \rightarrow L_2CuCo(CO)_4 + NaCl \quad (1)$$

$(tmed)CuCo(CO)_4$ (tmed = *N,N,N′,N′*-tetramethylethylenediamine) (**1**) showed that one of the carbonyl groups asymmetrically bridges the Cu–Co bond.[3] This is consistent with a low-frequency ν(CO) vibration observed at 1820 cm^{-1} in its solid-state infrared spectrum.

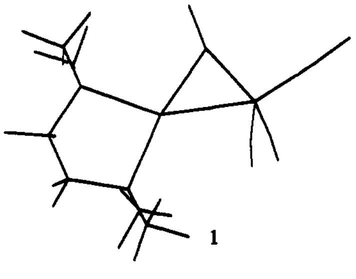

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Table I. Crystallographic Data for $[Cu(dmpe)_2][Cu(Co(CO)_4)_2]$

chem formula	$C_{20}H_{32}O_8P_4Co_2Cu_2$	V, Å^3	6788 (3)
fw	769.2	Z	16
space group	$C2/c$	D_{calcd}, g/cm^3	1.505
a, Å	18.437 (5)	μ(Mo Kα), cm^{-1}	24.20
b, Å	9.880 (2)	wavelength, Å	0.71073
c, Å	38.109 (9)	R_F,^{a} %	5.70
β, deg	102.07 (2)	R_{wF},^{a} %	6.23

[a] $R_F = \sum|\Delta|/\sum|F_o|$ and $R_{wF} = \sum(|\Delta|w^{1/2})/\sum(|F_o|w^{1/2})$, where $\Delta = |F_o| - |F_c|$.

In an attempt to synthesize the analogous $(dmpe)CuCo(CO)_4$ complex using dmpe, we instead obtained an ion-paired complex, $[Cu(dmpe)_2][Cu(Co(CO)_4)_2]$ (eq 2), whose structure and reactivity we report herein.

$$CuCl + dmpe + NaCo(CO)_4 \rightarrow \tfrac{1}{2}[Cu(dmpe)_2][Cu(Co(CO)_4)_2] + NaCl \quad (2)$$

Experimental Section

Methods and Materials. All manipulations were carried out either in an argon drybox or on a double-manifold Schlenk vacuum line, using freshly distilled solvents. Reagent grade tetrahydrofuran and hexane were purified by distillation under nitrogen from sodium benzophenone ketyl. Dichloromethane was refluxed under nitrogen over phosphorus pentoxide and distilled prior to use. CuCl and 1,2-bis(dimethylphosphino)ethane (dmpe) were purchased from Aldrich Chemical Co. $Co_2(CO)_8$ and 1,2-bis(diphenylphosphino)ethane (dppe) were obtained from Strem Chemical Inc. $NaCo(CO)_4$ was prepared from NaOH and $Co_2(CO)_8$ according to published procedures.[5] Infrared spectra were recorded on an IBM FTIR32 spectrometer.

Synthesis of $[Cu(dmpe)_2][Cu(Co(CO)_4)_2]$. CuCl (0.65 g, 6.66 mmol) was loaded in a 100-mL Schlenk flask in the drybox. After addition of 70 mL of CH_2Cl_2, dmpe (1 g, 6.66 mmol) was added via syringe under N_2 to the solution. The reaction was then placed under a CO atmosphere for 30 min. After the addition of $NaCo(CO)_4$ (1.292 g, 6.66 mmol), the solution was stirred for 2 h and then filtered under N_2 to remove NaCl. The yellow filtrate was concentrated to ca. 10 mL, and 50 mL of hexane was added. The product precipitated as a yellow powder (1.7 g, 67%) and was recrystallized from CH_2Cl_2/hexane. Anal. Calcd for $C_{20}H_{32}O_8P_4Co_2Cu_2$: C, 31.23; H, 4.16; Cu, 16.52. Found: C, 30.85; H, 4.44; Cu, 17.89. The infrared bands of the carbonyl stretching frequencies in Nujol mull: 2027 (m), 1960 (s, sh), 1925 (vs, bd), 1879 (s) cm^{-1}.

Reaction of $[Cu(dmpe)_2][Cu(Co(CO)_4)_2]$ with dppe. The complex $[Cu(dmpe)_2][Cu(Co(CO)_4)_2]$ was reacted with 2 equiv of dppe in THF at −78 °C. The reaction was monitored by IR spectroscopy, and the final infrared spectrum revealed quantitative formation of $Co(CO)_4^-$ with concomitant formation of 1 equiv of $Cu(dppe)_2^+$.

X-ray Crystallographic Study of $[Cu(dmpe)_2][Cu(Co(CO)_4)_2]$. Crystal data and details of data collection are given in Table I. A pale yellow block (0.26 mm × 0.36 mm × 0.38 mm) was mounted in a capillary tube, at room temperature. Preliminary examination and data collection were performed on a Nicolet R3m/V X-ray diffractometer (oriented graphite monochromator; Mo Kα λ = 0.71073 Å radiation). Cell parameters were calculated from the least-squares fitting of the setting angles for 25 reflections ($2\theta_{av}$ = 21.6). ω scans for several intense reflections indicated acceptable crystal quality. Data were collected for $4.0° \leq 2\theta \leq 50.0°$ [ω(Wyckoff) scans, $-21 \leq h \leq 21$, $-11 \leq k \leq 0$, $-45 \leq l \leq 0$] at 296 K. The scan range for the data collection was 1.20° plus Kα separation, with a variable scan rate of 1.50–15.00° min^{-1}. A 10.0% decay in the intensity of 3 control reflections collected every 97 reflections was observed. The intensities of the data set were corrected by employing a correction curve based on the intensity decay of the control reflections. Background measurement by the stationary-crystal and stationary-counter technique was taken at the beginning and end of each scan for half of the total scan time. Lorentz and polarization corrections applied to 6506 reflections. No absorption correction was applied. A total of 3131 unique observed reflections (R_{int} = 0.06, $R_{int} = \sum|F^2 - (F^2)_{mean}|/\sum F^2$), with $|F| \geq 4.0\sigma|F|$, were used in further calculations. The structure was solved by direct methods (SHELXS, SHELXTL-PLUS program package).[6] Full-matrix least-squares anisotropic refinement for all non-hydrogen atoms [SHELXLS, SHELXTL-PLUS; number of least-squares parameters = 327, quantity minimized $\sum w(F_o - F_c)^2$, $w = \sigma^2(F) + gF^2$, $g = 0.0006$][6] yielded R_F = 0.057, R_{wF} = 0.062, and S = 1.47 at convergence (largest Δ/σ = 0.0022; mean Δ/σ = 0.0001; largest positive peak in the final Fourier difference map = 0.35 e Å^{-3}; largest negative peak in the final Fourier difference map = −0.33 e Å^{-3}). Hydrogen atoms were placed in idealized positions with isotropic thermal parameters fixed at 0.08. Neutral-atom scattering factors and anomalous dispersion terms were taken from the literature.[7]

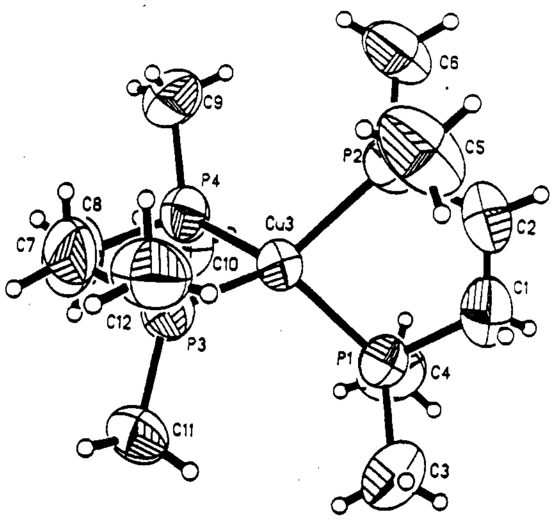

Figure 1. ORTEP diagram of the $[Cu(dmpe)_2]^+$ cation.

Tables listing observed and calculated structure factors are available as supplementary material.

Results

Reactions of CuCl/dmpe with $NaCo(CO)_4$. The reaction of CuCl with 1,2-bis(dimethylphosphino)ethane in THF in the presence of $NaCo(CO)_4$ yielded a yellow solution, which upon solvent reduction and addition of hexane provided a yellow powder. The infrared spectrum of this complex taken in Nujol mull exhibited ν(CO) frequencies similar to those reported from the analogous reaction carried out by Doyle and co-workers (see Experimental Section).[3] A similar ν(CO) spectrum was obtained in methylene chloride as well, with the four bands appearing at 2027 (m), 1958 (s), 1925 (s, sh), and 1890 (sh) cm^{-1}. It is of importance to note that in this instance there were no ν(CO) vibrations below 1880 cm^{-1} as seen in species **1**, where an asymmetrically bridging CO is present. A comparable observation was made by Doyle and co-workers.[3] Elemental analysis revealed the complex to contain one copper and one dmpe ligand per $Co(CO)_4^-$ unit.

Description of the Structure. In order to definitively assess the molecular structure of the complex, it has been subjected to a single-crystal X-ray diffraction investigation. Pale yellow crystals suitable for X-ray structural analysis were obtained from CH_2Cl_2/hexane. Several attempts were made to determine the structure at −85 °C; however, in every instance the crystal fractured during data collection within a few hours. It was therefore necessary to determine the structure at 23 °C. Nevertheless, all crystals examined (at least ten), including the one used for structure determination at ambient temperature, possessed the same unit cell and thus were typical of the entire sample (recall the complex was isolated in nearly 70% yield). The final atomic coordinates for all non-hydrogen atoms are provided in Table II. One whole cation and two half-anions were found in the unique volume of the unit cell. A staggered form of the anion is found to lie about the inversion center ($^1/_4$, $^3/_4$, $^1/_2$) with the copper atom occupying the special position. An eclipsed form of the anion sits about the 2-fold axis (0, y, $^1/_4$) with the copper atom occupying

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Table II. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3)

	x	*y*	*z*	*U*(eq)^a
Co(1)	2802 (1)	5649 (1)	4689 (1)	70 (1)
Cu(1)	2500	7500	5000	103 (1)
C(101)	2445 (6)	5009 (11)	5051 (3)	93 (5)
O(101)	2214 (5)	4516 (9)	5286 (3)	137 (5)
C(102)	2101 (7)	6487 (12)	4367 (3)	105 (6)
O(102)	1673 (6)	7030 (11)	4157 (2)	163 (5)
C(103)	3636 (7)	6544 (11)	4819 (3)	99 (5)
O(103)	4185 (5)	7099 (10)	4881 (3)	151 (5)
C(104)	3062 (6)	4199 (12)	4467 (3)	89 (5)
O(104)	3230 (5)	3277 (8)	4328 (2)	129 (4)
Co(2)	1113 (1)	8177 (1)	2299 (1)	77 (1)
Cu(2)	0	8203 (2)	2500	91 (1)
C(201)	1322 (7)	9030 (16)	2711 (4)	140 (7)
O(201)	1507 (6)	9609 (14)	2976 (3)	222 (7)
C(202)	1921 (7)	8263 (14)	2129 (3)	129 (7)
O(202)	2443 (6)	8287 (14)	2016 (3)	224 (8)
C(203)	445 (7)	8940 (12)	1962 (3)	95 (5)
O(203)	72 (5)	9456 (10)	1719 (2)	147 (5)
C(204)	952 (7)	6443 (14)	2340 (3)	107 (6)
O(204)	894 (7)	5301 (10)	2360 (3)	165 (6)
Cu(3)	178 (1)	3268 (1)	1247 (1)	59 (1)
P(1)	1332 (1)	2609 (3)	1507 (1)	75 (1)
P(2)	630 (1)	5075 (3)	1001 (1)	72 (1)
P(3)	−685 (1)	3577 (3)	1578 (1)	78 (1)
P(4)	−584 (1)	1872 (3)	875 (1)	74 (1)
C(1)	1894 (6)	4019 (4)	1404 (4)	147 (7)
C(2)	1614 (6)	4705 (14)	1086 (3)	127 (6)
C(3)	1670 (6)	2395 (12)	1986 (3)	105 (5)
C(4)	1699 (6)	1122 (12)	1345 (3)	119 (6)
C(5)	582 (8)	6703 (10)	1200 (3)	140 (7)
C(6)	425 (6)	5469 (10)	534 (2)	107 (5)
C(7)	−1514 (6)	2820 (16)	1307 (3)	134 (7)
C(8)	−1347 (5)	1637 (12)	1107 (3)	107 (5)
C(9)	−1021 (6)	2555 (11)	442 (3)	106 (5)
C(10)	−374 (6)	152 (10)	768 (3)	119 (6)
C(12)	−1041 (6)	5241 (11)	1675 (3)	120 (6)
C(11)	−569 (5)	2723 (10)	2007 (2)	86 (4)

^{a} Equivalent isotropic *U* defined as one-third of the traceof the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table III. Bond Lengths (Å) for [Cu(dmpe)$_2$][Cu(Co(CO)$_4$)$_2$]

Co(1)–Cu(1)	2.309 (1)	Co(1)–C(101)	1.765 (12)
Co(1)–C(102)	1.789 (11)	Co(1)–C(103)	1.753 (12)
C(1)–C(104)	1.780 (12)	Cu(1)–C(101)	2.472 (11)
Cu(1)–C(102)	2.573 (12)	Cu(1)–C(103)	2.520 (14)
Cu(1)–Co(1A)	2.309 (1)	Cu(1)–C(10A)	2.472 (11)
Cu(1)–C(10B)	2.573 (12)	Cu(1)–C(10C)	2.520 (14)
C(101)–O(101)	1.172 (16)	C(102)–O(102)	1.134 (15)
C(103)–O(103)	1.133 (16)	C(104)–O(104)	1.130 (14)
Co(2)–Cu(2)	2.335 (2)	Co(2)–C(201)	1.751 (15)
Co(2)–C(202)	1.747 (14)	Co(2)–C(203)	1.753 (11)
Co(2)–C(204)	1.751 (14)	Cu(2)–C(201)	2.536 (13)
Cu(2)–C(203)	2.472 (13)	Cu(2)–C(204)	2.632 (14)
Cu(2)–Co(2A)	2.335 (2)	Cu(2)–C(20A)	2.537 (13)
Cu(2)–C(20B)	2.472 (13)	Cu(2)–C(20C)	2.632 (14)
C(201)–O(201)	1.149 (19)	C(202)–O(202)	1.133 (19)
C(203)–O(203)	1.150 (14)	C(204)–O(204)	1.138 (17)
Cu(3)–P(1)	2.248 (3)	Cu(3)–P(2)	2.254 (3)
Cu(3)–P(3)	2.250 (3)	Cu(3)–P(4)	2.248 (3)
P(1)–C(1)	1.826 (14)	P(1)–C(3)	1.815 (10)
P(1)–C(4)	1.782 (12)	P(2)–C(2)	1.813 (11)
P(2)–C(5)	1.790 (11)	P(2)–C(6)	1.784 (9)
P(3)–C(7)	1.818 (11)	P(3)–C(12)	1.836 (12)
P(3)–C(11)	1.812 (9)	P(4)–C(8)	1.827 (12)
P(4)–C(9)	1.809 (10)	P(4)–C(10)	1.808 (11)
C(1)–C(2)	1.389 (18)	C(7)–C(8)	1.461 (19)

Table IV. Bond Angles (deg) for [Cu(dmpe)$_2$][Cu(Co(CO)$_4$)$_2$]

Cu(1)–Co(1)–C(101)	73.4 (4)	Cu(1)–Co(1)–C(102)	76.6 (4)
C(101)–Co(1)–C(102)	111.7 (6)	Cu(1)–Co(1)–C(103)	75.3 (4)
C(101)–Co(1)–C(103)	114.0 (5)	C(102)–Co(1)–C(103)	115.2 (5)
Cu(1)–Co(1)–C(104)	117.5 (3)	C(101)–Co(1)–C(104)	105.4 (5)
C(102)–C(1)–C(104)	105.9 (5)	C(103)–Co(1)–C(104)	103.5 (5)
Co(1)–Cu(1)–C(101)	43.2 (3)	Co(1)–Cu(1)–C(102)	42.6 (3)
C(101)–Cu(1)–C(102)	71.3 (4)	Co(1)–Cu(1)–C(103)	42.3 (3)
C(101)–Cu(1)–C(103)	72.5 (4)	C(102)–Cu(1)–C(103)	71.9 (4)
Co(1)–Cu(1)–Co(1A)	180.0 (1)	C(101)–Cu(1)–Co(1A)	136.8 (3)
C(102)–Cu(1)–Co(1A)	137.4 (3)	C(103)–Cu(1)–Co(1A)	137.7 (3)
Co(1)–Cu(1)–C(10A)	136.8 (3)	C(101)–Cu(1)–C(10A)	180.0 (1)
C(102)–Cu(1)–C(10A)	108.7 (4)	C(103)–Cu(1)–C(10A)	107.5 (4)
Co(1A)–Cu(1)–C(10A)	43.2 (3)	Co(1)–Cu(1)–C(10B)	137.4 (3)
C(101)–Cu(1)–C(10B)	108.7 (4)	C(102)–Cu(1)–C(10B)	180.0 (1)
C(103)–Cu(1)–C(10B)	108.1 (4)	Co(1A)–Cu(1)–C(10B)	42.6 (3)
C(10A)–Cu(1)–C(10B)	71.3 (4)	Co(1)–Cu(1)–C(10C)	137.7 (3)
C(101)–Cu(1)–C(10C)	107.5 (4)	C(102)–Cu(1)–C(10C)	108.1 (4)
C(103)–Cu(1)–C(10C)	180.0 (1)	Co(1A)–Cu(1)–C(10C)	42.3 (3)
C(10A)–Cu(1)–C(10C)	72.5 (4)	C(10B)–Cu(1)–C(10C)	71.9 (4)
Co(1)–C(101)–Cu(1)	63.5 (3)	Co(1)–C(101)–O(101)	176.4 (10)
Cu(1)–C(101)–O(101)	120.1 (9)	Co(1)–C(102)–Cu(1)	60.8 (3)
Co(1)–C(102)–O(102)	177.9 (13)	Cu(1)–C(102)–O(102)	119.8 (9)
Co(1)–C(103)–Cu(1)	62.4 (4)	Co(1)–C(103)–O(103)	175.2 (12)
Cu(1)–C(103)–O(103)	121.3 (9)	Co(1)–C(104)–O(104)	179.7 (11)
Cu(2)–Co(2)–C(201)	75.2 (4)	Cu(2)–Co(2)–C(202)	175.7 (4)
C(201)–Co(2)–C(202)	105.4 (6)	Cu(2)–Co(2)–C(203)	72.8 (4)
C(201)–Co(2)–C(203)	116.0 (6)	C(202)–Co(2)–C(203)	103.3 (6)
Cu(2)–Co(2)–C(204)	78.8 (5)	C(201)–Co(2)–C(204)	113.7 (7)
C(202)–Co(2)–C(204)	104.7 (6)	C(203)–Co(2)–C(204)	112.3 (5)
Co(2)–Cu(2)–C(201)	41.9 (4)	Co(2)–Cu(2)–C(203)	42.7 (3)
C(201)–Cu(2)–C(203)	72.8 (4)	Co(2)–Cu(2)–C(204)	40.7 (3)
C(201)–Cu(2)–C(204)	69.1 (5)	C(203)–Cu(2)–C(204)	69.5 (4)
Co(2)–Cu(2)–Co(2A)	178.7 (1)	C(201)–Cu(2)–Co(2A)	138.7 (4)
C(203)–Cu(2)–Co(2A)	137.9 (3)	C(204)–Cu(2)–Co(2A)	138.0 (3)
Co(2)–Cu(2)–C(20A)	138.7 (4)	C(201)–Cu(2)–C(20A)	142.4 (7)
C(203)–Cu(2)–C(20A)	96.1 (4)	C(204)–Cu(2)–C(20A)	141.5 (4)
Co(2A)–Cu(2)–C(20A)	41.9 (4)	Co(2)–Cu(2)–C(20B)	137.9 (3)
C(201)–Cu(2)–C(20B)	96.1 (4)	C(203)–Cu(2)–C(20B)	145.7 (6)
C(204)–Cu(2)–C(20B)	137.7 (4)	Co(2A)–Cu(2)–C(20B)	42.7 (3)
C(20A)–Cu(2)–C(20B)	72.8 (4)	Co(2)–Cu(2)–C(20C)	138.0 (3)
C(201)–Cu(2)–C(20C)	141.5 (4)	C(203)–Cu(2)–C(20C)	137.7 (4)
C(204)–Cu(2)–C(20C)	97.3 (6)	Co(2A)–Cu(2)–C(20C)	40.7 (3)
C(20A)–Cu(2)–C(20C)	69.1 (5)	C(20B)–Cu(2)–C(20C)	69.5 (4)
Co(2)–C(201)–Cu(2)	62.9 (4)	Co(2)–C(201)–O(201)	175.2 (13)
Cu(2)–C(201)–O(201)	121.9 (11)	Co(2)–C(202)–O(202)	178.4 (13)
Co(2)–C(203)–Cu(2)	64.5 (4)	Co(2)–C(203)–O(203)	172.1 (12)
Cu(2)–C(203)–O(203)	123.4 (10)	Co(2)–C(204)–Cu(2)	60.5 (4)
Co(2)–C(204)–O(204)	175.2 (13)	Cu(2)–C(204)–O(204)	124.3 (11)
P(1)–Cu(3)–P(2)	90.9 (1)	P(1)–Cu(3)–P(3)	120.4 (1)
P(2)–Cu(3)–P(3)	119.5 (1)	P(1)–Cu(3)–P(4)	120.6 (1)
P(2)–Cu(3)–P(4)	117.4 (1)	P(3)–Cu(3)–P(4)	90.9 (1)
Cu(3)–P(1)–C(1)	102.2 (4)	Cu(3)–P(1)–C(3)	124.9 (4)
C(1)–P(1)–C(3)	102.4 (5)	Cu(3)–P(1)–C(4)	118.6 (3)
C(1)–P(1)–C(4)	106.3 (6)	C(3)–P(1)–C(4)	100.3 (5)
Cu(3)–P(2)–C(2)	102.0 (4)	Cu(3)–P(2)–C(5)	118.7 (4)
C(2)–P(2)–C(5)	104.0 (6)	Cu(3)–P(2)–C(6)	124.6 (4)
C(2)–P(2)–C(6)	102.6 (6)	C(5)–P(2)–C(6)	102.0 (5)
Cu(3)–P(3)–C(7)	103.5 (4)	Cu(3)–P(3)–C(12)	124.0 (4)
C(7)–P(3)–C(12)	101.0 (6)	Cu(3)–P(3)–C(11)	118.6 (3)
C(7)–P(3)–C(11)	104.4 (5)	C(12)–P(3)–C(11)	102.4 (5)
Cu(3)–P(4)–C(8)	102.4 (4)	Cu(3)–P(4)–C(9)	116.5 (4)
C(8)–P(4)–C(9)	104.3 (5)	Cu(3)–P(4)–C(10)	125.7 (4)
C(8)–P(4)–C(10)	102.3 (6)	C(9)–P(4)–C(10)	102.8 (5)
P(1)–C(1)–C(2)	115.8 (8)	P(2)–C(2)–C(1)	115.5 (9)
P(3)–C(7)–C(8)	112.4 (8)	P(4)–C(8)–C(7)	114.7 (9)

the special position (0, 0.8203, $^1/_4$). A view of the cation, along with the atom-labeling scheme, is given in Figure 1, whereas the two isomeric anions and their atom-labeling schemes are depicted in Figure 2. Bond lengths and bond angles for the complex are listed in Tables III and IV.

The coordination sphere of the tetracoordinated copper ion, Cu(dmpe)$_2^+$, is best described as a highly distorted tetrahedron. The two planes, each containing the phosphorus atoms of the dmpe ligand and the copper center, are perpendicular to one another. The average P–Cu–P bond angle for phosphorus atoms of different dmpe ligands is 119.5 (1)°, being substantially larger than 109.5°, whereas the P–Cu–P angles of the dmpe ligands at 90.9 (1)° are much less than the ideal tetrahedral angle. The average Cu–P bond distance is 2.250 (3) Å.

The analysis shows that the staggered form of Cu(Co(CO)$_4$)$_2^-$ anion is found to lie about the inversion center with Cu(1) occupying the special position ($^1/_4$, $^3/_4$, $^1/_2$) with overall symmetry D_{3d}. The two cobalt atoms are linearly attached to the copper atom. The Cu(1)–Co(1) bond length is 2.309 (1) Å. The coordination about the cobalt atom is trigonal bipyramidal with one CO group and one Cu atom occupying the axial positions. The three equatorial carbonyls are bent by an angle of 14.9 (4)° toward the copper atom; the six Cu–Co–C angles average 75.1 (4)°.

The eclipsed form of the Cu(Co(CO)$_4$)$_2^-$ anion is found to sit on the 2-fold axis with overall symmetry of C_{2v}. The Co(2)–

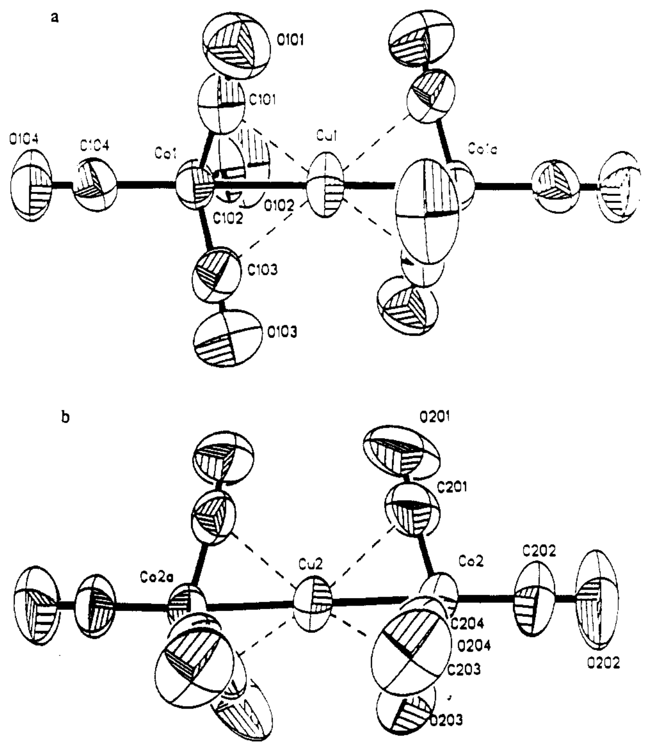

Figure 2. ORTEP diagrams of the $[Cu(Co(CO)_4)_2]^-$ anion: (a) staggered form; (b) eclipsed form.

Table V. Comparison of $Cu[Co(CO)_4]_2^-$ (Staggered) and $Cu[Co(CO)_4]_2^-$ (Eclipsed) Bond Angles and Bond Lengths

	staggered	eclipsed
Co–Cu–Co, Å	2.309 (1)	2.335 (2)
ax Co–C, Å	1.780 (12)	1.747 (14)
eq Co–C, Å	1.769 (11)	1.752 (13)
eight Co–C, Å	1.772 (13)	1.751 (16)
six Cu–Co–C, deg	75.1 (4)	75.6 (4)

Cu(2)–Co(2a) angle is 178.7 (1)°, less than 180° as observed in the staggered form. The Cu(2)–Co(2) bond is 2.335 (2) Å, which is significantly longer than those of the staggered form. The geometry of the cobalt atom is trigonal bipyramidal, with one CO group and one Cu atom occupying the axial positions. The three equatorial carbonyls are bent toward the copper atom by an angle of 14.4 (4)°; the six Cu–Co–C angles average 75.6 (4)°. A comparison of bond angles and bond lengths between the staggered and eclipsed forms are listed in Table V.

Reactivity. Interaction of 2 equiv of 1,2-bis(diphenylphosphino)ethane (dppe) with $Cu(Co(CO)_4)_2^-$ in THF at −78 °C leads to rapid formation of the $Co(CO)_4^-$ anion (eq 3). The IR

$$Cu(Co(CO)_4)_2^- + 2dppe \rightarrow Cu(dppe)_2^+ + 2Co(CO)_4^- \quad (3)$$

spectrum of the $Cu(Co(CO)_4)_2^-$ is characterized by four ν(CO) bands at 2024 (m), 1951 (vs), 1930 (sh), and 1891 (w) cm^{-1} in THF. The formation of the $Co(CO)_4^-$ anion occurred readily, as judged by the appearance of its diagnostic IR band at 1886 cm^{-1} within a few minutes. The IR spectra for this reaction are shown in Figure 3. These results indicate that the Cu–Co bonds of $Cu(Co(CO)_4)_2^-$ anions are extremely labile even at very low (−78 °C) temperature.

On the other hand, displacement of the Cu(I) cation in $Cu(Co(CO)_4)_2^-$ by the poorer coordinating THF ligand occurs much more slowly, with only 50% of the free $Co(CO)_4^-$ anion observed after 3 h at 50 °C. Similarly the complex was noted to be thermally quite stable in the less interacting CH_2Cl_2 solvent, where decomposition occurred over extended time periods under refluxing conditions. Furthermore, $[Cu(dmpe)_2][Cu(Co(CO)_4)_2]$ was insoluble in, and unreactive toward, deoxygenated water, as shown by the lack of detection of $Cu(Co(CO)_4)_2^-$ or $Co(CO)_4^-$ in water by infrared spectroscopy, with the salt being recovered unaltered.

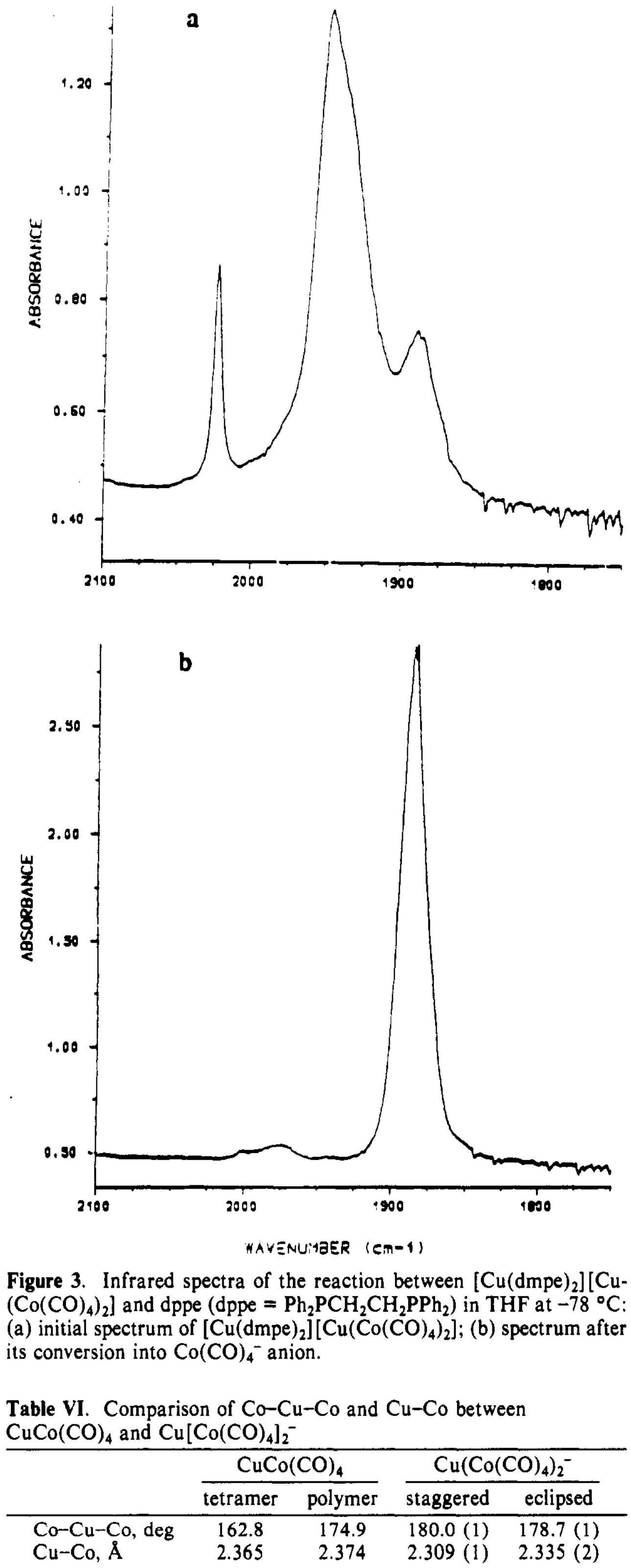

Figure 3. Infrared spectra of the reaction between $[Cu(dmpe)_2][Cu(Co(CO)_4)_2]$ and dppe (dppe = $Ph_2PCH_2CH_2PPh_2$) in THF at −78 °C: (a) initial spectrum of $[Cu(dmpe)_2][Cu(Co(CO)_4)_2]$; (b) spectrum after its conversion into $Co(CO)_4^-$ anion.

Table VI. Comparison of Co–Cu–Co and Cu–Co between $CuCo(CO)_4$ and $Cu[Co(CO)_4]_2^-$

	$CuCo(CO)_4$		$Cu(Co(CO)_4)_2^-$	
	tetramer	polymer	staggered	eclipsed
Co–Cu–Co, deg	162.8	174.9	180.0 (1)	178.7 (1)
Cu–Co, Å	2.365	2.374	2.309 (1)	2.335 (2)

Discussion

Klufers has reported the synthesis and characterization of $CuCo(CO)_4$ in two crystalline modifications, a Cu_4Co_4 eight-membered ring and a polymeric chain structure.[8,9] The tetrameric species has a square-planar arrangement of Cu atoms bridged by $Co(CO)_4$, with a Co–Cu–Co bond angle of 162.8° and a Cu–Co bond length of 2.365 Å. The polymeric structure is that of a zigzag chain with a Co–Cu–Co bond angle of 174.9° and a Cu–Co bond

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(8) Klufers, P. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 307.

(9) Klufers, P. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 70.

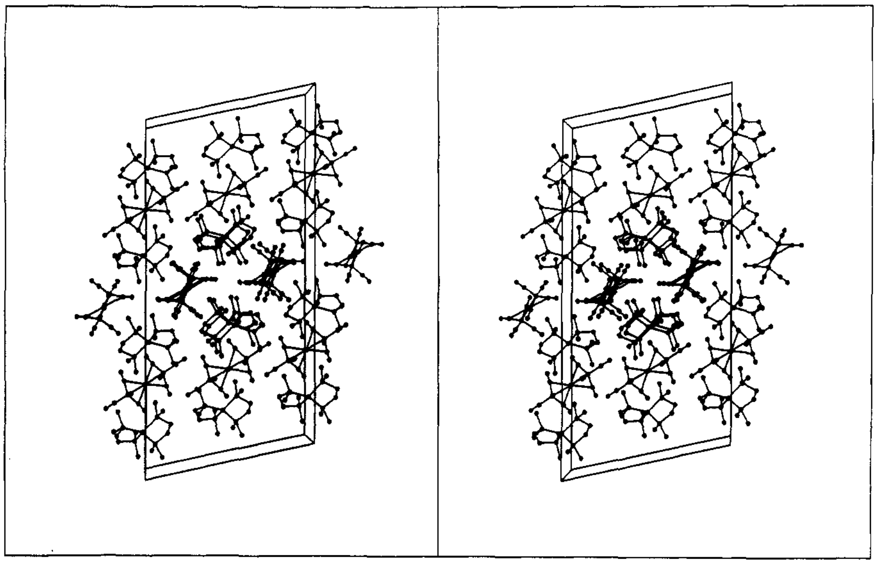

Figure 4. Unit cell packing diagram of $[Cu(dmpe)_2][Cu(Co(CO)_4)_2]$.

length of 2.374 Å. Table VI lists a comparison of bond angles and bond lengths between $[CuCo(CO)_4]_n$ and $Cu(Co(CO)_4)_2^-$. As is readily noted in Table VI, in the latter species the Co–Cu–Co unit is more linear and concomitantly the average Co–Cu bond distances are shorter.

Coordination units similar to $Cu(Co(CO)_4)_2^-$ have been found in the neutral, isoelectronic $Zn(Co(CO)_4)_2$,[10] $Cd(Co(CO)_4)_2$,[11] and $Hg(Co(CO)_4)_2$[12] derivatives. These complexes all exist solely in the staggered conformation with D_{3d} symmetry. The Co–Zn–Co angle is 177.8 (1)°, and the two Zn–Co bond lengths average 2.305 (2) Å. Correspondingly, the Co–Hg–Co angle is 178.4 (3)°, and the mean Hg–Co bond distance is 2.499 (7) Å. Hence, unlike these neutral complexes, the $Cu(Co(CO)_4)_2^-$ ions are present in the crystal lattice in both staggered and eclipsed conformations. A unit cell diagram is shown in Figure 4. It consists of two independent formula units, with each cation residing on a general position within the unit cell, whereas one of the two independent anions has Cu at the inversion center and the other has Cu on the 2-fold axis. There are no unusual interionic contacts, and there appear to be no distinct packing forces that affect the geometry of the anionic units.

The $Cu(Co(CO)_4)_2^-$ anion, as is also true for the $M(Co(CO)_4)_2$ (M = Zn and Hg) derivatives, may be regarded as containing covalent M–Co bonds, i.e., the limit of ion-pair formation.[13] Hence, the $Cu(Co(CO)_4)_2^-$ structure presented herein is quite analogous to that of $CuCl_2^-$ and represents an additional example of the structural relationship between $Co(CO)_4^-$ and halides.[14] On the other hand, $Mg[Mo(CO)_3C_5H_5]_2(C_5H_5N)_4$[15] and $Al[W(CO)_3C_5H_5]_3(C_4H_8O)_3$[16] are ion pairs with direct linkage of the metal atoms (Mg, Al) to a carbonyl oxygen atom. The IR absorption peaks around 1650 cm^{-1} in both complexes are assigned to the asymmetric mode of the doubly coordinated carbonyls. However, in the solid-state or solution spectra of $[Cu(dmpe)_2][Cu(Co(CO)_4)_2]$, there are no ν(CO) absorption peaks lower than 1880 cm^{-1}, indicating that no interaction exists between the copper center of $Cu(dmpe)_2^+$ and the carbonyl ligand of $Cu(Co(CO)_4)_2^-$.

In conclusion, it is apparent that the product resulting from reaction 1 is quite sensitive to the nature of the L_2 ligand. Furthermore, we obtained no evidence for $[Cu(dmpe)_2][Cu(Co(CO)_4)_2]$ being an intermediate in the synthesis of the corresponding $(dmpe)CuCo(CO)_4$ derivative. That is, under no conditions did $[Cu(dmpe)_2][Cu(Co(CO)_4)_2]$ transform into $(dmpe)CuCo(CO)_4$. Hence, it is reasonable to suggest that all $(diphosphine)CuCo(CO)_4$ derivatives reported in ref 3 should be reformulated as $[Cu(diphosphine)_2][Cu(Co(CO)_4)_2]$ complexes.

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Supplementary Material Available: Tables of hydrogen atom coordinates, anisotropic thermal parameters, and crystal data and data collection and refinement parameters for $[Cu(dmpe)_2][Cu(Co(CO)_4)_2]$ (5 pages); tables of calculated and observed structure factors (22 pages). Ordering information is given on any current masthead page.

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