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THE STRUCTURE OF BIS[(TRI-n-BUTYLPHOSPHINE)TRICARBONYLCOBALT]

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SUMMARY

The red compound, catalytically active in the hydroformylation of olefins, which is isolated from the reaction of $Co_2(CO)_8$ with Bu_3P at elevated temperatures under CO and H_2 pressure is shown, on the basis of a three-dimensional X-ray study, to be bis[(tri-n-butylphosphine)tricarbonylcobalt], $[Co(CO)_3Bu_3P]_2$. The compound crystallizes with four molecules in space group T_h^6–$Pa3$ of the cubic system in a cell with edge 16.79(5) Å. The observed density of 1.05(5) g/cm^3 agrees tolerably with the calculated value of 0.97 g/cm^3. The structure has been solved by standard methods and refined by least-squares techniques to a conventional R factor of 0.13 for the 382 visually observed reflections. The overall molecular symmetry is D_{3d}, with a linear P–Co–Co–P bonding arrangement coincident with a threefold crystallographic axis and with a center of symmetry between the cobalt atoms. Each cobalt is situated near the center of a trigonal bipyramid, the cobalt being bound to one phosphorus atom, three carbonyl groups, and the other cobalt atom. The Co–Co bond length is 2.66(1) Å. The other bond lengths and angles in the structure have their expected values.

INTRODUCTION

Slaugh and Mullineaux[1] have recently described cobalt carbonyl complexes containing a complementary tertiary phosphine, arsine, or phosphite ligand that have catalytic properties for the hydroformylation of olefins which are considerably different from those of the conventional catalyst, dicobalt octacarbonyl. In the course of their investigations of the possible catalyst species they treated $Co_2(CO)_8$ with Bu_3P ($Bu{=}n\text{-}C_4H_9$) at elevated temperatures under CO and H_2 pressure. A red compound was isolated. This same red compound is the principal complex isolated from the recovered hydroformylation products. This material was shown, on the basis of a three-dimensional X-ray study, to be $[Co(CO)_3Bu_3P]_2$, and the results of this structure investigation are reported here.

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EXPERIMENTAL

Unit cell and collection of intensity data

The samples used in this study were kindly supplied by Slaugh and Mullineaux. Crystals were obtained by recrystallization from isooctane. The red crystals exhibit a dodecahedral and on occasions an octahedral habit. Both habits are characteristic of the cubic system. Precession and Weissenberg photographs, taken at room temperature with Mo-Kα radiation ($\lambda = 0.7107$ Å), confirm that the material is cubic with $a = 16.79(5)$ Å. The systematically extinct reflections, $0kl$, k odd; $h0l$, l odd; $hk0$, h odd, are consistent with the space group T_h^6–$Pa3$. A density of 1.05 ± 0.05 g/cm^3 was obtained with water as the pycnometric fluid. The large variation in densities observed for different crystals may be the result of varying amounts of decomposition products on the surfaces of the crystals. Such decomposition is observed, even on freshly prepared samples. The observed density is near that of 0.97 g/cm^3 calculated for four units in the cell of $[Co(CO)_3Bu_3P]_2$ as established from this study.

A crystal of dodecahedral habit, mean diameter about 0.9 mm, was selected, mounted, and sealed into an argon-filled X-ray capillary tube. Intensity data were collected at room temperature by the equi-inclination Weissenberg method for the layers $0kl$ through $14kl$. The radiation used was Zr-filtered Mo-Kα. Intensities were estimated visually and were reduced in the usual way to values of F^2, where $|F|$ is the structure amplitude. No extinction or absorption corrections were applied. (The value of $\mu \cdot R$, where μ is the linear absorption coefficient and R is the average "radius", is about 0.36, and so absorption corrections should be small.) Application of the symmetry conditions $F^2(hkl) = F^2(klh) = F^2(lhk)$ made possible the correlation of intensity data from the separate layers. The agreement among multiply observed intensities provided a basis for the estimation of the standard deviation of a given $F(hkl)^2$. Of the 715 possible independent reflections within the sphere $\lambda^{-1} \cdot \sin\theta_{Mo} \leqslant 0.52$ Å^{-1}, 382 were observed and their intensities estimated.

Solution and refinement of the structure

The three-dimensional Patterson function* was readily interpreted if a heavy scatterer, assumed to be a cobalt atom, were placed along the body diagonal of the cube, about 1.3 Å from the center of symmetry at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$. This immediately leads to a reasonable Co–Co bond length of 2.6 Å. In addition other features of the Patterson map suggested the placement of a medium scatterer, assumed to be phosphorus, on the body diagonal about 2 Å from the cobalt. This leads to the linear arrangement P–Co–Co–P and to the reasonable assumption that the red material is *trans*-bis-(phosphine)-substituted $Co_2(CO)_8$. Such a formulation is consistent with the analytical data of Slaugh and Mullineaux[1]. The observed density is consistent with the placement of four such dimers within the cell. This requires the location of 24 CO groups and 24 butyl groups. Since the order of the space group is 24, this requires

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* Programs used in this work include Zalkin's FORDAP Fourier program and the Busing-Levy least-squares and error function programs. All of these were initially written for the IBM 704 and were used with a "Compatibility Package" on the IBM 7090. A few additional calculations were made using versions of these same programs for the Northwestern CDC 6400 computer. Fig. 1 was prepared using Johnson's ORTEP thermal ellipsoid plotting program.

that only six non-hydrogen atoms be located, namely the C and O of the carbonyl group and the four C atoms of the butyl group. These atomic positions were readily found on a subsequent difference Fourier map. At this point it was virtually certain that the material was $[Co(CO)_3Bu_3P]_2$, but the proposed structure was refined by least-squares and Fourier procedures in order to provide quantitative information on the structure and to eliminate any possibility that additional atoms, for example from solvent molecules, were present.

The function minimized was $\Sigma w \cdot (|F_o|-|F_c|)^2$, where the weights, w, were taken as inversely proportional to the estimated variances of the $|F_o|$ and where for unobserved reflections w was taken as 0. The atomic scattering factors for Co, P, O, and C were taken from the usual tabulation[3]. The effects of anomalous dispersion were included in $|F_c|$[4]. The values of $\Delta f'$ and $\Delta f''$ for Co and P were taken from the calculations of Cromer[5]. Individual isotropic thermal parameters were used throughout the refinement. Subsequent difference Fourier maps gave little indication of anisotropy in the vibrations of the Co and P atoms and it was not felt that the quality of the data justified application of anisotropic thermal parameters to the light atoms. The refinement converged rapidly to values of $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ and $R_2 = [\Sigma w \cdot (|F_o|-|F_c|)^2/\Sigma w \cdot F_o^2]^{\frac{1}{2}}$ of 0.13 and 0.19, respectively. A final difference Fourier map showed peaks ranging in height from −0.6 to +0.6 e/Å^3 in general positions and one peak of height 2.4 e/Å^3 at $x = 0.04$ along the body diagonal. This latter peak is about 60% of the height of a carbon atom in this structure. If account is

TABLE 1

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (IN ELECTRONS) FOR $[Co(CO)_3Bu_3P]_2$
The entries of each column are, in order, h, k, $|F_o|$, and $|F_c|$.

••••L = 0••••			
0	0		1252
2	0	219	175
4	0	195	172
8	0	80	77
10	0	32	27
12	0	125	101
14	0	44	28
2	1	159	160
4	1	141	111
8	1	32	29
14	1	23	25
2	2	132	91
4	2	94	84
6	2	55	44
8	2	57	63
10	2	46	36
12	2	75	61
14	2	27	18
2	3	147	201
4	3	128	160
6	3	85	81
8	3	15	31
10	3	67	67
14	3	38	40
4	4	80	82
6	4	70	57
8	4	63	66
10	4	36	35
2	5	41	45
4	5	215	99
6	5	152	182
8	5	97	101
4	7	89	90
6	7	103	103
8	7	37	53
2	8	84	80
4	8	112	110
6	8	70	67
12	8	65	59
2	9	46	53
4	9	85	78
6	9	32	28
2	10	113	115
4	10	32	28
6	10	31	24
8	10	43	41
10	10	55	47
12	10	43	24
2	11	52	45
4	11	22	18
6	11	30	30
2	12	66	61
4	12	14	10
10	12	34	29
2	13	43	30
4	13	29	27
6	13	20	24
2	14	33	37
2	15	26	25
4	15	29	34
••••L = 1••••			
1	1	367	417
2	1	109	60
3	1	28	53
4	1	101	64
5	1	70	66
9	1	49	50
10	1	39	34
11	1	70	75
13	1	55	38
2	2	44	39
3	2	156	119
4	2	55	46
6	2	59	42
8	2	24	32
9	2	39	31
10	2	12	14
11	2	16	19
12	2	22	23
13	2	30	27
15	2	35	33
2	3	40	59
3	3	26	31
4	3	42	22
5	3	67	64
6	3	79	80
7	3	45	39
8	3	26	29
9	3	49	46
11	3	31	37
2	4	45	35
3	4	134	105
4	4	81	64
5	4	207	197
6	4	36	47
7	4	89	77
8	4	41	42
9	4	72	61
10	4	34	37
12	4	20	29
13	4	41	37
15	4	39	33
2	5	17	34
5	5	45	40
6	5	34	32
9	5	57	57
3	6	210	95
4	6	58	59
5	6	109	103
7	6	136	131
8	6	47	45
9	6	44	37
10	6	38	39
3	7	44	35
4	7	21	29
6	7	20	15
7	7	24	21
9	7	40	51
11	7	18	21
2	8	21	20
3	8	56	53
4	8	17	20
5	8	95	81
6	8	16	23
7	8	34	31
8	8	26	28
9	8	30	27
10	8	15	16
3	9	109	112
4	9	19	22
6	9	39	45
7	9	55	54
8	9	21	15
9	9	62	59
11	9	39	42
2	10	31	16
3	10	62	53
4	10	37	33
8	10	24	14
2	11	22	24
3	11	37	46
4	11	24	23
7	11	22	11
8	11	17	11
9	11	32	30
11	11	39	34
5	12	32	30
7	12	32	29
3	13	30	34
4	13	14	17
3	14	43	37
5	14	20	23
7	14	24	20
••••L = 2••••			
2	2	219	206
3	2	99	36
4	2	46	43
5	2	133	137
7	2	33	33
9	2	11	22
10	2	64	65
12	2	41	37
13	2	14	19
14	2	34	29
3	3	13	34
4	3	142	147
5	3	31	41
6	3	34	33
7	3	41	42
8	3	59	59
11	3	57	51
12	3	24	25
13	3	40	43
14	3	21	24
3	4	16	11
4	4	51	44
5	4	73	70
7	4	40	76
8	4	52	54
10	4	41	35
11	4	19	15
14	4	22	12
3	5	22	17
4	5	173	153
5	5	42	32
6	5	89	101
7	5	65	65
8	5	60	67
9	5	64	78
11	5	47	39
12	5	20	15
14	5	22	27
3	6	14	8
4	6	23	26
5	6	23	14
3	7	56	47
4	7	49	53
5	7	21	21
6	7	62	66
7	7	54	48
8	7	34	42
9	7	53	63
11	7	16	17
4	8	27	16
5	8	49	45
6	8	45	40
7	8	64	63
8	8	58	57
10	8	40	42
11	8	22	27
12	8	38	35
4	9	57	55
5	9	24	22
6	9	19	23
9	9	12	13
11	9	13	18
12	9	22	11
13	9	22	19
3	10	18	25
4	10	39	42
5	10	41	43
7	10	25	30
8	10	29	30
10	10	43	39
12	10	22	30
3	11	24	26
5	11	25	26
7	11	20	18
3	12	54	55
4	12	21	21
6	12	27	21
9	12	15	20
10	12	20	24
6	13	37	34
3	14	27	17
6	14	21	12
4	15	33	27
••••L = 3••••			
3	3	85	69
4	3	149	123
5	3	89	74
6	3	65	88
7	3	19	17
8	3	35	31
9	3	16	17
11	3	28	36
13	3	32	28
4	4	59	62
5	4	122	115
7	4	86	74
8	4	50	57
9	4	30	33
10	4	34	34
12	4	41	42
13	4	16	25
15	4	16	19
4	5	54	46
5	5	50	43
6	5	52	43
8	5	30	32
9	5	20	22
11	5	23	20
13	5	23	25
4	6	76	65
5	6	37	33
6	6	22	22
7	6	32	27
8	6	76	74
9	6	40	34
10	6	54	64
4	7	20	17
6	7	63	58
7	7	20	16
8	7	29	27
9	7	14	22
4	8	43	39
5	8	40	44
7	8	24	25
8	8	34	40
9	8	24	26
10	8	20	29
4	9	49	44
5	9	20	24
6	9	62	73
7	9	29	29
8	9	23	34
11	9	41	42
5	10	22	20
7	10	25	25
4	11	41	31
5	11	34	27
6	11	34	35
8	11	29	30
7	12	31	0
4	13	23	26
5	13	21	15
6	13	23	18
5	14	30	27
••••L = 4••••			
4	4	109	112
5	4	66	36
6	4	10	20
7	4	31	21
9	4	23	26
12	4	31	46
14	4	13	16
5	5	23	18
6	5	20	20
7	5	20	19
8	5	35	39
9	5	65	59
10	5	30	34
11	5	52	47
13	5	39	26
14	5	22	25
7	6	13	20
5	7	23	24
6	7	21	13
7	7	32	20
9	7	62	55
10	7	42	37
11	7	40	42
13	7	23	24
5	8	20	32
7	8	47	51
9	8	15	17
10	8	14	12
12	8	16	30
5	9	34	31
7	9	16	12
11	9	17	19
5	10	63	63
7	10	50	59
9	10	16	23
10	10	21	18
6	11	27	30
5	12	36	30
7	12	29	35
8	12	20	30
6	13	20	23
••••L = 5••••			
5	14	24	11
5	5	60	56
10	5	29	24
13	5	21	16
7	6	24	29
9	6	34	34
10	6	41	30
11	6	32	23
12	6	43	36
5	7	32	32
7	7	40	12
8	7	32	33
6	8	20	29
10	8	20	35
12	8	30	27
6	9	39	36
7	9	16	16
8	9	39	37
10	9	21	21
7	10	25	24
8	10	23	22
6	11	67	65
8	11	30	36
6	13	49	48
••••L = 6••••			
6	6	24	26
7	6	21	14
9	7	24	23
11	7	31	44
13	7	33	35
7	8	26	23
8	8	12	0
9	8	30	37
6	9	36	34
7	9	33	33
6	10	32	44
7	11	42	24
••••L = 7••••			
7	7	32	29
8	7	44	40
9	7	12	5
10	7	43	46
11	7	20	14
8	8	21	23
10	8	27	32
8	9	41	37
8	10	16	25
8	11	27	30
••••L = 8••••			
8	8	21	24

TABLE 2

FINAL PARAMETERS FOR $[Co(CO)_3Bu_3P]_2$

Atom	x	y	z	B (Å^2)
Co	0.45418(20)[a]	x	x	4.84(19)
P	0.37930(41)	x	x	5.51(32)
C (of CO)	0.5120(18)	0.3728(19)	0.4849(18)	7.0(7)
O (of CO)	0.5486(15)	0.3211(15)	0.5067(15)	9.5(6)
C_1	0.4197(21)	0.3494(22)	0.2834(22)	9.3(9)
C_2	0.5042(21)	0.3148(20)	0.2877(21)	8.5(8)
C_3	0.5282(22)	0.2840(23)	0.2022(23)	9.7(9)
C_4	0.6115(26)	0.2475(25)	0.2016(28)	12.2(1.2)

[a] Numbers in parentheses here and in subsequent tables are estimated standard deviations in the least significant digits.

TABLE 3

PRINCIPAL INTERATOMIC DISTANCES AND ANGLES

Distances (Å)		Angles (°)	
Co–P	2.178(15)	Co–Co–P	180(0)
Co–C	1.753(33)	Co–C–O	178(3)
Co–O	2.878(28)	C–Co–P	92.3(1.0)
P–C_1	1.818(37)	Co–P–C_1	117(1)
C_1–C_2	1.53(4)	P–C_1–C_2	114(3)
C_2–C_3	1.58(5)	C_1–C_2–C_3	108(3)
C_3–C_4	1.53(5)	C_2–C_3–C_4	112(3)
C–O	1.12(3)		
Co–Co	2.665(14)	C_1–P–C_1'	101(1)

taken of the expected increased electron density at special positions in the cell, then this peak has a height about twice background, and no significance need be attached to it*. In view of the large thermal motion of the butyl group, no attempt was made to locate the hydrogen atoms in this difference Fourier map. Consequently, the contributions of hydrogen atoms to the structure factors were not taken into account. This fact, along with the high symmetry, probably accounts for large discrepancies between $|F_o|$ and $|F_c|$ for a few low-angle reflections.

Table 1 lists the final values of $|F_o|$ and $|F_c|$ (in electrons) for the 383 observed intensities. Table 2 lists the final structure parameters, along with standard deviations of these parameters as estimated from the inverse matrix. Table 3 lists principal interatomic distances and angles, along with their associated standard deviations.

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* The detection of possibly occluded solvent molecules does not seem feasible from the present X-ray data. The presence of such molecules is certainly consistent with the high observed density. Yet the amount of possibly occluded solvent appears to be small. Freshly crystallized material was lightly dried and was then analyzed for any isooctane solvent that might have been present. An upper limit of 4 wt.% was set by mass-spectrometric analysis. This corresponds to an upper limit of 1 molecule of isooctane per 4 molecules of the dimer.

DESCRIPTION OF THE STRUCTURE

Figure 1 displays the molecular structure and the principal interatomic distances and angles. Each cobalt atom is bonded to one phosphorus atom, to three carbonyl groups, and to another cobalt atom. A given cobalt atom may be considered to be situated near the center of a trigonal bipyramid. Bond lengths and angles in this compound appear to be normal, within the estimated standard deviations. For example, the Co–P distance of 2.18(2) Å compares favorably with Co–P distances of 2.17 to 2.22 Å in $CoH(N_2)(PPh_3)_3$[6]; similarly, the Co–C distance of 1.75(3) Å compares well with those of 1.75 to 1.79 Å in $Co(SiCl_3)_4(CO)_4$[7]. In both of these structures the Co is near the center of a trigonal bipyramid. The Bu_3P group in the present compound has its expected geometry. In addition, all intermolecular contacts (neglecting hydrogen atoms) appear to be normal and all are greater than about 3.8 Å.

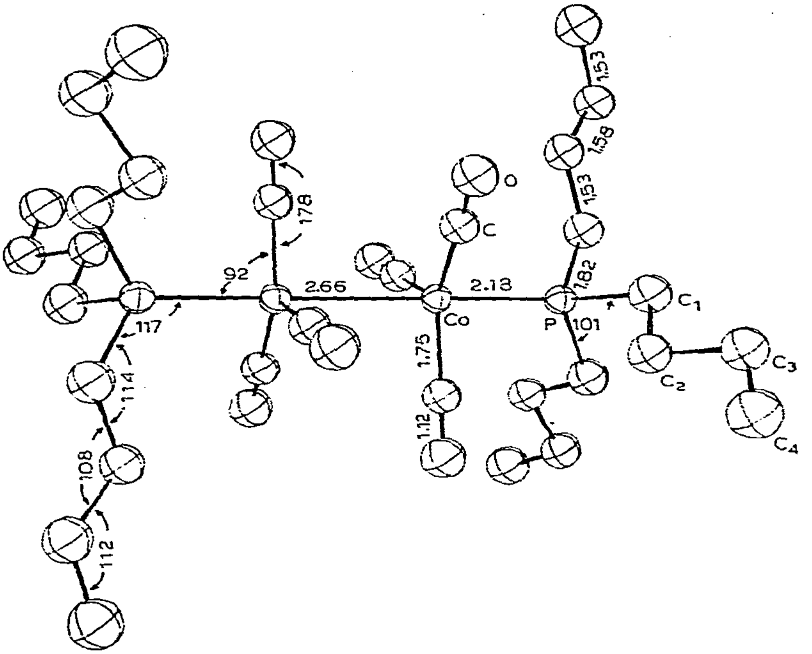

Fig. 1. A perspective drawing of one molecule of $[Co(CO)_3Bu_3P]_2$. The P–Co–Co–P axis is a threefold axis and there is a center of symmetry midway between the Co atoms. The sizes of the various spheres provide an indication of the relative thermal motions of the atoms.

The most interesting feature of the present structure is the presence of a metal–metal bond. The parent complex, $Co_2(CO)_8$, contains two carbonyl bridges and has a Co–Co interaction of 2.52 Å[8]. However, it is known[9] that this carbonyl-bridged form of $Co_2(CO)_8$ is in rapid equilibrium in solution with the species containing a metal–metal bond. The stabilization of the metal–metal bonded species upon substitution of phosphine for carbonyl may be significant, especially for the hydroformylation reaction. However, equilibrium studies in solution would be necessary to establish this, since the solids precipitated from the solutions of both the parent and the phosphine substituted product are those that are least soluble and not necessarily those that are present in highest proportion.

The Co–Co bond length of 2.66(1) Å in the present structure exceeds somewhat those Co–Co interactions in neutral species tabulated by Lewis[10]. It is, of course, shorter than the Co–Co bond in highly charged species, such as the $Co_2(CNCH_3)_{10}^{4+}$ ion[11]. It is interesting that the Mn–Mn bond length in Et_3P–$(CO)_4Mn$–$Mn(CO)_4$–PEt_3, the *trans*-Et_3P substitution product of $Mn_2(CO)_{10}$, does not differ significantly from that in $Mn_2(CO)_{10}$ itself[12]. On this basis it is probable that the Co–Co bond length in the present species is near to that of the metal–metal bonded species of $Co_2(CO)_8$. Half the Mn–Mn bond distance in $Mn_2(CO)_{10}$, 1.46 Å, has been taken as an appropriate single bond radius for the Mn atom[13]. Accordingly, half the present Co–Co bond length, namely 1.33 Å, may be an appropriate single bond radius for the Co atom in transition metal complexes.

Compounds of the type $Co_2(CO)_6(PR_3)_2$ were previously prepared by Hieber and Freyer[14] and their spectra were analyzed by Vohler[15]. Vohler correctly concluded that these compounds do not contain carbonyl bridges, but rather contain metal–metal bonds. He suggested that the overall symmetry of the complexes was either D_{3h} (carbonyl groups eclipsed) or D_{3d} (carbonyl groups staggered). In the present compound, the P–Co–Co–P axis is a threefold axis and the presence of a center of symmetry between the two cobalt atoms imparts symmetry D_{3d} to the molecules.

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