For 1: systematic absences indicated a choice of *Cc* or *C2/c* space groups (hkl, $h + k = 2n + 1$; $h0l$, $l = 2n + 1$). *Cc* was chosen on the basis of successful refinement. Data were collected in the $+h,+k,\pm l$ quadrant. Due to the large number of atoms in the asymmetric unit (two independent molecules) only O(1) and the Rh, Fe, and P atoms were refined anisotropically. The carbon atoms were refined isotropically, and the hydrogen atoms were not located. The maximum peak in the final difference Fourier map had a height of 0.83 e Å^{-3} and was located 0.78 Å from Rh (1).

For 2: the structure was successfully solved in $P\bar{1}$. Data were collected in the $\pm h,\pm k,+l$ hemisphere. All 36 hydrogen atoms were either located or placed in idealized positions and refined with isotropic thermal parameters. All other non-hydrogen atoms were refined anisotropically. The largest peak in the final difference Fourier map was 0.79 e Å^{-3} and was not chemically significant.

For 3: the monoclinic space group $P2_1/n$ (No. 1014) was uniquely determined by systematic absences ($h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$). Data were collected in the $+h,+k,\pm l$ quadrant. Due to a combination of poor crystal quality and large number of atoms in the structure only the Rh, Fe, and P atoms were refined anisotropically. The O and C atoms were refined iso-

tropically, and the H atoms were not located. The highest peak in the final difference Fourier map was 1.00 e Å^{-3} and was located 1.26 Å from C(16). Scattering factors were taken from ref 33. Supplementary material is available.[34]

Supplementary Material Available: Tables of bond lengths and angles and thermal parameters for 1–3 and H-atom positions and a complete ORTEP drawing for 2 (19 pages); listings of observed and calculated structure factors for 1–3 (81 pages). Ordering information is given on any current masthead page.

(33) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, *England*, 1974; Vol. 4.
(34) See paragraph at end of paper regarding supplementary material.

Synthesis and Reactivity of Cobalt Dimers of the Type Co$_2$(CO)$_3$(L-L)$_2$I$_2$. Crystal Structure of [Co$_2$(CO)$_2$(μ-CO)(μ-I)(Me$_2$PCH$_2$PMe$_2$)(Ph$_2$PCH$_2$PPh$_2$)]I

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The cobalt dimers Co$_2$(CO)$_3$(L-L)$_2$, L-L = Ph$_2$PCH$_2$PPh$_2$ (dppm) and Me$_2$PCH$_2$PMe$_2$ (dmpm), are oxidized by iodine in the presence of bis(diphenylphosphino)methane to yield the ionic complexes [Co$_2$(CO)$_3$(L-L)(L-L)'I]I. In a similar fashion, Co$_2$(CO)$_6$(dppm) reacts with elemental sulfur to yield Co$_2$(CO)$_3$(dppm)$_2$S. The complex [Co$_2$(CO)$_3$(dmpm)(dppm)I]I crystallizes in the $P2_1/n$ space group with dimensions $a = 10.956$ (3) Å, $b = 15.881$ (6) Å, $c = 21.393$ (5) Å, and $\beta = 97.20$ (2)° with four molecules per unit cell. Of a total of 4796 unique reflections collected, 2965 reflections with $F_o^2 > 3\sigma(F_o^2)$ were used to refine the structure. The structure converged at $R = 0.051$ and $R_w = 0.065$. The geometry around the cobalt atoms is very similar to that reported for [Rh$_2$(CO)$_3$(dppm)$_2$Cl]$^+$, [Rh$_2$(CO)$_3$(dppm)$_2$H]$^+$, and Ir$_2$(CO)$_3$(dppm)$_2$S. The molecule may be described as an A-frame structure with a neutral ligand, CO, occupying the additional bridging site. The observed Co–Co bond distance is 2.555 (2) Å consistent with a single bond between the metal atoms. Reduction of the ionic complex with zinc yields a pyrophoric green solid that analyzes approximately for Co$_2$(CO)$_3$(dppm)$_2$.

Transition-metal dimers linked by two or more bridging diphosphine ligands represent a large and important class of molecules. These include multiply bonded dimers such as Re$_2$Cl$_4$(dppm)$_2$[1] and Mo$_2$Cl$_4$(dppm)$_2$,[2] dimers containing a single bond between metals such as Co$_2$(CO)$_6$(dppm),[3] Fe$_2$(CO)$_7$(dppm),[4] "A-frame" dimers containing the M$_2$(μ-X)L$_2$ moiety (structures I and II below) such as Rh(CO)$_2$(dppm)$_2$S,[5] [Rh$_2$(CO)$_2$(dppm)$_2$Cl]$^+$,[6] and [Pd$_2$-

(dppm)$_2$Me$_2$Cl]$^+$,[7] and dimers of gold and silver with and without a formal metal–metal bond.[8]

Bis(diphenylphosphino)methane has played an important role in the development of this chemistry. It is readily available commercially or by a simple synthetic procedure[9] and is air-stable; thus it is an ideal ligand for exploratory syntheses. Many other bridging bidentate ligands have been used to advantage in investigating the chemistry of metal dimers including 2-hydroxypyridine derivatives,[2b,10] carboxylates,[2b,11] and phosphorus ylides.[12] However, none

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have enjoyed the widespread application of dppm. Arsenic derivatives of dppm have used in the development of A-frame chemistry;[13] more recently, the smaller diphosphines $Ph_2PCH_2PMe_2$ and $Me_2PCH_2PMe_2$ (dmpm)[14] have been synthesized and investigated as bridging ligands for metal dimers.

The "A-frame" structure is characterized by two metal atoms linked by a bridging group containing a single donor atom and a single terminal ligand on each metal. The metals may or may not be connected by a formal M–M bond. This arrangement is shown schematically as structure I.
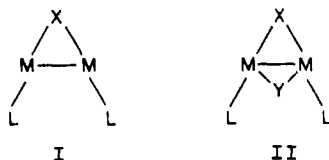
Many complexes of this class will add a small neutral molecule in the extra bridging site to yield the structure shown schematically as II. All of these complexes are stabilized by the presence of bridging diphosphines. Structures I and II are well established for rhodium,[5,6,15] iridium,[16] palladium[7], and platinum.[17] For cobalt, structure II has been postulated for $[Co_2(CO)_3(I)(dppm)_2]I$ (**1**).[3a] In this paper we confirm this structure for an analogue of **1**, namely, $[Co_2(CO)_3(I)(dppm)(dmpm)]^+$ (**2**) and describe the solution chemistry for cobalt "A-frames" of type II.

Experimental Section

All reactions were performed under an atmosphere of dry nitrogen. Solvents were either distilled from Na/K benzophenone or dried over molecular sieves and purged with N_2 before use. Dicobalt octacarbonyl was purified by sublimation and used immediately. The ligands dppm and dmpm were synthesized by literature methods.[9,18] Carbon-13 and phosphorous-31 NMR spectra were recorded on an IBM WP200. All ^{13}C-enriched compounds were synthesized from $Co_2(CO)_8$ enriched to 15–18% in [13]CO.

All NMR solvents were degassed by three freeze–pump–thaw cycles prior to use. Chemical shifts in parts per million are reported from Me_4Si (^{13}C NMR spectra) or 85% aqueous H_3PO_4 (^{31}P NMR spectra).

Preparation of Compounds. $Co_2(CO)_2(\mu\text{-}CO)(\mu\text{-}I)\text{-}(dppm)_2^+I^-$. A solution of 5.05 g (7.5 × 10⁻³ mol) of $Co_2(CO)_6$dppm and 2.93 (7.6 × 10⁻³ mol) of dppm in 20 mL of dry THF was treated dropwise with a solution of 1.9 g (7.5 × 10⁻³ mol) of I_2 in 20 mL of THF. Evolution of CO gas was vigorous. When the addition was complete and evolution of CO gas barely noticeable, the flask containing the reaction mixture was equipped with a reflux condenser under slow N_2 purge and heated to 70–80 °C. Additional CO gas was evolved followed by the formation of the red precipitate of product. After 12 h at 80 °C the solution was

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Table I. Crystal Data for Compound 2 ($C_{33}H_{36}Co_2I_2O_3P_4$)

Crystal Data

fw 976.22	a = 10.956 (3) Å
cryst dimens: 0.10 × 0.20 × 0.25 mm	b = 15.881 (6) Å
peak width at half-height = 0.30°	c = 21.393 (5) Å
Mo Kα radiatn (λ = 0.710 73 Å)	β = 97.20 (2)°
temp = 23 ± 1 °C	V = 3692.8 Å³
monoclinic space group $P2_1/n$	Z = 4
	ρ = 1.76 g/cm²
	μ = 28.3 cm⁻¹

Data Collection

instrument	Enraf–Nonius CAD4 diffractometer
monochromator	graphite crystal, incident beam
attenuator	Zr foil, factor 20.7
takeoff angle	2.8°
detector aperture	2.0–2.4 mm horizontal
	2.0 mm vertical
crystal–detector dist	21 cm
scan type	w–θ
scan rate	4–28°/min (in Ω)
max 2θ	45.0°
no. of reflctns measd	5165 total, 4796 unique
correctns	Lorentz–polarization
soln	direct methods
hydrogen atoms	not included
refinement	full-matrix least squares
minimization function	$\sum w(|F_0| - |F_c|)^2$
least-squares weights	$4F_0^2/\sigma^2(F_0^2)$
"Ignorance" factor	0.060
anomalous dispersion	all non-hydrogen atoms
reflctns included	2975 with $F_0^2 > 3.0\sigma(F_0^2)$
parameters refined	217
unweighted agreement factor	0.051
weighted agreement factor	0.065
factor including unobsd data	0.117
esd of observn of unit weight	1.52
convergence, largest shift	0.02σ
high peak in final diff map	0.98 (15) e/Å³
computer hardware/software	PDP-11/60 based TEXRAY system

cooled and the product collected by filtration and washed twice with 15 mL of hexane. The reddish brown microcrystalline powder was dried under vacuum and stored under N_2 (yield 7.5 g, 81.3%).

$Co_2(CO)_2(\mu\text{-}CO)(\mu\text{-}I)(dmpm)(dppm)^+I^-$. A solution of 1.0 g (2.37 × 10⁻³ mol) of $Co_2(CO)_6$dmpm and 0.91 g (2.38 × 10⁻³ mol) of dppm in 20 mL of dry THF was treated dropwise with stirring with a solution of 0.60 g (2.37 × 10⁻³ mol) of I_2 in 2 mL of THF. When evolution of CO gas had ceased, the flask was equipped with a reflux condensor and heated to 85 °C for 12 h. The solution was allowed to cool under N_2, and then 30 mL of toluene was added to the solution. The mixture was cooled to 0 °C for a few hours and the product obtained upon filtration. The red brown crystalline product was washed with pentane, dried under vacuum, and stored under N_2 (yield 1.34 g, 58.33%).

$Co_2(CO)_2(\mu\text{-}CO)(\mu\text{-}S)(dppm)_2$. A solution of 0.437 g (6.5 × 10⁻⁴ mol) of $Co_2(CO)_6$dppm, 0.250 g (6.5 × 10⁻⁴ mol) of dppm, and 0.21 g (6.5 × 10⁻⁴ mol) of elemental S in 30 mL of 1:1 THF/benzene was heated to 65 °C for 2.5 h. The solution was cooled and filtered at ambient temperature. Then 20 mL of pentane was added to the solution which was then cooled at 0 °C overnight. The solution formed dark red crystals of the product that were filtered, washed with a small amount of cold pentane, and dried under vacuum (yield 0.47 g, 72%). Anal. Calcd for $C_{53}H_{44}Co_2O_3P_4S$: C, 63.48; H, 4.42; P, 12.35; O, 4.78; S, 3.19. Found: C, 63.60; H, 4.44; P, 12.29; O, 4.79; S, 3.22.

$Co_2(CO)_2(\mu\text{-}CO)(dppm)_2$. A slurry containing 1 g of mossy zinc and 1 g of $[Co_2(CO)_2(\mu\text{-}CO)(\mu\text{-}I)(dppm)_2]I$ was generated in acetonitrile under nitrogen. After several hours, the slurry takes on a green color, and after 2 days a large quantity of green powder was present in the flask. The powder was slurried and decanted from the zinc. Complete retrieval of the zinc was very difficult. Filtration yields 0.45 g of a pyrophoric green solid. Anal. Calcd

for $C_{53}H_{44}Co_2O_3P_4$: C, 65.58; H, 4.53; P, 12.77. Found: C, 63.42; H, 4.98; P, 10.56.
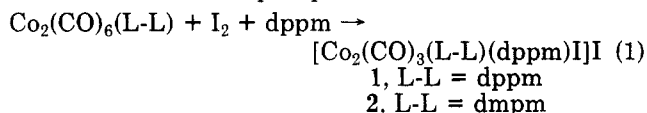
X-ray Structure Determination of 2. Crystals of **2** suitable for an X-ray structure determination were obtained by recrystallization from methylene chloride solution. Data collection and structure refinement were performed by the Molecular Structure Corp.[19] Relevant experimental and crystal data are given in Table I. Data were collected in the range $3° < 2\theta < 45°$ for $h,k,\pm l$. Three standard reflections were monitored every 41 min; these remained constant within experimental error during data collection. The space group $P2_1/n$ was determined by the systematic absences $0k0$, $k = 2n + 1$, and $h0l$, $h + l = 2n + 1$. The linear absorption coefficient is 28.3 for Mo Kα radiation; no absorption correction was made since the crystal was fairly well-shaped.

The structure was solved by a combination of direct methods and Fourier techniques. Scattering factors were taken from Cromer and Waber.[20] Anomalous dispersion effects were included in F_c,[21] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[22] Only the 2975 reflections having intensities greater than 3.0 times their standard deviation were used in the refinements. The final cycle of refinement included 217 variable parameters and converged (largest parameter shift was 0.02 times its estimated standard deviation) with unweighted and weighted agreement factors of $R = 0.051$ and $R_w = 0.065$. The standard deviation of an observation of unit weight was 1.52.

Results and Discussion

Synthesis. Incorporation of two or more bridging diphosphines into a cobalt dimer is not an easy task. With the ligands used in this study, direct reaction of $Co_2(CO)_8$ or $Co_2(CO)_6(L\text{-}L)$ with diphosphines does not lead to any binuclear products containing two of the bidentate ligands.[3a] For dppm, this lack of reactivity may be due in part to the steric bulk of the phosphine; however, the same result is obtained for the permethyldiphosphine, $Me_2PCH_2PMe_2$. King et al.[23] have synthesized dimers with the formula $Co_2(L\text{-}L)_5$ and $Co_2(L\text{-}L)_3(CO)_2$ (where L-L = F_2PNRPF_2). However, the fluorophosphine ligands are more reactive toward metal carbonyls than dppm or dmpm and thus go to the more substituted products, e.g. $Co_2(CO)_2(L\text{-}L)_3$.

The synthesis of the title compounds $Co_2(CO)_3dppm_2I_2$ (1) and $Co_2(CO)_3(dmpm)(dppm)I_2$ (2) is best described as an oxidative trapping reaction. It was noted previously[3a] that **1** could be synthesized in low yield from the reaction of $Co_2(CO)_6(dppm)$ with I_2. The presence of 2 equiv of dppm in the product suggested that some $Co_2(CO)_6(dppm)$ is sacrificed in the reaction and that the liberated dppm traps and stabilizes the cobalt(I) dimer. Indeed if the reaction is performed in the presence of free dppm, yields of greater than 70% are routinely obtained. The dimer $Co_2(CO)_6dmpm$ may also be oxidized in this fashion to introduce the second phosphine

$$Co_2(CO)_6(L\text{-}L) + I_2 + dppm \rightarrow$$
$$[Co_2(CO)_3(L\text{-}L)(dppm)I]I \quad (1)$$
$$1, \text{ L-L} = dppm$$
$$2, \text{ L-L} = dmpm$$

It should be noted that so far in our laboratory dppm has been the only effective trapping ligand. The bridging diphosphine ligand dmpm, the chelating ligand $Ph_2PCH_2CH_2PPh_2$(diphos), and triphenylphosphine all

Table II. Comparison of Co, Rh, and Ir Dimers Containing Diphosphines

compd	M–M, Å	ν_{CO}, cm^{-1}	ref
$Co_2(CO)_3(\mu\text{-I})(dppm)_2^+$ (1)		1988 s, 1944 vs, 1816 m	this work
$Co_2(CO)_3(\mu\text{-I})(dppm)(dmpm)$ (2)	2.555 (2)	1972 s, 1950 vs, 1812 m	this work
$Rh_2(CO)_3(\mu\text{-Cl})(dppm)_2^+$	2.8415 (7)	1992 s, 1977 vs, 1863 m	15
$Rh_2(CO)_3(\mu\text{-H})(dppm)_2$	2.731 (2)	1970 s, 1955 vs, 1860 s	25
$Ir_2(CO)_3(\mu\text{-Cl})(dppm)_2$		1984 s, 1968 vs, 1816 s	26a
$Ir_2(CO)_3(\mu\text{-H})(dppm)_2$	2.7661 (4)	1979 m, 1967 vs, 1850 s	31, 32
$Co_2(CO)_3(\mu\text{-S})(dppm)_2$ (3)		1959 s, 1948 vs, 1772 m	this work
$Ir_2(CO)_3(\mu\text{-S})(dppm)_2$	2.843 (2)	1950 s, 1937 s, 1760 s	16
$Rh_2(CO)_2(\mu\text{-Cl})(dppm)_2^+$	3.150	1987 s, 1970 s	26, 28
$Ir_2(CO)_2(\mu\text{-S})(dppm)_2$		1918 vs, 1902 vs	16
$Co_2(CO)_3(dppm)_2$ (4)		1935 s, 1900 vs, 1750 s	this work
$Rh_2(CO)_3(dppm)_2$	2.739	1940, 1920, 1835	27
$Ir_2(CO)_3(dppm)_2$		1950 s, 1936 vs, 1857 s	32

Table III. $^{13}C^a$ and $^{31}P^b$ NMR Data for Compounds 1–4

	complex	^{13}C bridging CO	^{13}C terminal CO	^{31}P
1	$Co_2(CO)_3(dppm)_2I^+I^-$	239.46	199.35	51.5
2	$Co_2(CO)_3(dmpm)(dppm)I^+I^-$	239.77	202.50	46, 41 AA'BB' pattern
3	$Co_2(CO)_3(dppm)_2S$	249.22	211.83	48.3
4	$Co_2(CO)_3(dppm)_2$			36.95

^{a} Chemical shifts from Me$_4$Si. ^{b} Chemical shifts from 85% phosphoric acid.

have failed to yield an isolable product when used in place of dppm in eq 1. Conductively measurements, infrared spectroscopy, elemental analysis, and comparison with known rhodium analogues led to the assignment of A-frame type structure II for **1** with CO occupying the second bridging site.

In addition to the oxidation of $Co_2(CO)_6dppm$ by I_2, it is also possible to effect an oxidation by elemental sulfur in the presence of dppm as a trapping agent. Elemental analysis and spectroscopic data are consistent with formulation of this compound, $Co_2(CO)_2(\mu\text{-CO})(\mu\text{-S})(dppm)_2$, as an A-frame complex. Table II compares the relevant spectroscopic data for compounds **1–3** along with many similar rhodium and iridium complexes. Table III shows NMR data for these compounds. A bridging carbonyl is observed by infrared spectroscopy ($\nu_{CO} = 1772$ cm^{-1}) for compound **3**.

Unlike compounds **1** and **2** which are 1:1 salts, compound **3** is neutral due to the presence of S^{2-} in place of I$^-$. On the basis of the similarity of its infrared spectrum with other type II structures (see Table II) compound **3** is proposed to also have an A-frame type II structure. The ^{31}P NMR (Table III) spectrum of **3** shows a single peak

(19) Crystallographic services were provided by the staff of the Molecular Structure Corp.: Dr. M. W. Extine, Dr. P. N. Swepston, Dr. W. Pennington, Dr. J. M. Troup, and Ms. B. B. Warrington.

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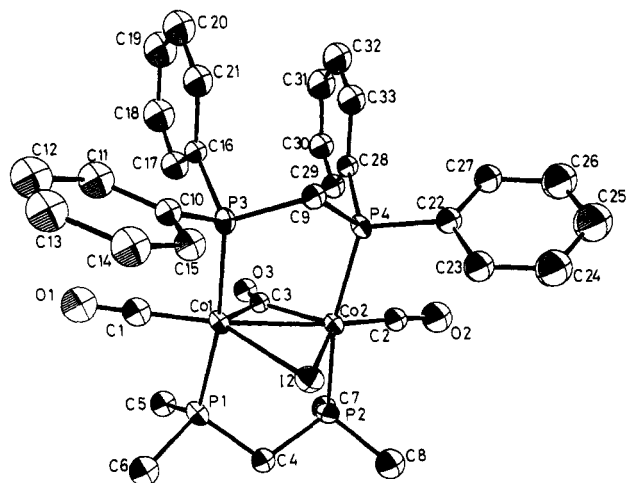(28) Cowie, M.; Dwight, S. K. *Inorg. Chem.* **1979**, *18*, 2700.

Figure 1. Perspective drawing and numbering scheme for [Co(CO)$_3$(dmpm)(dppm)I]$^+$. The thermal ellipsoids are drawn to represent 50% of the electron density.

Table IV. Atomic Positions

atom	x	y	z
I1	0.46381 (9)	0.28320 (6)	0.00214 (5)
I2	0.15215 (7)	0.19174 (5)	0.33979 (4)
Co1	0.0872 (1)	0.0642 (1)	0.26376 (7)
Co2	0.3054 (1)	0.0675 (1)	0.32213 (7)
P1	0.0032 (3)	−0.0006 (2)	0.3397 (2)
P2	0.2593 (3)	0.0078 (2)	0.4099 (1)
P3	0.1345 (3)	0.1364 (2)	0.1800 (1)
P4	0.3885 (3)	0.1323 (2)	0.2449 (1)
O1	−0.1374 (9)	0.0204 (7)	0.1872 (5)
O2	0.5539 (9)	0.0365 (6)	0.3764 (5)
O3	0.2313 (7)	−0.0877 (5)	0.2578 (4)
C1	−0.046 (1)	0.0382 (9)	0.2184 (6)
C2	0.452 (1)	0.0486 (8)	0.3532 (6)
C3	0.217 (1)	−0.0166 (7)	0.2721 (5)
C4	0.095 (1)	0.0052 (8)	0.4171 (5)
C5	−0.023 (1)	−0.1125 (9)	0.3252 (6)
C6	−0.146 (1)	0.0402 (9)	0.3569 (6)
C7	0.313 (1)	−0.1014 (9)	0.4227 (6)
C8	0.323 (1)	0.0622 (9)	0.4821 (7)
C9	0.275 (1)	0.1994 (7)	0.1967 (5)
C10	0.013 (1)	0.2114 (7)	0.1516 (5)
C11	−0.071 (1)	0.1852 (9)	0.1015 (6)
C12	−0.178 (1)	0.2388 (10)	0.0825 (7)
C13	−0.192 (1)	0.3107 (9)	0.1145 (7)
C14	−0.107 (1)	0.3363 (9)	0.1646 (6)
C15	−0.002 (1)	0.2839 (8)	0.1831 (6)

Table V. Selected Bond Distances (Å) and Angles (deg)

Bond Distances			
I2–Co1	2.639 (1)	P1–C6	1.834 (11)
I2–Co2	2.649 (1)	P2–C7	1.841 (12)
Co1–Co2	2.555 (2)	P2–C8	1.831 (12)
Co1–P1	2.219 (3)	P3–C9	1.834 (10)
Co1–P3	2.241 (3)	P3–C10	1.834 (10)
Co1–C1	1.699 (11)	P3–C16	1.822 (9)
Co1–C3	1.911 (9)	P4–C9	1.849 (10)
Co2–P2	2.217 (3)	P4–C22	1.822 (10)
Co2–P4	2.236 (3)	P4–C28	1.816 (10)
Co2–C2	1.683 (11)	O1–C1	1.166 (12)
Co2–C3	1.896 (9)	O2–C2	1.183 (11)
P1–C4	1.828 (10)	O3–C3	1.185 (10)
P1–C5	1.821 (12)		

Bond Angles			
Co1–I2–Co2	57.80 (4)	P2–Co2–P4	168.5 (1)
I2–Co1–Co2	61.30 (4)	P2–Co2–C2	84.1 (4)
I2–Co1–P1	90.54 (9)	P2–Co2–C3	91.3 (3)
I2–Co1–P3	91.63 (8)	P4–Co2–C2	85.3 (3)
I2–Co1–C1	133.2 (4)	P4–Co2–C3	97.6 (3)
I2–Co1–C3	108.5 (3)	C2–Co2–C3	119.3 (5)
Co2–Co1–P1	95.72 (9)	Co1–P1–C4	114.2 (3)
Co2–Co1–P3	94.83 (8)	Co1–P1–C5	113.6 (4)
Co2–Co1–C1	165.5 (4)	Co1–P1–C6	116.3 (4)
Co2–Co1–C3	47.6 (3)	Co2–P2–C4	114.4 (3)
P1–Co1–P3	168.9 (1)	Co2–P2–C7	115.2 (4)
P1–Co1–C1	84.2 (4)	C32–P2–C8	114.2 (4)
P1–Co1–C3	89.6 (3)	Co1–P3–C9	113.4 (3)
P3–Co1–C1	86.4 (4)	Co1–P3–C10	111.5 (3)
P3–Co1–C3	100.0 (3)	Co1–P3–C16	117.9 (3)
C1–Co1–C3	117.9 (5)	Co2–P4–C9	111.7 (3)
I2–Co2–Co1	60.90 (4)	Co2–P4–C22	112.3 (3)
I2–Co2–P2	88.97 (8)	Co2–P4–C28	116.8 (3)
I2–Co2–P4	94.95 (8)	Co1–C1–O1	180 (1)
I2–Co2–C2	131.7 (4)	Co2–C2–O2	178.2 (9)
I2–Co2–C3	108.6 (3)	Co1–C3–Co2	84.3 (4)
Co1–Co2–P2	96.13 (9)	Co1–C3–O3	137.3 (8)
Co1–Co2–P4	95.19 (8)	Co2–C3–O3	138.1 (8)
Co1–Co2–C2	167.3 (4)	P1–C4–P2	111.1 (5)
Co1–Co2–C3	48.1 (3)	P3–C9–P4	106.4 (5)

at 48.3 ppm which is upfield compared to 1, and the CO stretching frequencies of the carbonyls occur at a lower wavenumber than those of 1. These facts indicate a greater electron density on the cobalt atoms of 3 due to the greater donating ability of the sulfido group (S^{2-}) in 3 over that of the iodo group (I$^-$) in 1.

Crystal Structure of [Co$_2$(CO)$_3$(I)(dmpm)(dppm)]$^+$ (2). X-ray diffraction quality crystals of 2 were obtained by slow evaporation of a concentrated methylene chloride solution under a nigrogen atmosphere. Table I summarizes the relevant crystallographic data for this compound. A perspective drawing of the molecule along with the numbering scheme employed is shown in Figure 1. Atomic coordinates and selected bond distances and angles are given in Tables IV and V.

The crystal structure for 2 confirms the *trans*-diphosphine arrangement with bridging carbonyl and iodide ligands are previously postulated.[3a] Also the Co–Co distance, 2.555 (2) Å, is consistent with a single bond between the metals. This is only slightly longer than observed in Co$_2$(CO)$_8$, 2.525 Å.[24] As seen from the data in Table V, the Co$_2$I moiety forms a nearly equilateral triangle (the

internal angles are 57.8, 61.3, and 60.9°). All three carbonyl ligands lie essentially in the same plane as the Co$_2$I triangle.

The series of compounds, Co$_2$(CO)$_3$(I) (dppm)(dmpm)$^+$, Rh$_2$(CO)$_3$(Cl)(dppm)$_2^+$, and Ir$_2$(CO)$_3$(S)(dppm)$_2$ are isoelectronic and simple electron counting predicts a M–M single bond in each case. This is reflected in the metal–metal bond lengths, 2.555 (2), 2.8415 (7), and 2.84 (2) Å, respectively. In all other respects the structure of 2 is remarkably similar to the rhodium and iridium complexes above. The average Co–P bond length in 2 is 2.23 (1) Å while the rhodium and iridium analogues have M–P(ax) of 2.33 and 2.32 Å, respectively. All three structures have a planar M$_2$(CO)$_2$(μ-CO)(μ-X) core; the cobalt dimer 2 shows a distortion away from the "A-frame" structure by having a slightly more linear arrangement along the metal–metal band. In 2 the average M–M–CO angle is 166.4° while the rhodium and iridium complexes the corresponding angles are 162.2 and 153.9°, respectively.

Solution Chemistry of Cobalt "A-Frames". An important feature of the A-frame chemistry of the rhodium and iridium analogues of 1–3 is the ability to reversibly coordinate a neutral ligand in the bridging site. Thus Rh$_2$(CO)$_2$(μ-Cl)(dppm)$_2^+$ and Ir$_2$(CO)$_2$(μ-S)(dppm)$_2$ react with CO to yield complexes of type II (vide supra). With dppm as the diphosphine and halide or sulfide bridging groups, type II structures have a 17e count and a M–M bond for Co, Rh, and Ir, while type I structures have a 16e count. For Rh and Ir dimers, a 16e count implies separate square-planar metal centers. This is confirmed by the significant lengthening in the metal–metal distance in Rh$_2$(CO)$_2$(μ-Cl)(dppm)$_2^+$ compared to Rh$_2$(CO)$_3$(μ-Cl)-

$(dppm)_2^+$. A 16e count for cobalt dimers implies a Co–Co double bond. Molecules for which a Co–Co double bond is postulated are very rare and extremely reactive. For example $Co_2(\mu_5\text{-}C_5H_5)_2(\mu\text{-}CO)_2$[29a] is proposed as an intermediate in the photochemistry of $(\eta^5\text{-}C_5H_5)Co(CO)_2$. This dimer formally has a double bond and a single carbonyl stretch in the infrared at 1798 cm^{-1} consistent with a bridging carbonyl. Similarly, $Co_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)(\mu\text{-}C\text{-}(CH_3)_2$[29b] has a bridging carbonyl frequency of 1797 cm^{-1}. Attempts to thermally activate 1, 2, and 3 for loss of CO to generate a type I complex have been unsuccessful. Heating these molecules to 80 °C in THF under N_2 for several hours leaves them unchanged. The rhodium and iridium complexes may shuttle between structures I and II while at this time only structure II has been identified for cobalt complexes. The difficulty in obtaining compounds of type I for cobalt may reflect the instability of cobalt–cobalt double bonds. This may be aggravated by the tendency for dppm to pull the metal atoms away from each other.

The rhodium complex $Rh_2(CO)_3(Cl)(dppm)_2^+$ is readily reduced to yield the neutral complex $Rh_2(CO)_3(dppm)_2$.[27] When I and excess zinc metal are stirred in acetonitrile at ambient temperature, an emerald green powder is obtained within a few hours. This powder, which analyzes approximately for $Co_2(CO)_3(dppm)_2$ (4), is insoluble in most solvents and is barely soluble in THF. It reacts with halogenated hydrocarbon solvents such as CH_2Cl_2 and $CHCl_3$ to give a number of as yet uncharacterized products (as seen by ^{31}P NMR and solution IR). Furthermore, 4 is pyrophoric in air in the solid state and reacts readily with I_2 in THF to give 1 again. In the presence of CO, 4 reacts to yield $Co_2(CO)_6(dppm)$, $[Co(CO)_3(dppm)]^+[Co(CO)_4]^-$ and some free dppm (again as seen by ^{31}P NMR and solution IR). The ^{31}P NMR spectrum of 4 in THF solution shows a peak at 36.4 ppm which is upfield of that of 1. The infrared spectrum is very similar to 1 but is shifted to a lower frequency, indicating more electron density on the cobalt complex. The bridging carbonyl stretching frequency in 4 occurs at 1750 cm^{-1}; this is shifted significantly to lower wavenumber compared to its rhodium and iridium analogues (Table II). However, it is only slightly shifted from the bridging carbonyl bonds in the neutral cobalt dimers that are postulated to have a cobalt–cobalt double bond.[29] The rhodium complex $Rh_2(CO)_3(dppm)_2$[27] has an unusual structure with dppm ligands in a cis rather than a trans arrangement. Furthermore the bridging carbonyl is semibridging, and the Rh–Rh distance is consistent with a single bond.[27]

There are two possible limiting dimeric structures for 4, one which contains a Co–Co double bond and a normal bridging carbonyl and another which has a Co–Co single bond and an η^2-bridging carbonyl acting as a four-electron donor. This type of arrangement is well-known for the manganese dppm-bridged dimer $Mn_2(CO)_4(\eta^2\text{-}\mu\text{-}CO)(dppm)_2$.[30] In the manganese dimer, the bridging carbonyl band is observed at 1645 cm^{-1} in the infrared spectrum. Alternatively the extreme insolubility of 4 may be consistent with a polymeric or cluster structure. At the present time we regard 4 as containing a double bond between cobalts.

In solution, complex 1 is quite unreactive to substitution with a number of reagents such as acetylenes, CO, H_2, phosphines, and alkenes. For example, refluxing 1 with PMe_2Ph in THF for 3 h failed to give any products as identified by infrared spectroscopy.

Supplementary Material Available: Tables of positional and thermal parameters, complete bond distances and angles, and least-squares planes (9 pages); a listing of observed and calculated structure factors (21 pages). Ordering information is given on any current masthead.

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