

References and Notes

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Reactions of μ -Diphenylethyne-hexacarbonyldicobalt with Bis(diphenylphosphino)methane and Bis(diphenylarsino)methane. Crystal Structures of (tolan)(dpm)Co₂(CO)₄ and (tolan)(dam)₂Co₂(CO)₂C₂H₄Cl₂

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The bidentate ligands bis(diphenylphosphino)methane (dpm) and bis(diphenylarsino)methane (dam) displace two or four carbonyl groups from μ -tolan-hexacarbonyldicobalt, (tolan)(CO)₆Co₂ (tolan = diphenylethyne). Single-crystal x-ray diffraction studies have yielded the molecular geometries of μ -bis(diphenylphosphino)methane- μ -tolan-tetracarbonyldicobalt and di- μ -bis(diphenylarsino)methane- μ -tolan-dicarbonyldicobalt. The crystal data for the phosphino complex (tolan)(dpm)Co₂(CO)₄ are as follows: space group $P2_1/n$ (C_{2h}^5 ; No. 14, nonstandard setting) with $a = 19.97$ (2) Å, $b = 20.41$ (2) Å, $c = 15.45$ (2) Å, $\beta = 97.57$ (7)°, $V = 3742$ Å³, $Z = 4$. A unique quadrant of 3144 diffraction intensities with $I > 3\sigma(I)$ and $2\theta < 40^\circ$ (Mo K α radiation), collected on a Picker FACS-1 diffractometer, was used to solve and refine the structure by conventional Patterson, Fourier, and full-matrix least-squares techniques. Phenyl groups were constrained as idealized rigid groups with isotropic thermal parameters; remaining atoms were refined anisotropically to final discrepancy indices $R_F = 0.088$ and $R_{wF} = 0.102$. The bidentate phosphine ligand bridges between the cobalt atoms. The cobalt-cobalt bond length is 2.459 (2) Å and the cobalt-phosphorus bond lengths are 2.210 (3) and 2.215 (3) Å, while those from cobalt to "acetylene" carbon atoms are 1.97 (1), 1.95 (1), 1.94 (1), and 1.92 (1) Å. The carbon-carbon distance is 1.33 (1) Å. The arsino complex (tolan)(dam)₂Co₂(CO)₂ was crystallized as the dichloroethane monosolvate: space group $P\bar{1}$ (C_1^1 , No. 2) with $a = 14.207$ (4) Å, $b = 17.321$ (5) Å, $c = 13.736$ (4) Å, $\alpha = 73.63$ (2)°, $\beta = 112.44$ (2)°, $\gamma = 99.78$ (2)°, $V = 2990$ Å³, $Z = 2$. Structure solution and refinement employed 4158 intensities measured in a unique hemisphere on the diffractometer ($I > 3\sigma(I)$ and $2\theta < 40^\circ$ using Mo K α radiation). Refinement with rigid rings was terminated with $R_F = 0.086$ and $R_{wF} = 0.075$. The arsine ligands both bridge between the cobalt atoms which are 2.518 (4) Å apart. Cobalt-arsenic bond lengths are 2.326 (4), 2.330 (4), 2.332 (4), and 2.348 (3) Å. The cobalt to "acetylene" carbon distances are 1.97 (1), 1.98 (1), 1.95 (1), and 1.95 (1) Å while the carbon-carbon distance is 1.37 (3) Å.

Introduction

The replacement of up to two carbonyl groups on alkynehexacarbonyldicobalt is facile with a large range of ligands.¹ To progress beyond two, monodentate ligands must have good

π -acceptor properties. Thus trialkyl or triaryl phosphites² or trifluorophosphine³ replaces a maximum of four carbonyl groups. The preparation of complexes in which two carbonyl groups have been replaced by a bridging ligand has been

Table I. Experimental Data for X-Ray Diffraction Studies

A. Crystal Parameters at 18 °C Assuming $\lambda(\text{Mo K}\alpha)$ 0.710 69 Å				
	(tolan)(dpm)Co ₂ (CO) ₄		(tolan)(dam) ₂ Co ₂ (CO) ₂ ·C ₂ H ₄ Cl ₂	
<i>a</i> , Å	11.97 (2)	11.97 ^a	14.207 (4)	14.207 ^a
<i>b</i> , Å	20.41 (2)	20.41	17.321 (5)	17.321
<i>c</i> , Å	15.45 (2)	18.25	13.736 (4)	18.830
α , deg	90	90	73.63 (2)	135.64
β , deg	97.57 (7)	122.98	112.44 (2)	97.14
γ , deg	90	90	99.78 (2)	99.89
<i>V</i> , Å ³	3742	3742	2990	2990
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 1	<i>P</i> 1
Mol wt	<i>C</i> ₂ <i>h</i> ^s , No. 14		<i>C</i> _i ⁱ , No. 2	
<i>Z</i>	796.84		1395.67	
ρ_{calcd} , g cm ⁻³	4		2	
ρ_{obsd} , g cm ⁻³ (by flotation in aqueous ZnI ₂)	1.40		1.55	
μ , cm ⁻¹	1.35 (2)		1.54 (2)	
Crystal dimensions	10.49		30.30	
(100)→(100), mm	0.2		0.1	
(010)→(010), mm	0.2		0.1	
(001)→(001), mm	0.2		0.1	
Estd transmission factors	0.80–0.86%		0.74–0.81%	

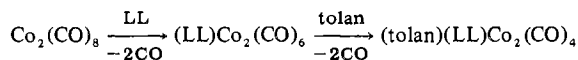
B. Measurement of Intensity Data

Radiation: Mo K α
 Monochromator: Highly oriented graphite $2\theta_{002} = 12.1^\circ$
 Crystal to detector distance: 25 mm
 Detector: scintillation counter and pulse height analyzer set for 100% of Mo K α peak
 Attenuators: Ni foil used for intensities $>10^4$ Hz
 Takeoff angle: 3.0°
 Detector aperture: 4 mm \times 4 mm
 Scan type: coupled θ (crystal)– 2θ (detector), $1.0^\circ \text{ min}^{-1}$
 Scan length: $\Delta(2\theta) = (\text{base width (see below)}) + 0.692 \tan \theta^\circ$
 starting (base width/2.0) below Mo K α peak

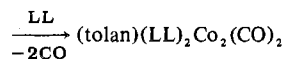
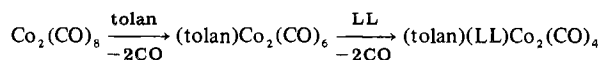
	(tolan)(dpm)Co ₂ (CO) ₄	(tolan)(dam) ₂ Co ₂ (CO) ₂
Rotation axis	[001]	[100]
Reflections measd	$\pm h, \pm k, \pm l$	$+h, \pm k, \pm l$
Min 2θ , deg	4	4
Max 2θ , deg	40	40
Scan length, deg	2.1	2.0
Std reflections (every 50 cycles)	600, 060, 006	800, 0, 11, 0, 006
Variation of standards	10% (random)	10% (random)
Reflections collected	3942	6047
Reflections where $I > 3\sigma(I)$	3144	4158

^a Reduced cells.

described.⁴ The bridging acetylene was emplaced after the bidentate ligand

LL = dpm, dam, or [(C₆H₅)₂Sb]₂CH₂

Here we report the preparations of 1:1 and 1:2 complexes by an alternative route: prior attachment of the acetylene moiety



LL = dpm or dam

The ligands (CH₃)₂AsC≡C(As(CH₃)₂)CF₂CF₂ (*f₄fars*), (C₆H₅)₂PC≡C(P(C₆H₅)₂)CF₂CF₂ (*f₄fos*), and *cis*-(CH₃)₂AsC(CF₃)=C(CF₃)As(CH₃)₂ (*dab*) have also been shown to yield 1:2 complexes by this route.²

We have determined the crystal and molecular structures of (tolan)(dpm)Co₂(CO)₄ and (tolan)(dam)₂Co₂(CO)₂ both to confirm the overall geometry and to compare the (tolan)Co₂

units in these structures with the parent (alkyne)Co₂(CO)₆ fragment.^{5–7}

Experimental Section

Dicobalt octacarbonyl (Co₂(CO)₈) purchased from Alfa-Ventron, Beverly, Mass., and tolan (diphenylethyne), from Eastman Organic Chemicals, Rochester, N.Y., were used to prepare (tolan)Co₂(CO)₆.⁸ [(C₆H₅)₂P]₂CH₂ (dpm) and [(C₆H₅)₂As]₂CH₂ (dam) were obtained from Alfa-Ventron. Solution infrared spectra were obtained on a Perkin-Elmer Model 457 recording spectrometer.

Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Preparation of (tolan)(dpm)Co₂(CO)₄. (tolan)Co₂(CO)₆, 0.47 g (1.0 mmol), and dpm, 0.39 g (1.0 mmol), were dissolved in 50 mL of *n*-hexane, and the solution was refluxed under N₂ for 1.5 h. The solution was concentrated and cooled to room temperature. The red precipitate was filtered off, washed with cold hexane, and recrystallized from a hexane-dichloroethane mixture; yield 70%; mp 200 °C dec.

Anal. Calcd for C₄₃H₃₂Co₂O₄P₂: C, 65.35; H, 4.05; Co, 14.79; P, 7.77. Found: C, 65.23; H, 4.16; Co, 14.70; P, 7.83.

The infrared spectrum showed the following maxima. In C₂Cl₄ solution: 3070 (sh), 3058 (w), 3020 (vw), 3010 (sh), 2033 (s), 2000 (s), 1975 (s), 1592 (w), 1483 (w), 1435 (w) cm⁻¹. From a solution in CS₂: 1366 (vw), 1328 (vw), 1304 (vw), 1276 (vw), 1002 (vw), 968 (vw), 922 (vw), 840 (vw), 785 (w), 740 (m), 720 (w), 695 (m), 632 (vw), 625 (vw) cm⁻¹.

Table II. Final Positional Parameters^a for (tolan)(dpm)Co₂(CO)₄

Atom	x	y	z
Co1	0.29013 (12)	0.40511 (7)	0.16834 (9)
Co2	0.36081 (12)	0.33636 (7)	0.05663 (9)
P1	0.42922 (23)	0.37725 (14)	0.27022 (18)
P2	0.49280 (24)	0.28213 (14)	0.14186 (18)
C12	0.4670 (9)	0.2911 (4)	0.2562 (6)
CA1	0.2091 (8)	0.3650 (5)	0.0625 (7)
CA2	0.2373 (8)	0.3199 (5)	0.1235 (6)
CCOA	0.1893 (10)	0.4198 (6)	0.2341 (8)
OCOA	0.1191 (7)	0.4296 (4)	0.2776 (6)
CCOB	0.3145 (9)	0.4857 (6)	0.1308 (8)
OCOB	0.3230 (7)	0.5372 (4)	0.1031 (7)
CCOC	0.4184 (12)	0.3993 (7)	-0.0016 (9)
OCOC	0.4467 (10)	0.4392 (6)	-0.0451 (8)
CCOD	0.3367 (11)	0.2793 (7)	-0.0252 (8)
OCOD	0.3143 (10)	0.2431 (6)	-0.0808 (7)
C1A1	0.5647 (5)	0.4191 (4)	0.2817 (5)
C1A2	0.6516 (6)	0.3967 (3)	0.3431 (4)
C1A3	0.7564 (5)	0.4270 (4)	0.3511 (5)
C1A4	0.7743 (5)	0.4798 (4)	0.2976 (6)
C1A5	0.6874 (7)	0.5022 (3)	0.2362 (5)
C1A6	0.5826 (6)	0.4718 (4)	0.2282 (4)
C1B1	0.3960 (6)	0.3800 (4)	0.3820 (4)
C1B2	0.3747 (6)	0.3241 (3)	0.4285 (5)
C1B3	0.3412 (7)	0.3298 (4)	0.5110 (5)
C1B4	0.3291 (7)	0.3914 (5)	0.5469 (4)
C1B5	0.3505 (7)	0.4473 (3)	0.5004 (5)
C1B6	0.3840 (6)	0.4416 (3)	0.4179 (5)
C2A1	0.6420 (5)	0.2983 (4)	0.1465 (5)
C2A2	0.7196 (7)	0.2622 (3)	0.2020 (5)
C2A3	0.8337 (6)	0.2770 (4)	0.2086 (5)
C2A4	0.8702 (5)	0.3280 (5)	0.1597 (6)
C2A5	0.7927 (8)	0.3641 (4)	0.1042 (6)
C2A6	0.6786 (7)	0.3493 (4)	0.0976 (5)
C2B1	0.4844 (7)	0.1938 (3)	0.1218 (5)
C2B2	0.5412 (6)	0.1694 (4)	0.0559 (5)
C2B3	0.5285 (7)	0.1041 (5)	0.0310 (5)
C2B4	0.4589 (8)	0.0632 (3)	0.0721 (6)
C2B5	0.4021 (7)	0.0877 (4)	0.1380 (6)
C2B6	0.4149 (7)	0.1530 (4)	0.1629 (5)
CP11	0.1177 (6)	0.3869 (4)	-0.0030 (4)
CP12	0.1273 (6)	0.4446 (4)	-0.0492 (6)
CP13	0.0407 (8)	0.4638 (4)	-0.1131 (6)
CP14	-0.0554 (6)	0.4253 (4)	-0.1308 (5)
CP15	-0.0649 (6)	0.3676 (4)	-0.0845 (6)
CP16	0.0216 (7)	0.3484 (3)	-0.0206 (5)
CP21	0.1859 (6)	0.2604 (3)	0.1580 (5)
CP22	0.1525 (8)	0.2094 (4)	0.1006 (4)
CP23	0.1080 (8)	0.1524 (4)	0.1313 (6)
CP24	0.0971 (7)	0.1462 (4)	0.2194 (7)
CP25	0.1306 (8)	0.1971 (5)	0.2768 (4)
CP26	0.1750 (7)	0.2542 (4)	0.2462 (5)

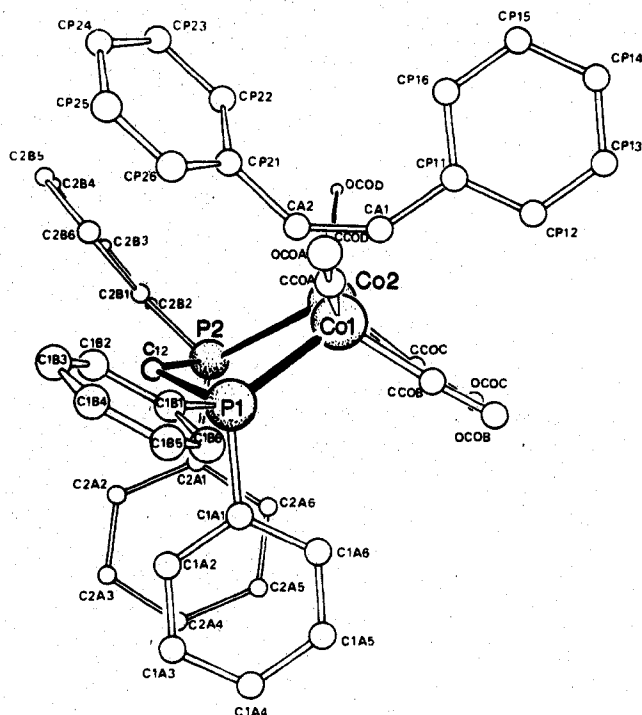
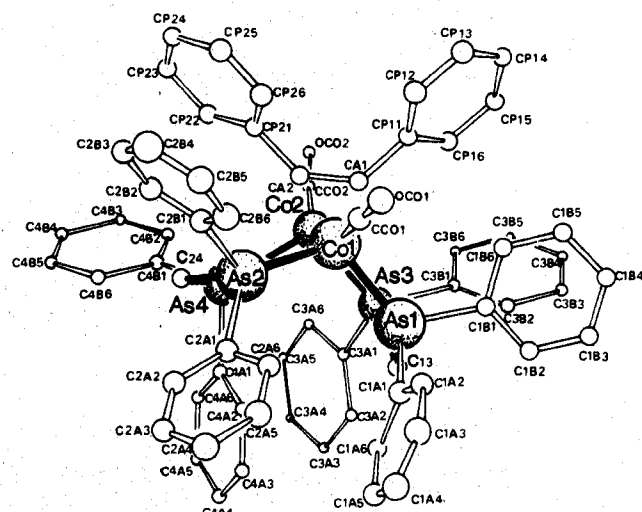
^a The estimated standard deviations in parentheses are right justified to the least significant digits of the fractional coordinates.

Preparation of (tolan)(dam)₂Co₂(CO)₂·C₂H₄Cl₂. (tolan)Co₂(CO)₆, 0.47 g (1 mmol), was treated with dam, 0.94 g (2.0 mmol), in 50 mL of refluxing toluene under N₂ for 48 h. The red solution was filtered hot, and the solvent removed under nitrogen. The residue was extracted with 1,2-dichloroethane, hexane was added, and the solution concentrated. The brown microcrystalline product, which was obtained upon cooling the solution, was recrystallized from a C₂H₄Cl₂-hexane mixture; yield 57%; mp 192–193 °C.

Anal. Calcd for C₆₈H₅₈As₄Cl₂Co₂O₂: C, 58.52; H, 4.19. Found: C, 58.33; H, 4.12.

The infrared spectrum in CH₂Cl₂ showed maxima at 1920 (s), 1590 (w), 1078 (w), 1028 (w), 1004 (w) cm⁻¹.

Collection of X-Ray Diffraction Data. Weissenberg and precession photographs of the three zero and three first levels were obtained to check the mosaicity of the crystals and obtain approximate cell dimensions. The crystal was approximately aligned on a fully automated Picker Nuclear FACS-1 diffractometer, and accurate setting

Figure 1. Atom labeling in (tolan)(dpm)Co₂(CO)₄.Figure 2. Atom labeling in (tolan)(dam)₂Co₂(CO)₂.

angles for 12 Bragg reflections, at both positive and negative 2θ , were measured. At the 30–35° 2θ angles involved, the $K\alpha_1$ - $K\alpha_2$ doublet was not resolved. The angles were used in a least-squares calculation to obtain the quoted cell parameters and a refined orientation matrix.

Details of the unit cell measurement, space group determination, and intensity data collection are collected in Table I. The Picker Disc Operating System was used for all automatic diffractometer operations. The data were processed using a locally written program:

$$I(\text{intensity}) = N - Bt_s/t_b$$

$$\sigma(I) = [N + B(t_s/t_b)^2 + (0.02N)^2]^{1/2}$$

where N and B are the counts accumulated during the scan period t_s and total background counting time t_b , respectively. Data for which $I < 3\sigma(I)$ were discarded and the remainder were corrected for Lorentz and polarization effects:

$$(Lp)^{-1} = \sin 2\theta_s(\cos^2 2\theta_m + 1)/(\cos^2 2\theta_m + \cos^2 2\theta_s)$$

where $2\theta_m$ and $2\theta_s$ are diffraction angles at the monochromator and

Table III. Final Thermal Parameters^a for (tolan)(dpm)Co₂(CO)₄

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co1	61.0 (13)	17.8 (4)	42.4 (8)	3.3 (6)	-3.2 (8)	0.6 (5)
Co2	71.2 (15)	25.1 (5)	35.6 (8)	4.9 (6)	-2.9 (8)	0.0 (5)
P1	60.9 (25)	17.4 (8)	33.0 (14)	2.9 (11)	-0.2 (16)	-2.3 (9)
P2	65.1 (26)	19.1 (9)	35.3 (15)	5.0 (12)	1.7 (16)	-4.6 (9)
C12	82 (10)	13 (3)	38 (6)	12 (4)	8 (6)	0 (3)
CA1	53 (9)	22 (3)	46 (6)	-8 (4)	0 (6)	5 (4)
CA2	66 (10)	19 (3)	35 (6)	2 (4)	-10 (6)	2 (4)
CCOA	82 (12)	22 (4)	49 (7)	-10 (5)	8 (8)	3 (4)
OCOA	101 (9)	43 (3)	80 (6)	12 (4)	33 (6)	-3 (4)
CCOB	55 (10)	26 (4)	64 (8)	8 (5)	-12 (7)	6 (5)
OCOB	113 (10)	23 (3)	113 (7)	5 (4)	5 (6)	17 (4)
CCOC	117 (15)	43 (5)	52 (8)	1 (7)	3 (9)	14 (5)
OCOC	167 (13)	72 (5)	114 (9)	7 (6)	22 (9)	51 (6)
CCOD	116 (14)	39 (5)	50 (8)	8 (6)	-18 (8)	-12 (5)
OCOD	218 (15)	69 (5)	76 (7)	4 (7)	-19 (8)	-37 (5)

Atom	$B, \text{Å}^2$	Atom	$B, \text{Å}^2$	Atom	$B, \text{Å}^2$
C1A1	3.8 (2)	C2A1	4.1 (2)	CP11	4.0 (2)
C1A2	5.2 (3)	C2A2	5.2 (3)	CP12	7.0 (4)
C1A3	5.8 (3)	C2A3	6.4 (3)	CP13	7.5 (4)
C1A4	5.9 (3)	C2A4	7.1 (3)	CP14	6.2 (3)
C1A5	6.9 (4)	C2A5	8.3 (4)	CP15	6.9 (3)
C1A6	4.6 (3)	C2A6	6.6 (3)	CP16	5.6 (3)
C1B1	3.5 (2)	C2B1	4.1 (2)	CP21	4.4 (3)
C1B2	4.9 (3)	C2B2	6.5 (3)	CP22	6.3 (3)
C1B3	6.9 (3)	C2B3	8.4 (4)	CP23	8.8 (4)
C1B4	6.6 (3)	C2B4	7.2 (4)	CP24	7.9 (4)
C1B5	6.5 (3)	C2B5	7.4 (4)	CP25	7.3 (4)
C1B6	5.4 (3)	C2B6	6.2 (3)	CP26	5.6 (3)

^a Anisotropic thermal parameters are applied in the expression $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. They are multiplied by 10^4 . Estimated standard deviations in parentheses are right justified to the least significant digits of the thermal parameter.

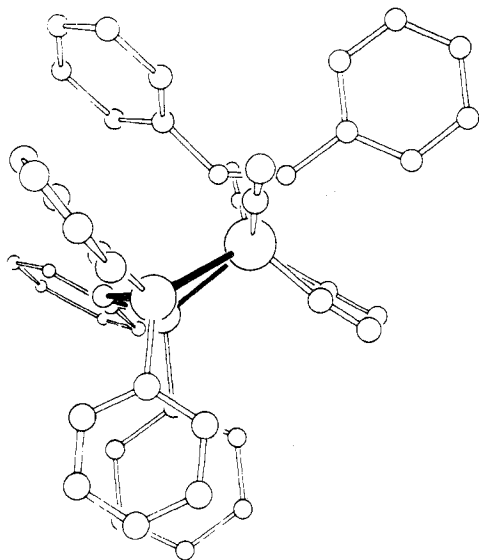


Figure 3. Projection of (tolan)(dpm)Co₂(CO)₄ directly down the cobalt-cobalt vector.

sample crystals, respectively. In view of the relatively invariant transmission factors of the very small crystals, absorption corrections were not applied.

Solution and Refinement of Structures

The scattering factors for neutral atoms were taken from the listings of Cromer and Waber,⁹ and real and imaginary anomalous dispersion corrections were applied for the "heavy" atoms.¹⁰ We used the following equations

$$R_F = \frac{\sum \|F_o\| - |F_c|}{\sum \|F_o\|}$$

$$R_{wF} = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\sum w|F_o|^2} \right]^{1/2}$$

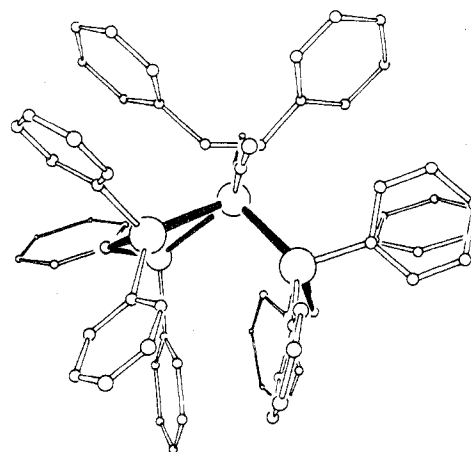


Figure 4. Projection of (tolan)(dam)₂Co₂(CO)₂ directly down the cobalt-cobalt vector.

The standard deviation in an observation of unit weight is

$$\text{"goodness of fit"} = \left[\frac{\sum w(|F_o| - |F_c|)^2}{(m - n)} \right]^{1/2}$$

where m is the number of reflections, n is the number of refined variables, and $w[F(hkl)] = \sigma^{-2}[F(hkl)]$.

Fourier and Patterson syntheses were calculated using FORDAP by Zalkin; structure factor and least-squares calculations were performed using NUCLS (by J. A. Ibers). All computing was carried out on the Concordia University CDC 6400 computer.

a. (tolan)(dpm)Co₂(CO)₄. The positions of the two independent cobalt atoms were determined from a three-dimensional Patterson synthesis. A structure factor calculation ($R = 49.9\%$) was used as the basis for a Fourier synthesis which revealed the position of the two phosphorus atoms, the carbonyl groups, the "acetylene" carbon atoms, and most of the carbon atoms of the six phenyl rings. After one cycle of full-matrix least-squares refinement and a structure factor calculation ($R = 25.2\%$), a difference Fourier showed the remaining

Table IV. Final Positional Parameters^a for (tolan)(dam)₂Co₂(CO)₂·C₂H₄Cl₂

Atom	x	y	z	Atom	x	y	z
Co1	0.31578 (17)	0.27155 (15)	0.46306 (20)	C3A2	0.0345 (8)	0.2653 (6)	-0.0068 (11)
Co2	0.14594 (17)	0.19851 (15)	0.38388 (20)	C3A3	-0.0128 (10)	0.2248 (8)	-0.0893 (8)
As1	0.30253 (14)	0.37498 (12)	0.30865 (17)	C3A4	-0.0952 (8)	0.1283 (6)	0.0228 (12)
As2	0.42387 (13)	0.17762 (12)	0.47964 (16)	C3A5	-0.0777 (9)	0.1564 (8)	-0.0745 (10)
As3	0.08522 (14)	0.28668 (12)	0.21369 (16)	C3A6	-0.0479 (9)	0.1688 (8)	0.1053 (8)
As4	0.20748 (13)	0.10286 (12)	0.33533 (16)	C3B1	-0.0186 (10)	0.3647 (9)	0.1761 (10)
C13	0.1956 (13)	0.3564 (11)	0.1695 (14)	C3B2	0.0062 (9)	0.4474 (10)	0.1533 (12)
C24	0.3502 (11)	0.0776 (10)	0.4368 (13)	C3B3	-0.0663 (14)	0.5008 (6)	0.1306 (13)
CA1	0.1891 (13)	0.2602 (11)	0.4926 (15)	C3B4	-0.1636 (12)	0.4716 (10)	0.1307 (12)
CA2	0.2363 (13)	0.1893 (13)	0.5361 (14)	C3B5	-0.1885 (8)	0.3890 (12)	0.1535 (12)
CCO1	0.4017 (12)	0.3201 (10)	0.5566 (15)	C3B6	-0.1160 (12)	0.3355 (7)	0.1762 (12)
OCO1	0.4556 (10)	0.3572 (8)	0.6184 (12)	C4A1	0.2322 (10)	0.1247 (8)	0.1995 (8)
CCO2	0.0260 (12)	0.1531 (10)	0.3909 (14)	C4A2	0.3091 (8)	0.1812 (7)	0.1805 (9)
OCO2	-0.0486 (9)	0.1292 (8)	0.4039 (12)	C4A3	0.3237 (8)	0.1980 (7)	0.0819 (12)
C1A1	0.4159 (8)	0.4193 (7)	0.2565 (11)	C4A4	0.2613 (11)	0.1582 (8)	0.0023 (8)
C1A2	0.4955 (11)	0.4643 (8)	0.3175 (9)	C4A5	0.1844 (9)	0.1017 (8)	0.0213 (9)
C1A3	0.5815 (8)	0.4910 (7)	0.2891 (12)	C4A6	0.1698 (8)	0.0849 (6)	0.1199 (11)
C1A4	0.5880 (9)	0.4728 (8)	0.1997 (13)	C4B1	0.1454 (10)	-0.0068 (6)	0.3423 (10)
C1A5	0.5085 (12)	0.4278 (9)	0.1387 (10)	C4B2	0.0425 (9)	-0.0229 (7)	0.3285 (10)
C1A6	0.4224 (9)	0.4010 (7)	0.1671 (10)	C4B3	-0.0019 (7)	-0.1010 (9)	0.3298 (10)
C1B1	0.2661 (9)	0.4800 (7)	0.3092 (13)	C4B4	0.0566 (11)	-0.1629 (6)	0.3450 (11)
C1B2	0.2528 (10)	0.5456 (10)	0.2203 (9)	C4B5	0.1595 (10)	-0.1468 (7)	0.3587 (10)
C1B3	0.2222 (10)	0.6171 (8)	0.2220 (10)	C4B6	0.2039 (7)	-0.0688 (8)	0.3574 (10)
C1B4	0.2047 (10)	0.6230 (7)	0.3125 (14)	CP11	0.1431 (10)	0.3062 (7)	0.5375 (11)
C1B5	0.2180 (10)	0.5574 (10)	0.4013 (10)	CP12	0.1904 (7)	0.3177 (8)	0.6420 (10)
C1B6	0.2486 (9)	0.4858 (8)	0.3997 (8)	CP13	0.1457 (11)	0.3627 (9)	0.6799 (8)
C2A1	0.5336 (8)	0.1997 (9)	0.4190 (10)	CP14	0.0536 (11)	0.3964 (7)	0.6131 (13)
C2A2	0.5615 (11)	0.1421 (6)	0.3841 (11)	CP15	0.0063 (8)	0.3849 (8)	0.5086 (11)
C2A3	0.6462 (12)	0.1580 (8)	0.3525 (11)	CP16	0.0510 (10)	0.3399 (8)	0.4707 (8)
C2A4	0.7031 (8)	0.2316 (10)	0.3558 (11)	CP21	0.2601 (9)	0.1228 (6)	0.6374 (8)
C2A5	0.6752 (10)	0.2892 (7)	0.3907 (11)	CP22	0.2152 (7)	0.0450 (8)	0.6375 (8)
C2A6	0.5905 (10)	0.2733 (7)	0.4223 (10)	CP23	0.2392 (9)	-0.0148 (5)	0.7334 (11)
C2B1	0.5115 (8)	0.1312 (8)	0.6311 (7)	CP24	0.3081 (9)	0.0032 (7)	0.8292 (8)
C2B2	0.4990 (8)	0.0512 (7)	0.6842 (10)	CP25	0.3531 (8)	0.0810 (8)	0.8291 (8)
C2B3	0.5644 (10)	0.0220 (6)	0.7895 (10)	CP26	0.3291 (8)	0.1408 (6)	0.7332 (11)
C2B4	0.6422 (9)	0.0728 (9)	0.8417 (8)	CI1	0.5712 (7)	0.6864 (6)	0.1136 (7)
C2B5	0.6547 (8)	0.1529 (8)	0.7885 (11)	CS1	0.4374 (21)	0.6635 (23)	0.0866 (31)
C2B6	0.5893 (10)	0.1821 (5)	0.6832 (11)	CS2	0.3852 (41)	0.7326 (20)	0.0720 (27)
C3A1	0.0170 (8)	0.2372 (7)	0.0905 (9)	CI2	0.3727 (10)	0.7871 (7)	-0.0665 (11)

^a The estimated standard deviations in parentheses are right justified to the least significant digits of the fractional coordinates.

atoms (other than hydrogen). Two further cycles of refinement reduced the *R* value to 10.2%. At this point idealized six-membered rings (C-C bond length 1.39 Å; all angles 120°) were fitted to the observed ring atom positions by a least-squares procedure and refinement was continued using isotropic thermal parameters for each ring atom and anisotropic thermal parameters for the remaining atoms. The anomalous dispersion corrections for cobalt were included from this point. Refinement converged with $(\Delta/\sigma)_{\max} < 0.10$ after four cycles of refinement at *R* = 8.8% and *R_w* = 10.2%. The "goodness of fit" was 2.45. A final difference Fourier showed no features with an electron density greater than 0.9 e Å⁻³.

A table of observed and calculated structure factors is available as supplementary material. Table II gives the final positional parameters and their estimated standard deviations, and Table III gives the thermal parameters and esd's.

b. (tolan)(dam)₂Co₂(CO)₂·C₂H₄Cl₂. Solution and refinement of this structure closely paralleled that of the phosphino complex. The solution of the Patterson for the six heavy atoms was facilitated by the wide separation of intramolecular peak groupings caused by the sheath of phenyl groups. One cycle of refinement of the heavy atoms was followed by a structure factor calculation (*R* = 30.2%). This yielded a difference Fourier map from which the remaining non-hydrogen atom positions were obtained (including the dichloroethane).

Two cycles of isotropic refinement were used to improve the positions prior to the use of rigid rings. The parameters were separated randomly into seven matrices during these two cycles after which *R* = 12.7%.

Refinement with all ten phenyl rings constrained as rigid groups with individual atomic isotropic parameters, and all other atoms anisotropic, converged at *R* = 8.6% and *R_w* = 7.5% with the "goodness

of fit" 3.04. The final difference Fourier showed residual peaks of less than 1.0 e Å⁻³.

A table of observed and calculated structure factors is available as supplementary material. The final positional parameters are in Table IV, and thermal parameters in Table V.

Results and Discussion

Figures 1 and 2 show the atom labelling with the molecules viewed approximately along the cobalt-cobalt vector. Figures 3 and 4 show the molecules viewed directly along this bond. In neither structure are there unusually short intermolecular distances: the shortest nonbonded contacts are intramolecular. The intramolecular bond lengths and angles are collected in Tables VI and VII.

(tolan)(dpm)Co₂(CO)₄. The molecular structure is derived from that of (tolan)Co₂(CO)₆ by replacement of two pseudoaxial carbonyls, one on each cobalt, by phosphorus atoms. Examination of Figure 3 reveals that the five-membered ring

Co1-Co2-P2-C12-P1 is nonplanar, being folded up at the line joining the phosphorus atoms and twisted slightly: the two ends of the molecule are not perfectly eclipsed. The cobalt to carbonyl-carbon distances are normal, averaging 1.71 Å for the pseudoaxial groups (A and D), and 1.77 Å for the pseudoequatorial groups (B and C). The average cobalt-phosphorus distance of 2.213 Å is similar to the value of 2.233 Å in Co₄(CO)₁₀(Ph₂PC₂CF₃)₂.¹¹

(tolan)(dam)₂Co₂(CO)₂. In this structure all of the pseudoequatorial carbonyl groups have been replaced by

Table V. Final Thermal Parameters^a for (tolan)(dam)₂Co₂(CO)₂·C₂H₄Cl₂

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co1	31.6 (17)	29.0 (13)	62.6 (25)	7.5 (12)	5.7 (17)	-15.6 (15)
Co2	36.0 (18)	27.5 (13)	54.7 (24)	7.5 (12)	4.6 (16)	-14.6 (14)
As1	42.9 (15)	27.5 (10)	63.9 (20)	5.0 (10)	14.2 (14)	-10.5 (12)
As2	33.0 (14)	29.1 (10)	60.9 (19)	10.8 (9)	3.9 (13)	-16.1 (11)
As3	43.7 (15)	30.5 (11)	55.6 (20)	13.3 (10)	2.3 (14)	-10.5 (12)
As4	35.3 (14)	27.1 (10)	55.1 (19)	7.6 (10)	2.8 (13)	-12.9 (11)
C13	53 (15)	34 (10)	63 (18)	-1 (10)	19 (13)	-15 (11)
C24	33 (12)	45 (10)	55 (16)	30 (9)	-30 (11)	-15 (10)
CA1	59 (15)	22 (9)	66 (19)	7 (9)	28 (14)	-23 (11)
CA2	53 (16)	64 (13)	37 (17)	19 (11)	10 (13)	-18 (12)
CCO1	62 (15)	40 (9)	102 (20)	12 (9)	39 (14)	-34 (11)
OCO1	88 (12)	52 (8)	135 (17)	-4 (8)	16 (11)	-46 (10)
CCO2	61 (14)	31 (9)	62 (18)	-5 (9)	19 (13)	-38 (11)
OCO2	53 (10)	67 (9)	159 (18)	-12 (7)	58 (11)	-22 (10)
C11	221 (11)	119 (11)	148 (6)	-11 (9)	62 (6)	-12 (8)
CS1	86 (26)	180 (29)	288 (62)	20 (23)	96 (33)	-18 (35)
CS2	711 (11)	104 (22)	423 (42)	93 (38)	499 (62)	3 (24)
Cl2	435 (18)	130 (9)	362 (20)	52 (10)	49 (15)	18 (10)

Atom	$B, \text{Å}^2$	Atom	$B, \text{Å}^2$	Atom	$B, \text{Å}^2$
C1A1	3.8 (4)	C2B1	3.5 (4)	C4A1	3.1 (4)
C1A2	5.2 (5)	C2B2	3.5 (4)	C4A2	4.7 (5)
C1A3	5.5 (5)	C2B3	4.7 (4)	C4A3	4.8 (5)
C1A4	7.1 (6)	C2B4	5.2 (5)	C4A4	5.4 (5)
C1A5	7.5 (6)	C2B5	5.7 (5)	C4A5	6.0 (6)
C1A6	6.0 (6)	C2B6	5.5 (5)	C4A6	4.4 (5)
C1B1	4.6 (5)	C3A1	3.5 (4)	C4B1	4.0 (4)
C1B2	5.6 (5)	C3A2	4.3 (5)	C4B2	4.3 (5)
C1B3	6.3 (6)	C3A3	5.1 (5)	C4B3	6.3 (6)
C1B4	7.3 (6)	C3A4	4.7 (5)	C4B4	5.7 (5)
C1B5	6.0 (6)	C3A5	5.5 (5)	C4B5	5.3 (5)
C1B6	5.4 (5)	C3A6	4.8 (5)	C4B6	4.5 (5)
C2A1	4.0 (4)	C3B1	3.5 (4)	CP11	3.0 (4)
C2A2	6.5 (6)	C3B2	7.0 (6)	CP12	4.9 (5)
C2A3	7.6 (7)	C3B3	9.5 (8)	CP13	6.5 (6)
C2A4	7.0 (6)	C3B4	8.2 (7)	CP14	5.2 (5)
C2A5	5.7 (5)	C3B5	8.5 (7)	CP15	6.2 (6)
C2A6	3.9 (4)	C3B6	7.1 (6)	CP16	5.7 (5)
CP21	3.4 (4)	CP22	3.2 (4)	CP23	4.0 (4)
CP24	5.1 (5)	CP25	4.6 (5)	CP26	3.7 (4)

^a Anisotropic thermal parameters are applied in the expression $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. They are multiplied by 10⁴. Estimated standard deviations in parentheses are right justified to the least significant digits of the thermal parameter.

arsenic. Figure 4 shows that both five-membered rings Co1-Co2-As3-C13-As1 and Co1-Co2-As4-C24-As2 are nonplanar but folded in opposite directions. One of the rings, that containing As2 and As4, is essentially similar in conformation to that in the dpm complex. The other does not possess the twist; that is, Co1, Co2, As1, and As3 are coplanar. The mean cobalt to carbonyl carbon distance is 1.75 Å. The Co to As bond lengths average 2.334 Å which is close to the value of 2.323 Å in Co₂(CO)₆(CH₃)₂AsC=C(As(CH₃)₂)CF₂CF₂.¹² The tolan unit has a rather unusual conformation with both phenyl rings turned in the same direction. It is also displaced slightly such that the CA1-CA2 vector deviates by about 12° from a perpendicular to the plane containing the cobalt atoms and carbonyl groups.

The Bridging Ligands. There are relatively few crystallographic data on complexes of dpm and dam compared with the ethane analogues. A comparison of these moieties in our structures with those in other molecules in which they bridge or are chelating is of interest. We wish to know, if possible, whether the cobalt-cobalt bond is under tension or compression as a result of the presence of the bridging ligands. Table VIII displays relevant structural parameters.¹³⁻²²

In cases with four-membered chelate rings, where most strain is present, a planar skeleton is expected, provided torsional effects caused by nonbonded interactions between

substituent groups are not significant. Such torsional effects are presumably responsible for the nonplanarity observed in cyclobutane²³ but might be reduced in chelate complexes due to longer skeletal bond lengths. The Ni and Fe complexes indeed show planar rings, while in the Pt and Mo complexes cyclic strain is sufficiently reduced that the rings pucker. In the binuclear complexes in which the ring strain is further reduced (or eliminated) the rings fold along the line joining donor atoms by even larger angles with steric repulsion between phenyl rings imposing the upper limit. In those complexes where the fold angle lies between 40 and 46.4°, the phenyl rings are found approximately face to face in quite close contact. A typical distance between the phosphorus-bonded carbon atoms is 3.58 Å in dpm(CuCl)₂, while the closest approach of ring atoms in (dam)₂Rh₂(CO)₂Cl₂ is 3.54 Å.

In (tolan)(dpm)Co₂(CO)₄ the chelate ring conformation is very similar to that found in (dam)₂Rh₂(CO)₂Cl₂. Rings 1A and 2A are nearly parallel and perpendicular to the Co-Co bond, with a distance between C1A1 and C2A1 of 3.43 (1) Å. The other two phenyl rings 1B and 2B lie in approximately the same plane as P1, P2, and C12.

In (tolan)(dam)₂Co₂(CO)₂ none of the phenyl rings are found in this limiting face to face position; indeed examination of crude molecular models suggests that such conformations are all unfavorable. As a consequence, the fold angles are limited to 28 and 30°. If the chelating rings are closer to planarity than would be preferred in the absence of the steric

Table VI. Bond Lengths (Å) and Angles (deg) in (tolan)(dpm)Co₂(CO)₄^a

Distances			
Co1-Co2	2.459 (2)	CA1-CA2	1.33 (1)
Co1-CCOA	1.70 (1)	Co2-CCOD	1.71 (1)
Co1-CCOB	1.78 (1)	Co2-CCOC	1.76 (1)
Co1-CA1	1.97 (1)	Co2-CA2	1.94 (1)
Co1-CA2	1.95 (1)	Co2-CA1	1.92 (1)
CCOA-OCOA	1.16 (2)	CCOC-OCOC	1.13 (2)
CCOB-OCOB	1.14 (2)	CCOD-OCOD	1.14 (2)
Co1-P1	2.210 (3)	Co2-P2	2.215 (3)
P1...P2	2.946 (4)		
P1-C12	1.84 (1)	P2-C12	1.84 (1)
P1-C1A1	1.822 (7)	P2-C2A1	1.809 (7)
P1-C1B1	1.822 (7)	P2-C2B1	1.829 (7)
CA1-CP11	1.46 (1)	CA2-CP21	1.49 (1)
Angles			
P1-Co1-Co2	93.2 (1)	P2-Co2-Co1	98.8 (1)
P1-Co1-CCOB	109.2 (4)	P2-Co2-CCOC	111.8 (5)
P1-Co1-CCOA	98.5 (4)	P2-Co2-CCOD	97.8 (5)
P1-Co1-CA2	101.7 (3)	P2-Co2-CA2	97.5 (3)
CA1-Co1-Co2	50.0 (3)	CA1-Co2-Co1	51.6 (3)
CA1-Co1-CCOB	101.4 (5)	CA1-Co2-CCOC	103.8 (6)
CA1-Co1-CCOA	105.0 (5)	CA1-Co2-CCOD	100.0 (6)
CA1-Co1-Co2	39.7 (4)	CA1-Co2-Co2	40.2 (4)
Co2-Co1-CCOB	102.2 (4)	Co1-Co2-CCOC	97.8 (5)
CCOB-Co1-CCOA	101.0 (5)	CCOC-Co2-CCOD	99.1 (6)
CCOA-Co1-CA2	98.5 (5)	CCOD-Co2-CA2	102.0 (5)
CA2-Co1-Co2	50.7 (3)	CA2-Co2-Co1	50.8 (3)
Co2-Co1-CCOA	148.8 (4)	Co1-Co2-CCOD	149.8 (4)
Co1-P1-C12	109.7 (3)	Co2-P2-C12	108.9 (3)
Co1-P1-C1A1	121.8 (3)	Co2-P2-C2A1	123.8 (3)
Co1-P1-C1B1	115.4 (3)	Co2-P2-C2B1	111.9 (3)
C12-P1-C1A1	103.4 (4)	C12-P2-C2A1	103.5 (4)
C12-P1-C1B1	103.2 (4)	C12-P2-C2B1	104.3 (4)
C1A1-P1-C1B1	101.3 (4)	C2A1-P2-C2B1	102.6 (4)
P1-C12-P2	106.4 (5)		
CP11-CA1-CA2	143.2 (9)	CP21-CA2-CA1	137.7 (9)
CP11-CA1-Co1	133.8 (7)	CP21-CA2-Co1	136.9 (7)
CP11-CA1-Co2	133.5 (7)	CP21-CA2-Co2	135.2 (7)
CA2-CA1-Co1	69.4 (6)	CA1-CA2-Co1	70.9 (6)
CA2-CA1-Co2	70.7 (6)	CA1-CA2-Co2	69.1 (6)
Co1-CA1-Co2	78.5 (4)	Co1-CA2-Co2	78.5 (4)
Co1-CCOA-OCOA	179 (1)	Co2-CCOD-OCOD	176 (1)
Co1-CCOB-OCOB	175 (1)	Co2-CCOC-OCOC	173 (1)

^a Estimated standard deviations in parentheses are right justified to least significant digits of the preceding number.

limitations, one effect is to place the Co-Co bond under a compressional stress.

The Co₂(tolan) Groups. Table IX contains various geometrical parameters for selected molecules containing "acetylene" bridging between singly bonded metal atoms.^{7,24-27} Further structural data for acetylene bridging two cobalt atoms are available in the literature.^{11,28-32} Cobalt-cobalt distances range from 2.447 (4) Å in Co₃(CO)₉C₃HCO₂(CO)₆²⁶ to 2.488 (4) Å in C₆F₆Co₂(CO)₆.³¹ The value of 2.459 (2) Å for (tolan)(dpm)Co₂(CO)₄ is within this range but the bond length observed in (tolan)(dam)₂Co₂(CO)₂, 2.518 (4) Å, is significantly longer. We are inclined to ascribe this lengthening to electronic effects since the arguments presented above suggest the bond would be under steric compression. It should be noted that the available evidence suggests that poorer π-electron acceptors replacing the carbonyl groups of Co₂(CO)₆(C₂H₂) appear to prefer the pseudoaxial sites.^{2,33} Similarly, triphenylphosphine replacing PF₃ groups in Rh₂(PF₃)₆(C₂H₂) prefers these sites.²⁵ The inaccessibility of these electronically preferred sites to the bidentate bridging ligands may lie at the root of the Co-Co bond length anomalies.

Given the magnitude of their esd's, the C-C distance and the carbon-phenyl distances and the angles at these

Table VII. Bond Lengths (Å) and Bond Angles (deg) in (tolan)(dam)₂Co₂(CO)₂-C₂H₄Cl₂^a

Distances			
Co1-Co2	2.518 (4)	CA1-CA2	1.37 (3)
Co1-CCO1	1.71 (2)	Co2-CCO2	1.78 (2)
Co1-CA1	1.96 (2)	Co2-CA2	1.97 (2)
Co1-CA2	1.96 (2)	Co2-CA1	1.93 (2)
CCO1-OCO1	1.17 (2)	CCO2-OCO2	1.13 (2)
Co1-As1	2.326 (4)	Co2-As3	2.332 (4)
Co1-As2	2.330 (3)	Co2-As4	2.348 (3)
As1...As3	3.165 (3)	As2...As4	3.240 (3)
As1-C13	2.01 (2)	As3-C13	1.99 (2)
As1-C1A1	1.96 (1)	As3-C3A1	1.95 (1)
As1-C1B1	1.98 (1)	As3-C3B1	1.99 (1)
As2-C24	1.98 (2)	As4-C24	2.01 (2)
As2-C2A1	1.97 (1)	As4-C4A1	1.95 (1)
As2-C2B1	1.98 (1)	As4-C4B1	1.95 (1)
CA1-CP11	1.48 (2)	CA2-CP21	1.50 (2)
CS1-Cl1	1.79 (3)	CS2-Cl2	1.82 (4)
CS1-CS2	1.44 (6)		
Angles			
As1-Co1-Co2	96.2 (1)	As3-Co2-Co1	99.7 (1)
As1-Co1-As2	110.0 (1)	As3-Co2-As4	98.7 (1)
As1-Co1-CCO1	98.2 (6)	As3-Co2-CCO2	97.7 (6)
As1-Co1-CA1	108.4 (6)	As3-Co2-CA1	108.3 (6)
CA2-Co1-Co2	50.3 (6)	CA2-Co2-Co1	49.8 (6)
CA2-Co1-As2	92.1 (6)	CA2-Co2-As4	101.7 (6)
CA2-Co1-CCO1	107.9 (9)	CA2-Co2-CCO2	104.8 (8)
CA2-Co1-CA1	41.0 (8)	CA2-Co2-CA1	41.1 (9)
Co2-Co1-As2	99.5 (1)	Co1-Co2-As4	96.9 (1)
As2-Co1-CCO1	96.9 (6)	As4-Co2-CCO2	103.6 (6)
CCO1-Co1-CA1	104.3 (8)	CCO2-Co2-CA1	101.8 (8)
CA1-Co1-Co2	49.1 (6)	CA1-Co2-Co1	50.1 (6)
Co2-Co1-CCO1	152.9 (6)	Co1-Co2-CCO2	150.6 (6)
Co1-As1-C13	116.4 (5)	Co1-As2-C24	113.4 (5)
Co1-As1-C1A1	124.1 (4)	Co1-As2-C2A1	125.6 (4)
Co1-As1-C1B1	116.5 (5)	Co1-As2-C2B1	114.4 (4)
C13-As1-C1A1	99.1 (7)	C24-As2-C2A1	103.6 (6)
C13-As1-C1B1	100.6 (7)	C24-As2-C2B1	100.0 (6)
C1A1-As1-C1B1	95.7 (5)	C2A1-As2-C2B1	95.8 (5)
Co2-As3-C13	113.1 (6)	Co2-As4-C24	110.9 (5)
Co2-As3-C3A1	116.4 (4)	Co2-As4-C4A1	122.8 (4)
Co2-As3-C3B1	122.9 (4)	Co2-As4-C4B1	121.7 (4)
C13-As3-C3A1	101.0 (7)	C24-As4-C4A1	97.6 (6)
C13-As3-C3B1	102.6 (7)	C24-As4-C4B1	98.8 (6)
C3A1-As3-C3B1	97.5 (6)	C4A1-As4-C4B1	100.1 (6)
As1-C13-As3	104.7 (9)	As2-C24-As4	108.4 (8)
CP11-CA1-CA2	132 (2)	CP21-CA2-CA1	140 (2)
CP11-CA1-Co1	135 (1)	CP21-CA2-Co1	136 (1)
CP11-CA1-Co2	139 (1)	CP21-CA2-Co2	135 (1)
CA2-CA1-Co1	69 (1)	CA1-CA2-Co1	70 (1)
CA2-CA1-Co2	71 (1)	CA1-CA2-Co2	68 (1)
Co1-CA1-Co2	81 (1)	Co1-CA1-Co2	80 (1)
Co1-CCO1-OCO1	175 (2)	Co2-CCO2-OCO2	172 (2)
Cl1-CS1-CS2	112 (3)	Cl2-CS2-CS1	102 (3)

^a Estimated standard deviations in parentheses are right justified to the least significant digits of the preceding number.

"acetylenic" carbon atoms of the Co₂C₂ fragment do not reveal significant differences from compound to compound. We have, therefore, attempted to identify a parameter which is more sensitive to changes in the substituents on cobalt. The angle, θ, a representation of the deviation from linearity of the acetylene, is based on the crystallographically determined positions of the six ring atoms in the tolan cases and the five atoms comprising the *t*-Bu-C group in Co₂(CO)₆((*t*-Bu)₂C₂). While this angle is expected to decrease as the acetylene acts more effectively as a σ donor or π acceptor, steric effects can account for such anomalies as appear in Table IX. Repulsion between *tert*-butyl groups in Co₂(CO)₆((*t*-Bu)₂C₂) could be responsible for the larger angle observed for this compound. The angle θ in (tolan)(dam)₂Co₂(CO)₂ is at the other end of

Table VIII. Geometrical Parameters Associated with Bis(phosphino)- and Bis(arsino)methane Ligands

Compd	Ref	Comments	Bite, deg	M-X, ^a Å	X···X, ^a Å	M-M, ^b Å	M···M, ^c Å	X-C-X, ^a deg	Dihedral angle, ^d deg
[(C ₆ H ₁₁) ₂ P] ₂ CH ₂] ₂ Ni	13	<i>e</i> , ring 1	77.7 (1)	2.193 (2), 2.198 (2)	2.778 (2)			96.4 (3)	0
		<i>e</i> , ring 2	77.3 (1)	2.215 (2), 2.214 (2)	2.766 (2)			94.8 (3)	0
(dpm)Fe(CO) ₃	14	<i>e</i>	73.5 (1)	2.209 (3), 2.225 (3)	2.651 (2)			90.8 (2)	0
(dpm)PtPh ₂	15	<i>e</i>	73 (1)	2.30, 2.30	2.74			95 (1)	7.8
(dpm)Mo(CO) ₄	16	<i>e</i>	67.3 (1)	2.535 (3), 2.501 (2)	2.792 (3)			95.6 (4)	18.6
(dpm)(CuCl) ₂	17	<i>f</i>		2.197 (5), 2.195 (4)	3.049 (6)		2.908	110 (1)	40
(dpm)(CuI) ₂	18	<i>f</i>		2.22, 2.22	3.08 (1)		3.108 (7)	113	Nonplanar
(tolan)(dpm)Co ₂ (CO) ₄		<i>f</i>		2.210 (3), 2.215 (3)	2.946 (4)	2.459 (2)		106.4 (5)	44.6
(dpm)Fe ₂ (CO) ₇	19	<i>f</i>		2.250 (3), 2.257 (3)	2.999 (4)	2.709 (2)		109.0 (5)	45.3
(dam) ₂ Mo(CO) ₂ Br ₂	20	<i>e</i>	66.7 (1)	2.651 (5), 2.592 (5)	2.883 (5)			90 (1)	25
		<i>g</i>		2.608 (5)	3.28			113 (2)	
(dam)[Hg(C ₆ F ₅) ₂] ₂	21	<i>f</i>		3.40 (5)	3.35			113 (3)	
(dam) ₂ Rh ₂ (CO) ₂ Cl ₂	22	<i>f</i>		2.404 (1), 2.410 (1)	3.298 (1)		3.396 (1)	113.5 (4)	46.4
(tolan)(dam) ₂ Co ₂ (CO) ₂		<i>f</i> , ring 1		2.326 (4), 2.330 (3)	3.165 (3)	2.518 (4)		104.7 (9)	29.9
		<i>f</i> , ring 2		2.332 (4), 2.348 (3)	3.240 (3)	2.518 (4)		108.4 (8)	27.7

^a X = P or As. ^b Binuclear complexes with a metal-metal bond have an entry here. ^c Binuclear complexes without a metal-metal bond have an entry here. ^d Defined by the XCX plane and either the XM₂ plane or the XMMX least-squares plane. ^e Chelating. ^f Bridging. ^g Dangling.

Table IX. Geometrical Parameters Associated with the μ -alkyne-M₂ Group in Selected Molecules

Compd	Ref	M-M, Å	M-C, ^a Å	C-C, Å	C-R, ^a Å	R-C-C, ^b deg	θ , ^c deg	θ_1 , ^d deg	ϕ_2 , ^d deg
(tolan)(dpm)Co ₂ (CO) ₄	This work	2.459 (2)	1.95 (2)	1.33 (1)	1.48 (2)	143.2 (9), 137.7 (9)	101.3	4.9	-58.5
(tolan)(dam) ₂ Co ₂ (CO) ₂	This work	2.518 (4)	1.96 (2)	1.37 (3)	1.49 (1)	132 (2), 140 (2)	93.2	44.6	-64.7
((<i>t</i> -Bu) ₂ C ₂)Co ₂ (CO) ₆	7	2.463 (1)	1.996 (5)	1.335 (6)	1.51 (1)	144.5 (4), 144.8 (4)	108.6		
(tolan)Ni ₂ (C ₅ H ₅) ₂	24	2.329 (4)	1.89 (1)	1.35 (3)	1.45 (2)	142 (2), 138 (2)	103.2	16.1	53.4
(tolan)(Ph ₃)Rh ₂ (PF ₃) ₄	25	2.740 (1)	2.125 (5)	1.369 (7)	1.460 (7)	141.5 (5), 141.1 (5)	104.0	28.9	-34.3
(tolan)Co ₂ (CO) ₆	26	2.460 (5)	1.97 (2)	1.36 (3)	1.46 (3)	141 (2), 141 (2)	102 (1) ^e	13 (7) ^e	-47 (3)
(tolan)[P(OMe) ₂] ₂ O]Co ₂ (POMe) ₃	27	2.461 (7)	1.96 (3)	1.28 (5)	1.50 (4)	138 (3), 141 (3)	101	18	-47

^a Average value; figure in parentheses is crystallographic esd or rms deviation, whichever is larger. ^b In tolan compounds, the first figure refers to the least rotated phenyl ring. ^c Angle between the appropriate axes of the R groups; see text. ^d Angle between the phenyl ring plane and the plane defined by acetylene carbons and substituted phenyl ring carbons. ^e Rms deviation.

the range, as might be expected since four relatively efficient π -accepting CO groups have been replaced by arsenic atoms quasi-trans to the alkyne. However, the observation that the tolan in this complex differs in its conformation from all the other examples suggests an alternative explanation. The normal conformation appears to be that in which the phenyl rings are rotated relative to the plane of the alkyne (with its attached ring carbon atoms) in opposite directions, to produce a propeller-shaped unit, with very approximate local C₂ symmetry. This presumably minimizes interactions between ortho hydrogen atoms. In the dam complex, the tolan has very approximate C₃ symmetry and a fairly close (2.26 Å) contact between HP12 and HP16. This unusual conformation is probably another ramification of the crowding of phenyl rings around the molecule, and this same crowding might also account for the smallness of the θ angle.

In summary, the geometry of the Co₂- μ -alkyne group seems little affected by the substitution of carbonyl groups on cobalt. We are attempting to prepare carbonyl-free complexes in order to establish the extent to which this moiety is stable in the absence of good π -bonding ligands.

The 1,2-Dichloroethane. In the gas phase or in solution 1,2-dichloroethane exists as a mixture of *trans* and *gauche* forms.³⁴ The *gauche* form, which is present to 27 (5)%, reveals (by electron diffraction) a Cl-C bond length of 1.78 (1) Å and a C-C bond length of 1.48 (3) Å. The Cl-C-C angle is 110 (3)° and the torsion angle Cl-C-C-Cl is 71°.

The solvent molecule present in the dam complex crystal structure is present in the *gauche* form exclusively: the torsion angle is 78°.

The crystallographically determined geometry (Table VII) is in general agreement with the electron diffraction structure, although the accuracy is poor as a result of very large vi-

brational motion.

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Registry No. (tolan)(dmp)Co₂(CO)₄, 52659-27-5; (tolan)(dam)₂Co₂(CO)₂C₂H₄Cl₂, 62475-96-1; (tolan)Co₂(CO)₆, 14515-69-6.

Supplementary Material Available: Listings of the structure factors for both structures (28 pages). Ordering information is given on any current masthead page.

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Kinetic Studies on the Oxidation of the Thiolpentaquo chromium(III) Complex CrSH^{2+} with Fe^{3+} (and I_2) and the Reaction of Fe^{2+} with the μ -Disulfido-bis[pentaquo chromium(III)] Complex $\text{CrS}_2\text{Cr}^{4+}$

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Anaerobic oxidation of thiolpentaquo chromium(III), CrSH^{2+} , by hexaquoiron(III) at 25 °C and $I = 1.00 \text{ M}$ (LiClO_4) yields the chromium(III) products $\text{CrS}_2\text{Fe}^{3+}$ (which is assigned the formula $\text{CrS}_2\text{HFe}^{4+}$ at $[\text{H}^+] = 0.50\text{--}1.00 \text{ M}$) and $\text{CrS}_2\text{Cr}^{4+}$ with μ -disulfido (S-S) bridging ligands. Relative amounts of the two are dependent on the hydrogen ion concentration. At 25 °C with $[\text{H}^+] \geq 0.10 \text{ M}$, $\text{CrS}_2\text{HFe}^{4+}$ is the major product ($\geq 80\%$). The kinetics have been followed by monitoring formation of $\text{CrS}_2\text{HFe}^{4+}$ and $\text{CrS}_2\text{Cr}^{4+}$ at the 376-nm isosbestic for these complexes and conform to the rate law

$$\text{rate} = k_1 [\text{CrSH}^{2+}] [\text{Fe}^{3+}] [\text{H}^+]^{-1} \quad (\text{i})$$

where $k_1 = 1.50 (\pm 0.02) \times 10^{-2} \text{ s}^{-1}$ at 25 °C and $I = 1.00 \text{ M}$ (LiClO_4). The reaction of hexaquoiron(II) with $\text{CrS}_2\text{Cr}^{4+}$ also yields $\text{CrS}_2\text{HFe}^{4+}$ with a rate law

$$\text{rate} = k_2 [\text{CrS}_2\text{Cr}^{4+}] + k_3 [\text{CrS}_2\text{Cr}^{4+}] [\text{Fe}^{2+}] \quad (\text{ii})$$

where $k_2 = 9.8 (\pm 0.4) \times 10^{-5} \text{ s}^{-1}$ and $k_3 = 3.16 (\pm 0.05) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$. Oxidation of CrSH^{2+} by I_2 (with CrSH^{2+} excess) yielding $\text{CrS}_2\text{Cr}^{4+}$ as the sole product is too fast to follow by the stopped-flow method; $k_4 > 3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ with $[\text{H}^+] = 0.50 \text{ M}$ at 25 °C.

Many studies on redox reactions involving organic thiols and metal ions have been carried out.^{1,2} Little is known however about the redox behavior of simple ligands such as SH^- (or H_2S) when coordinated to a metal ion. The important complex CrSH^{2+} was first reported by Ardon and Taube in 1967.³ Further characterization together with studies of the aquation and anation (with NCS^-) have recently been reported.⁴ A communication from this laboratory on the synthesis and characterization of the μ -disulfido complexes $\text{CrS}_2\text{Cr}^{4+}$ and $\text{CrS}_2\text{HFe}^{4+}$ resulting from the I_2 and Fe(III) oxidation of CrSH^{2+} has already appeared.⁵ Iron(III) is also known to catalyze the aquation of $\text{Cr}(\text{H}_2\text{O})_5(\text{SC}_6\text{H}_4\text{NH}_3)^{3+}$.⁶ The present paper describes kinetic studies on the Fe(III) (and I_2) oxidation of CrSH^{2+} , as well as the Fe^{2+} displacement of Cr^{3+} from $\text{CrS}_2\text{Cr}^{4+}$ to give $\text{CrS}_2\text{HFe}^{4+}$.

Experimental Section

Materials. Solutions of the complex CrSH^{2+} typically ca. 0.04 M in 0.10 M HClO_4 and 0.9 M LiClO_4 were prepared as described elsewhere.^{3,4} The μ -disulfido complex $\text{CrS}_2\text{Cr}^{4+}$ was obtained by reacting I_2 with CrSH^{2+} and separating the product using a column of Sephadex SP C25.⁵ Concentrations of complex obtained were ca. $1 \times 10^{-3} \text{ M}$ in 0.1 M HClO_4 and 0.9 M LiClO_4 . Hexaquoiron(III) (G. F. Smith, Chemical Co.) was purified by elution from Amberlite IR-120(H) (BDH) cation-exchange column using 0.5 M HClO_4 , while hexaquoiron(II) perchlorate (G. F. Smith) was eluted from an air-free Dowex 50W-X8 (200–400 mesh) column using solutions of 0.1 M HClO_4 with 0.9 M LiClO_4 . Solutions of iron(II) were stored under N_2 . Lithium perchlorate was prepared from perchloric acid (Analar grade) and lithium carbonate and recrystallized until free from Cl^- and SO_4^{2-} impurities. Sephadex SP C25 resin (Pharmacia Fine

Table I. Reaction of CrSH^{2+} ($1.52 \times 10^{-2} \text{ M}$) with Fe(III) ($2.5 \times 10^{-4} \text{ M}$) at 25 °C and $I = 1.00 \text{ M}$ (LiClO_4): Yield of $\text{CrS}_2\text{Cr}^{4+}$ with Varying $[\text{H}^+]$

$[\text{H}^+]$, M	% $\text{CrS}_2\text{Cr}^{4+}$ ^a	$[\text{H}^+]$, M	% $\text{CrS}_2\text{Cr}^{4+}$ ^a
0.10	18	0.40	8
0.25	12	0.55	4

^a Percentage of total binuclear product formed.

Chemicals, 40–120 μ) was prepared for use by washing extensively with water and 0.1 M HClO_4 (3 \times resin volume) to remove any free polyelectrolytes and then equilibrating with 0.1 M HClO_4 for at least 24 h. Trapped air was removed by placing the slurry in a desiccator under vacuum.

Determination of Products Obtained from Fe(III) Oxidation of CrSH^{2+} . Because of the air sensitivity of both CrSH^{2+} and the products of the Fe(III) oxidation, isolation was performed anaerobically under N_2 . To a solution of CrSH^{2+} (ca. $2 \times 10^{-2} \text{ M}$, 3–4 mL) at $[\text{H}^+] = 0.1 \text{ M}$ and $I = 1.0 \text{ M}$ (LiClO_4) was added Fe(III) ($1.5 \times 10^{-2} \text{ M}$, 1 mL) and the mixture maintained at 25 °C for 20 min. The reaction mixture was cooled to 0 °C and passed down a deaerated Sephadex SP C25 column (18–20 cm long, 1.8-cm diameter, at 0 °C) which had been preequilibrated with 0.1 M HClO_4 . Four colored bands were observed. The first diffuse brownish green band was identified as unreacted CrSH^{2+} by its visible spectrum, peak positions 575 nm ($\epsilon 27.5 \text{ M}^{-1} \text{ cm}^{-1}$) and 435 nm ($\epsilon 43.1 \text{ M}^{-1} \text{ cm}^{-1}$).⁴ The second blue band was identified as Cr^{3+} , peak positions 575 nm ($\epsilon 13.7 \text{ M}^{-1} \text{ cm}^{-1}$) and 408 nm ($\epsilon 15.5 \text{ M}^{-1} \text{ cm}^{-1}$). The two remaining bands were both slow moving possibly because of the high charge. Washing the column first with 0.2 M HClO_4 eluted the Fe(II) product. This was identified by addition of thiocyanate and H_2O_2 which produced an