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$Co_8(CO)_{24}C_6$, A BIS(TRICOBALT NONACARBONYL)/DICOBALT HEXACARBONYL DERIVATIVE OF 2,4-HEXADIYNE FROM THE REACTION OF DICOBALT OCTACARBONYL WITH HEXACHLOROCYCLOPROPANE

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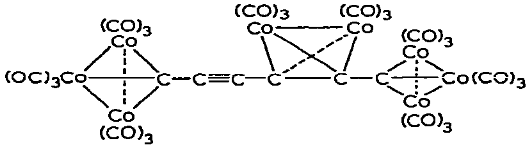
SUMMARY

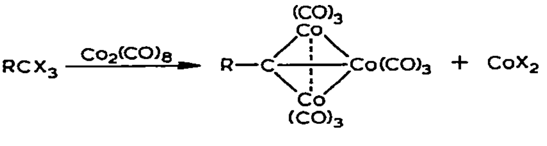
The reaction of dicobalt octacarbonyl with hexachlorocyclopropane in THF produced $Co_8(CO)_{24}C_6$ whose structure (A) was determined by means of single crystal X-ray crystallography.



(A)

The compound is obtained from hexane/benzene as black $Co_8(CO)_{24}C_6 \cdot \frac{1}{2}C_6H_6$, crystallising in the triclinic space group $P\bar{1}$ with $a = 15.57 \pm 0.02$ Å, $b = 16.32 \pm 0.02$ Å, $c = 9.77 \pm 0.01$ Å, $\alpha = 99.78 \pm 0.10°$, $\beta = 115.06 \pm 0.10°$, $\gamma = 74.39 \pm 0.10°$. The final discrepancy index is $R_F = 10.2\%$ for 2484 independent, nonzero reflections.

The dehalogenation of organic trihalides by dicobalt octacarbonyl yields novel methylidynetricobalt nonacarbonyl cluster compounds (eqn. 1)[1-3]. Recent



(1)

interest in halogenated cyclopropanes[4] led us to examine the possible dechlorination of hexachlorocyclopropane by dicobalt octacarbonyl.

In the reaction studied, 41 mmoles each of the reactants were mixed in tetra-

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* Fellow of the Alfred P. Sloan Foundation, 1968–1970.

hydrofuran (THF) solution under nitrogen. Carbon monoxide was given off slowly at room temperature; heating to 40° caused vigorous gas evolution. Work-up of the reaction mixture gave hexachlorocyclopropane (36% recovery), cobalt(II) chloride and 1.85 g of brown black crystals, (I), m.p. 132–133° (dec.), as well as 2.5 g of a brown powder (II) which was insoluble in THF and hexane.

Further attention is focussed on Compound(I). This material is soluble in THF and hot hexane; it is stable in air for periods up to a day but slowly decomposes on continued exposure to air. It was recovered unchanged after treatment with methanolic sulfuric acid (18 h at room temperature, 5 h at 60°). It contains no chlorine or hydrogen; analysis for carbon and cobalt indicated an empirical formula $C_3Co_4(CO)_{12}$, if one assumed that oxygen was the only other element present and that it was present solely in the form of C≡O groups. Experimental molecular weights were variable and uninformative. Spectral data also were not particularly helpful. Fig. 1 shows the infrared spectrum of (I) in the carbonyl region (0.5% solution in carbon tetrachloride; Perkin Elmer 521 spectrophotometer; ±0.5 cm^{-1} resolution). One can distinguish bands at 2096.8 (s), 2084.0 (s), 2069.0 (vs), 2062.0 (s), 2057.3 (s), 2051.0 (sh) 2040.8 (s), 2033.0 (s), 2014 (w) and 1981 (vw) cm^{-1}. Additional bands (in carbon disulfide) were observed at 1212 (vw), 1067 (vw) and 755 (m). In the ultraviolet spectrum (in benzene) λ_{max} was observed at 428 mμ, with ε being concentration dependent.

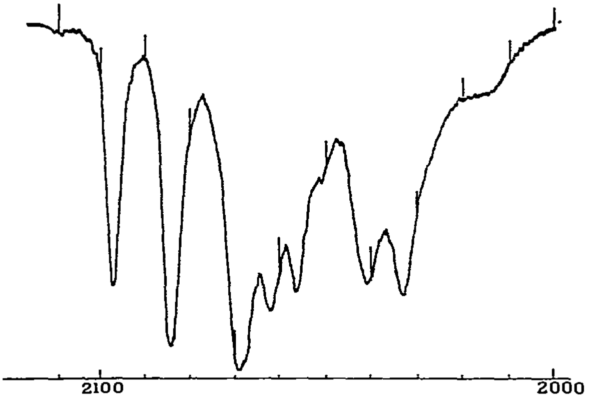

Fig. 1. The carbonyl region of the infrared spectrum of $Co_8(CO)_{24}C_6$ (0.5% in carbon tetrachloride).

Since the large number of CO frequencies in the infrared spectrum of (I) suggested that it was a rather complicated molecule, definitive structural information was sought by means of a single crystal X-ray analysis.

RESULTS OF THE STRUCTURAL STUDY

Unit cell and space group

The complex was isolated from hexane/benzene as a black-brown crystalline product, as needles by slow crystallization or as platelets when recrystallization proceeded rapidly. The two forms have the same unit cell dimensions and are crystallographically identical.

Optical and X-ray examination showed the crystals to be triclinic, belonging to either of the space groups $P1$ (C_1^1; no. 1) or $P\bar{1}$ (C_i^1; no. 2). The centrosymmetric $P\bar{1}$ was shown to be the correct space group from a plot of the intensity distribution[5] as a function of sin θ.

Unit cell dimensions are:

$$a = 15.57 \pm 0.02\ \text{Å};\ b = 16.32 \pm 0.02\ \text{Å};\ c = 9.77 \pm 0.01\ \text{Å}$$
$$\alpha = 99.78 \pm 0.10°;\ \beta = 115.06 \pm 0.10°;\ \gamma = 74.39 \pm 0.10°.$$

The unit cell volume is 2161 Å^3. The observed density ($\rho_{\text{obs}} = 1.95 \pm 0.02$ g·cm^{-3}) was only in fair agreement with that calculated for $Co_8(CO)_{24}C_6$ ($\rho_{\text{calc}} = 1.868$ g·cm^{-3} for $M = 1215.90$, $Z = 2$). However, solution of the crystal structure, *vide infra*, revealed the presence of one benzene molecule of crystallization per unit cell. The density calculated for $Co_8(CO)_{24}C_6 \cdot \frac{1}{2}C_6H_6$ ($\rho_{\text{calc}} = 1.928$ g·cm^{-3} for $M = 1254.96$ and $Z = 2$) is in excellent agreement with the observed value.

A Delaunay reduction[6] shows dimensions of the reduced cell to be:

$$a' = 14.46 \pm 0.02\ \text{Å};\ b' = 9.77 \pm 0.01\ \text{Å};\ c' = 19.29 \pm 0.02\ \text{Å};$$
$$\alpha' = 101.43 \pm 0.10°;\ \beta' = 119.35 \pm 0.10°;\ \gamma' = 102.68 \pm 0.10°.$$

The non-reduced cell is, however, used throughout this paper.

Collection and reduction of diffraction data

Two crystals were used for data collection. Crystal 1 (volume 9.5×10^{-6} cm^3) was mounted on its *b*-axis and crystal 2 (volume 1.3×10^{-6} cm^3) was mounted on its *c*-axis.

TABLE 1

RESULTS FOR THE PHASE PYRAMIDS

Set No.	Signs applied to reflections				Mode 1[a]				Mode 2[a]			
	$5\,2\,2$	$3\,\bar{5}\,2$	$4\,\bar{6}\,3$	$\bar{3}\,2\,3$	No. cycles	C	+ signs	− signs	No. cycles	C	+ signs	− signs
1	+	+	+	+	13	1.000	180	0	2	1.000	180	0
2	+	+	+	−	13	0.995	82	98	2	0.995	82	98
3	+	+	−	+	16	0.957	96	84	3	0.949	86	94
4	+	+	−	−	17	0.814	104	76	3	0.954	100	80
5	+	−	+	+	17	0.798	88	92	4	0.821	94	86
6	+	−	+	−	17	0.793	86	94	4	0.816	90	90
7	+	−	−	+	15	0.824	80	100	3	0.810	82	98
8	+	−	−	−	16	0.817	84	96	3	0.815	82	98
9	−	+	+	+	16	0.953	86	94	3	0.940	92	88
10	−	+	+	−	17	0.938	92	88	3	0.945	104	76
11	−	+	−	+	13	0.991	86	94	2	0.991	86	94
12	−	+	−	−	13	0.986	106	74	2	0.986	106	74
13	−	−	+	+	15	0.828	95	85	3	0.819	94	86
14	−	−	+	−	16	0.821	84	96	3	0.824	84	96
15	−	−	−	+	17	0.804	91	89	5	0.825	92	88
16	−	−	−	−	16	0.799	93	87	5	0.820	90	90

[a] In mode 1 no new signs are applied until the subsequent cycle. In Mode 2, newly determined signs are applied immediately.

(Continued p. 243)

TABLE 2

OBSERVED AND CALCULATED STRUCTURE FACTOR AMPLITUDES FOR $Co_8(CO)_{24}C_6 \cdot \frac{1}{2}C_6H_6$ (IN ELECTRONS × 5.00)

K	L	FO	FC
***************			
H = -15			
0	5	377	365
***************			
H = -14			
0	1	325	390
0	2	271	313
0	6	331	347
1	1	324	351
1	2	322	402
1	3	358	473
1	4	316	331
1	6	288	233
2	2	504	481
2	4	246	263
3	3	494	429
***************			
H = -13			
0	3	346	357
1	1	420	427
1	5	263	290
2	5	328	332
3	1	295	359
3	3	292	356
3	4	361	313
3	5	241	239
3	6	312	362
4	4	655	602
4	5	337	331
***************			
H = -12			
0	1	335	281
0	2	450	400
0	3	594	647
0	4	369	303
0	5	281	278
0	6	226	239
0	7	292	320
1	1	845	973
1	4	706	689
1	5	355	434
1	6	570	542
1	8	237	212
2	1	599	656
2	2	300	305
2	5	737	732
2	7	615	564
3	1	212	182
3	2	562	446
3	3	307	392
3	4	321	286
3	5	461	426
3	6	394	331
4	1	242	176
4	4	213	180
4	6	377	404
5	5	362	408
5	6	554	437
6	2	394	381

K	L	FC	FC
2	2	513	485
2	3	447	495
2	5	232	172
2	8	467	223
3	2	489	507
3	3	413	433
3	4	1026	1030
3	7	369	180
4	1	331	268
4	2	408	354
4	4	436	319
4	5	305	210
4	6	352	294
5	2	369	283
5	4	561	493
5	6	628	591
5	7	412	350
5	8	455	437
6	3	315	303
6	4	381	438
7	1	274	237
7	6	471	496
8	1	390	446
9	1	285	327
9	3	364	263
9	4	610	603
***************			
H = -8			
0	1	994	1075
0	2	811	808
0	3	370	317
0	4	327	323
0	5	220	168
0	6	1127	1115
0	7	807	772
0	9	324	355
1	2	458	469
1	3	290	344
1	4	324	371
1	5	845	839
1	6	278	253
1	7	623	577
1	8	367	315
2	2	264	237
2	3	253	143
2	4	572	570
2	5	284	146
2	6	659	623
2	7	681	627
3	1	259	188
3	2	403	440
3	8	349	396
4	2	458	497
4	3	286	283
4	5	314	247
4	7	613	667
5	1	337	375
5	2	799	818
5	3	554	537
5	8	595	617
6	1	233	286
6	2	737	644
6	3	1111	1044
6	5	367	260
7	1	405	388
7	2	578	540
7	3	292	234
7	4	412	395

K	L	FO	FC
2	4	414	417
2	5	268	226
2	7	327	288
2	8	393	410
3	1	253	294
3	2	416	429
3	3	969	1015
3	4	319	251
3	5	599	642
3	6	254	177
3	7	315	276
4	1	365	430
4	2	769	838
4	3	744	740
4	4	304	277
4	6	494	447
5	1	431	385
5	2	883	834
5	3	472	476
5	7	946	1018
5	8	273	145
6	1	253	210
6	2	790	792
6	3	577	596
6	5	395	358
6	6	846	880
6	8	394	450
7	1	921	1073
7	2	413	438
7	3	601	596
7	6	409	261
7	7	651	743
8	2	1087	1066
8	3	497	438
8	4	501	475
8	7	492	470
9	4	321	366
9	5	565	449
9	6	445	353
10	1	288	285
10	3	298	275
11	3	272	289
11	4	451	401
12	1	253	294
***************			
H = -5			
0	1	767	806
0	2	1404	1247
0	3	740	696
0	4	1656	1443
0	5	294	114
0	6	908	889
0	7	526	527
0	8	201	196
1	2	1287	1174
1	3	342	247
1	4	1087	930
1	5	1051	1015
1	6	591	536
1	9	330	375
2	1	358	389
2	2	275	281
2	3	707	650
2	4	1709	1575
2	6	290	234
2	8	250	350
3	2	635	676
3	5	1027	1013

K	L	FO	FC
9	3	376	377
9	4	347	148
9	6	437	449
10	1	423	487
11	3	729	684
12	2	637	510
12	4	652	577
13	3	706	682
14	1	222	283
***************			
H = -3			
0	4	1223	1136
0	5	568	554
0	9	430	500
1	2	702	640
1	3	531	456
1	4	336	209
1	5	594	579
1	6	312	315
1	8	483	584
1	9	394	375
2	1	813	808
2	2	342	300
2	3	2415	2262
2	4	564	509
2	5	197	206
2	7	·258	120
3	2	209	116
3	3	485	447
3	4	2035	1847
3	5	586	566
3	6	350	218
4	1	254	262
4	2	467	498
4	3	908	805
4	4	319	311
4	5	723	754
4	6	610	598
4	7	516	518
4	8	407	494
5	1	700	617
5	2	344	327
5	4	789	747
5	5	307	265
5	7	395	390
5	8	359	408
6	2	840	794
6	4	823	478
6	5	516	316
6	7	374	413
6	8	354	333
7	1	581	615
7	2	690	692
7	8	465	368
8	1	548	716
8	2	808	837
8	4	307	226
9	1	545	666
9	4	500	531
10	1	383	431
10	4	418	349
10	5	490	506
11	1	285	197
11	4	393	371
13	1	273	326
13	4	276	277
14	1	430	512
14	3	311	284

K	L	FO	FC
3	3	1291	1069
3	4	1340	1110
3	6	349	387
3	7	476	401
3	8	313	387
4	1	556	507
4	2	1830	1510
4	4	945	871
4	5	322	403
4	8	609	699
5	1	1147	1026
5	2	627	529
5	3	1558	1485
5	4	477	412
5	5	358	340
5	8	485	540
6	2	316	222
6	3	494	555
6	5	831	921
6	6	665	657
7	4	651	667
7	6	394	458
7	7	434	578
8	1	210	155
8	2	644	634
8	5	1282	1259
9	4	451	432
9	6	343	398
10	1	690	602
10	3	364	344
10	4	744	682
11	1	332	248
11	2	387	386
11	3	460	480
11	4	559	558
12	1	309	349
12	3	397	415
12	4	320	398
12	5	311	263
13	2	272	339
13	4	382	372
14	1	268	332
15	1	316	237
***************			
H = 0			
0	2	604	606
0	3	410	325
0	5	698	724
0	6	1060	1053
0	8	316	279
1	-7	507	517
1	-5	1849	1718
1	-4	738	632
1	-3	223	130
1	-2	633	533
1	4	1496	1320
1	6	726	679
2	-7	265	287
2	-6	1196	1255
2	-4	543	474
2	-3	965	563
2	-2	761	954
2	2	255	208
2	3	1246	1069
2	4	1472	1341
2	5	1027	1025
3	-8	417	419
3	-5	654	845

K	L	FO	FC
H = 1			
-15	1	256	227
-14	2	312	331
-13	0	329	341
-13	1	302	339
-13	2	306	261
-12	1	335	378
-12	2	666	671
-12	4	420	385
-12	5	522	435
-11	0	388	351
-11	1	599	567
-11	4	440	519
-11	6	475	545
-10	0	396	291
-10	1	833	941
-10	2	691	814
-10	4	486	408
-10	5	925	822
-10	6	387	431
-9	0	1144	1143
-9	2	928	987
-9	3	316	293
-9	4	252	193
-9	5	317	284
-9	6	564	804
-8	0	816	769
-8	1	1314	1438
-8	2	944	851
-8	3	800	798
-8	6	686	852
-7	1	403	484
-7	2	417	324
-7	8	288	296
-7	4	850	795
-6	0	453	421
-6	1	424	499
-6	2	1365	1311
-6	3	426	478
-6	5	624	604
-5	0	338	411
-5	2	339	356
-5	3	1425	1279
-5	4	728	752
-5	5	438	433
-5	6	699	682
-4	0	822	803
-4	1	945	1031
-4	2	545	828
-4	3	722	855
-4	5	505	479
-4	6	856	782
-4	7	606	628
-3	1	1297	1470
-3	2	2541	2807
-3	3	1008	865
-3	4	229	118
-3	5	541	838
-3	6	1055	1069
-3	7	1010	1042
-2	2	1812	1601
-2	3	930	879
-2	4	1240	1356
-2	6	628	879
-2	7	298	318
-2	8	228	298
-1	2	564	474
-1	3	477	511
-1	4	746	705
-1	5	1016	1040

K	L	FO	FC
8	-1	997	1135
8	0	642	491
8	1	527	629
8	4	1816	1753
8	6	312	234
9	-6	733	744
9	-5	691	667
9	-4	559	560
9	-2	235	194
9	-1	805	954
9	0	875	869
9	2	413	381
9	3	707	677
9	4	293	267
10	-7	341	410
10	-6	444	389
10	-4	661	663
10	-3	514	463
10	-2	1012	984
10	-1	311	129
10	0	773	657
10	2	367	336
10	3	406	343
10	4	1221	1118
11	-5	288	134
11	-3	249	359
11	-2	502	457
11	-1	1168	1285
11	2	258	123
11	3	316	378
11	4	385	361
12	-6	673	614
12	-2	559	451
12	0	217	303
12	2	367	380
13	-1	359	343
13	1	250	190
13	3	535	566
14	-4	292	289
14	1	366	368
15	2	312	334
***************			
H = 2			
-14	3	495	475
-13	1	315	281
-13	3	344	376
-12	0	226	175
-12	1	445	475
-12	2	682	730
-11	0	261	297
-11	1	536	639
-11	2	991	983
-11	3	712	685
-10	0	314	319
-10	1	244	257
-10	2	370	367
-10	3	485	496
-9	0	696	758
-9	1	220	130
-9	2	490	502
-8	1	244	269
-8	2	586	631
-8	3	636	562
-7	3	909	815
-7	4	910	800
-6	0	1066	1025
-6	1	434	447
-6	3	279	245

K	L	FO	FC
5	-3	226	352
5	0	2435	2373
5	1	1641	1789
5	2	321	252
5	3	757	713
5	4	746	730
5	6	543	522
6	-7	328	410
6	-6	2041	1796
6	-2	695	658
6	-1	512	447
6	0	1369	1377
6	1	1063	1111
6	2	1408	1418
6	3	312	263
6	4	371	338
6	6	430	443
7	-5	261	232
7	-4	530	435
7	-3	1982	1961
7	-2	1133	1044
7	0	1316	1351
7	1	406	479
7	3	344	343
7	6	509	497
8	-8	405	396
8	-6	453	470
8	-5	304	322
8	-4	675	550
8	-3	265	141
8	-2	538	488
8	0	885	790
8	1	1102	1170
8	2	445	414
8	3	392	255
8	6	547	511
9	-5	689	597
9	-3	330	368
9	-2	367	411
9	-1	306	197
9	0	898	973
9	1	990	1055
9	3	519	563
10	-5	515	495
10	-4	655	403
10	-3	245	233
10	-2	421	391
10	-1	219	130
10	1	461	594
10	3	472	450
10	4	486	428
11	-6	373	438
11	-5	638	565
11	-4	431	289
11	-1	709	804
11	0	364	411
11	2	427	470
11	5	281	331
12	-5	523	442
12	-3	691	707
12	-1	455	403
12	0	348	385
12	2	549	527
12	3	256	290
13	-3	507	570
13	1	353	317
13	3	421	363
14	-2	527	519
15	-3	299	259
15	0	218	159

K	L	FO	FC
4	-5	465	472
4	-4	178	163
4	-3	398	381
4	-2	1361	1155
4	-1	266	259
4	0	808	759
4	1	435	363
4	2	272	310
4	3	1668	1672
4	4	430	420
4	5	604	465
4	7	582	565
5	-8	492	478
5	-7	296	342
5	-6	325	309
5	-5	381	351
5	-4	219	138
5	-2	483	458
5	-1	827	940
5	1	286	276
5	3	336	276
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(Continued next page)

TABLE 2 (*Continued*)

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12	-2	271	301
12	0	486	546
13	-6	494	512
13	-5	307	285
13	-1	278	309
13	0	329	446
14	-5	568	587
14	-3	355	206
15	-3	351	285
H = 10			
-6	2	436	387
-4	0	232	174
-4	1	277	120
-4	3	206	226
-3	0	445	437
-3	1	232	282
-3	2	229	218
-3	3	363	447
-1	0	1284	1328
-1	1	550	638
-1	2	263	267
-1	3	456	472
0	0	519	508
0	1	334	397
0	4	444	428
1	-9	251	177
1	-7	532	483
1	-6	1132	1213
1	-5	387	434
1	-4	245	228
1	-3	360	312
1	-2	501	507
1	-1	420	506
1	0	681	694
1	1	523	450
1	3	343	272
1	4	409	360
2	-7	279	232
2	-6	320	273
2	-5	281	167
2	-4	403	388
2	-3	295	322
2	-2	772	813
2	-1	597	602
2	0	329	303
2	2	216	207
2	3	447	457
3	-9	219	328
3	-7	312	309
3	-4	312	233
3	-3	254	237
3	-2	1069	1125
3	-1	410	622
3	4	319	343
4	-7	272	277
4	-6	319	345
4	-5	212	191
4	-4	212	191
4	-3	212	261
4	-2	331	381
4	-1	560	583
4	0	758	162
4	2	304	309
5	-5	1044	921
5	-4	631	614
5	-3	605	635
5	-2	493	383
5	0	617	666
5	2	210	357
6	-7	422	427
6	-5	838	789
6	-4	412	324
6	-3	390	355
6	1	723	747
6	2	548	552
6	3	556	525
7	-6	300	198
7	-3	582	595
7	-2	305	292
7	-1	218	310
7	0	680	701
7	1	312	330
7	2	265	209
8	-8	555	527
8	-6	321	196
8	-5	493	471
8	-4	781	710
8	-3	711	685
8	1	370	380
8	2	210	272
8	3	426	381
9	-7	496	478
9	-4	347	376
9	-3	438	443
9	-2	630	574
9	1	470	481
10	-8	597	571
10	-7	328	254
10	-6	301	308
10	-4	416	308
10	-3	1078	1006
10	-1	227	200
10	0	303	481
10	1	265	269
10	2	343	337
11	-8	366	624
11	-5	686	617
11	-3	502	484
11	-2	389	387
11	-1	269	218
11	1	669	743
11	2	297	275
12	-4	672	643
12	-2	363	361
12	1	513	617
13	-1	448	486
H = 11			
-4	0	225	283
-3	0	568	628
-1	0	540	376
-1	1	266	125
-1	3	242	257
0	2	317	269
0	3	296	297
1	-9	278	201
1	-7	390	470
1	-6	218	292
1	-4	452	406
1	0	522	471
1	1	356	351
1	2	451	447
2	-8	658	788
2	-7	219	139
2	-6	333	308
2	-5	594	560
2	-4	667	630
2	-3	865	847
2	-2	347	331
2	-1	261	105
2	2	392	374
2	3	495	501
3	-8	298	332
3	-6	856	855
3	-3	707	628
3	-2	458	531
3	1	566	536
4	-7	395	419
4	-6	555	574
4	-5	535	574
4	-4	718	747
4	-3	263	201
4	0	360	377
4	1	524	595
4	2	316	331
5	-7	364	204
5	-4	273	217
5	-1	686	769
5	2	596	580
6	-8	375	456
6	-6	371	293
6	-5	371	189
6	-4	649	544
6	-2	885	824
6	0	440	452
6	2	285	264
7	-8	278	187
7	-7	1081	1181
7	-3	270	356
7	-1	662	696
8	-8	311	389
8	-6	762	748
8	-4	712	703
8	-3	601	653
8	2	543	492
9	-7	615	675
9	-6	327	381
9	-5	281	211
9	-3	904	774
9	-2	698	663
10	-7	329	386
10	-5	335	156
10	-3	465	469
10	-2	667	702
10	-1	219	286
10	0	275	187
11	-6	513	472
11	-5	328	274
11	-3	676	704
11	-1	272	205
13	-1	384	502
14	-3	306	307
H = 12			
-3	0	336	375
-1	1	243	281
-1	2	180	422
0	0	269	247
1	-7	378	551
1	-6	318	263
1	-5	438	446
1	-4	382	363
1	-2	491	550
1	-1	595	618
1	0	450	371
1	2	311	366
2	-6	225	182
2	-5	271	248
2	-4	511	535
2	-3	540	614
2	-1	248	195
3	-7	447	497
3	-6	341	317
3	-3	374	271
3	-1	507	472
3	0	336	229
4	-8	218	257
4	-6	219	287
4	-5	263	207
4	-4	287	270
4	-3	527	543
4	-2	633	626
4	-1	451	499
4	0	568	499
4	1	290	356
5	-6	412	388
5	-4	579	632
5	-3	532	530
5	-1	246	216
5	0	429	407
6	-8	305	276
6	-6	450	352
6	-5	490	440
6	-3	718	721
6	-2	754	718
6	0	619	576
7	-4	400	404
7	-2	339	351
8	-8	342	504
8	-5	341	276
8	-4	318	258
8	-2	471	485
9	-3	398	421
9	-1	256	261
10	-4	822	836
11	-3	613	615
11	0	416	458
12	-4	279	176
12	-3	287	268
12	-1	220	259
13	-5	331	269
13	-4	332	309
13	-2	297	180
H = 13			
-2	0	693	785
-1	1	386	394
0	0	391	451
1	-8	353	454
1	-5	280	297
1	-4	271	278
1	-3	265	208
2	-3	263	225
2	-2	236	225
2	-1	228	105
3	-8	395	473
3	-4	311	233
3	-3	435	492
3	-2	355	417
3	-1	394	440
4	-7	269	266
4	-6	236	207
4	-3	260	231
4	-1	267	248
5	-6	581	609
5	-1	235	268
6	-7	370	306
6	-3	361	212
6	-1	260	249
7	-3	252	267
7	-2	702	643
7	0	254	258
8	-7	485	480
8	-6	266	168
8	-3	395	318
8	-2	413	476
8	-1	401	478
9	-3	381	401
9	-2	419	335
9	0	273	281
10	-7	330	400
10	-2	464	470
11	-3	411	427
12	-4	312	250
12	-3	310	348
H = 14			
1	-7	213	289
1	-2	344	329
1	0	269	201
2	-8	417	482
3	-8	332	371
3	-4	379	312
3	-2	288	286
4	-7	311	328
4	-5	645	651
4	-4	219	218
4	-1	389	499
5	-4	286	219
5	-2	297	306
5	0	331	359
6	-4	470	813
6	-3	255	278
6	-1	555	629
6	0	245	286
7	-6	326	391
7	-5	503	394
7	-3	276	188
8	-3	318	360
9	-4	335	321
10	-5	408	331
10	-2	256	163
11	-5	275	148
11	-4	672	663
H = 15			
1	-4	313	347
1	-3	229	250
2	-5	221	208
2	-2	223	212
3	-8	343	315
3	-4	342	316
4	-4	221	220
4	-2	258	215
5	-2	407	446
7	-6	376	241
7	-5	322	211
8	-4	359	247

Diffraction data were collected with a 0.01°-incrementing Supper-Pace 'Buerger Automated Diffractometer' using a stationary-background, ω-scan, stationary-background counting sequence. The scan angle was chosen as $\omega = [1.5 + (0.7/L)]°$, where $1/L$ is the Lorentz factor. Other experimental details have been described fully in a previous publication[7].

Using equi-inclination Weissenberg geometry and Mo-$K\alpha$ radiation ($\bar{\lambda} = 0.7107$ Å), data for the zones $h(0\text{–}4)l$ were collected from crystal 1 and data for the zones $hk(0\text{–}8)$ were collected from crystal 2. (Data within each zone is complete to $\sin\theta = 0.38$, save for the few reflections with $\theta < 4°$ which are shielded from the counter by a Pb backstop.]

The standard deviation assigned to a reflection hkl, of intensity $I(hkl)$ was:

$$I(hkl) \geqslant 4900,\ \sigma[I(hkl)] = 0.1\ [I(hkl)]$$
$$I(hkl) < 4900,\ \sigma[I(hkl)] = 7.0\ [I(hkl)]^{\frac{1}{2}}$$

Reflections were omitted from the subsequent analysis if their net intensities were less than 3σ above background.

All data were corrected for Lorentz, polarization and absorption effects using a locally-modified version of Burnham's[8] GNABS. (Transmission factors varied from 0.346–0.643 for crystal 1 and from 0.736–0.826 for crystal 2). The corrected data were placed on a common scale using a least-squares procedure[9], the R-factor for scaling being 8%, based on F^2. Finally, the resulting 2484 independent non-zero reflections were placed on an absolute scale by means of a Wilson plot[10].

Solution and refinement of the structure

The structure was solved by Sayre's method[11] using a locally-modified version of the IBM 7094 program REL, by R. E. Long[12]. Normalized structure factors:

$$E\ (hkl) = F(hkl)\left[\sum_{j=1}^{j=N} f^2[j,\ \theta(hkl)]\right]^{-\frac{1}{2}}$$

were calculated, where the sum $j = 1 \rightarrow N$ is over all atoms in the unit cell, $\langle E^2(hkl)\rangle$ is normalized by adjustment of a scale factor, and $f[j,\ \theta(hkl)]$ is the scattering factor for the jth atom at the Bragg angle $\theta(hkl)$.

The origin of the unit cell was fixed by assigning positive phases to three strong reflections of appropriate parity, *i.e.*, 532 ($E = 3.42$), 365 ($E = 3.28$), 184 ($E = 3.16$). Possible signs for the 180 reflections with $E > 1.6$ were obtained using phase pyramids based on the 16 possible sign combinations for the reflections $52\bar{2}$ ($E = 2.75$), $3\bar{5}2$ ($E = 2.74$), $4\bar{6}3$ ($E = 2.67$), $\bar{3}23$ ($E = 2.63$). The results of this process are summarized in Table 1.

The consistency index, C, is defined as:

$$C = \frac{\langle |E_A \sum\limits_{A=B+C} E_B \cdot E_C| \rangle}{\langle |E_A| \cdot \sum\limits_{A=B+C} |E_B| \cdot |E_C| \rangle}$$

where sums are over all pairs of reflections B and C for which B + C = A, and where $\langle\ \rangle$ means the average over all values of A.

TABLE 3

(A). FINAL ATOMIC POSITIONS AND ISOTROPIC THERMAL PARAMETERS FOR $Co_8(CO)_{24}C_6\cdot\frac{1}{2}C_6H_6$

Atom	*x*	*y*	*z*	*B*
Co(1)	0.16407(30)	−0.41087(26)	−0.17361(47)	[a]
Co(2)	0.25755(29)	−0.31443(28)	−0.18739(47)	[a]
Co(3)	0.19284(32)	−0.28626(29)	0.01036(46)	[a]
Co(4)	−0.02146(31)	−0.21797(27)	−0.52122(47)	[a]
Co(5)	−0.02985(32)	−0.11670(26)	−0.30621(50)	[a]
Co(6)	−0.35465(29)	−0.37065(27)	−0.38500(48)	[a]
Co(7)	−0.32797(31)	−0.25259(30)	−0.18525(47)	[a]
Co(8)	−0.42348(32)	−0.22083(32)	−0.45390(53)	[a]
C(1)	0.1257(18)	−0.2896(16)	−0.2052(29)	1.6(5)
C(2)	0.0413(18)	−0.2399(16)	−0.2984(30)	1.4(5)
C(3)	−0.0569(21)	−0.2333(19)	−0.3579(34)	2.6(6)
C(4)	−0.1333(20)	−0.2589(18)	−0.3585(32)	2.1(5)
C(5)	−0.2066(21)	−0.2714(18)	−0.3617(33)	2.4(6)
C(6)	−0.2877(20)	−0.2825(19)	−0.3528(34)	2.4(6)
C(7)	0.1411(24)	−0.4728(22)	−0.3555(39)	3.5(7)
C(8)	0.2644(25)	−0.4893(23)	−0.0542(42)	4.2(8)
C(9)	0.0576(26)	−0.4244(23)	−0.1467(43)	4.2(8)
C(10)	0.2468(28)	−0.3511(25)	−0.3768(47)	5.3(9)
C(11)	0.3860(27)	−0.3700(24)	−0.0736(45)	4.4(8)
C(12)	0.2681(23)	−0.2212(20)	−0.2015(37)	3.8(6)
C(13)	0.2985(34)	−0.3421(31)	0.1740(57)	6.8(11)
C(14)	0.1999(30)	−0.1809(27)	0.0539(49)	6.6(9)
C(15)	0.0983(28)	−0.2822(25)	0.0641(46)	5.4(9)
C(16)	0.0587(29)	−0.1763(26)	−0.5553(48)	5.3(9)
C(17)	−0.0057(22)	−0.3234(20)	−0.6019(36)	3.4(6)
C(18)	−0.1482(33)	−0.1700(30)	−0.6868(55)	6.6(10)
C(19)	−0.1481(28)	−0.0400(26)	−0.4036(47)	5.5(9)
C(20)	−0.0246(26)	−0.0933(23)	−0.1119(43)	4.5(8)
C(21)	0.0493(26)	−0.0543(24)	−0.3032(44)	5.4(8)
C(22)	−0.3708(21)	−0.4132(19)	−0.5804(34)	2.7(6)
C(23)	−0.2527(23)	−0.4522(20)	−0.2758(37)	3.2(6)
C(24)	−0.4541(24)	−0.3921(22)	−0.3669(40)	3.7(7)
C(25)	−0.2263(30)	−0.3141(27)	−0.0392(50)	5.5(4)
C(26)	−0.2850(30)	−0.1583(27)	−0.1087(51)	6.0(10)
C(27)	−0.4231(23)	−0.2343(21)	−0.1194(38)	3.6(7)
C(28)	−0.4047(30)	−0.1157(28)	−0.4274(50)	6.3(10)
C(29)	−0.4462(49)	−0.2442(43)	−0.6523(81)	11.5(19)
C(30)	−0.5408(32)	−0.2094(29)	−0.4599(53)	7.1(10)
O(7)	0.1321(22)	−0.5186(20)	−0.4599(36)	6.9(7)
O(8)	0.3286(18)	−0.5393(17)	0.0131(30)	5.5(6)
O(9)	−0.0022(21)	−0.4349(19)	−0.1277(36)	6.5(7)
O(10)	0.2431(18)	−0.3699(16)	−0.4981(30)	4.9(6)
O(11)	0.4659(21)	−0.4074(19)	−0.0005(36)	6.5(7)
O(12)	0.2804(25)	−0.1524(22)	−0.2017(41)	8.6(9)
O(13)	0.3648(24)	−0.3705(21)	−0.2623(40)	7.5(8)
O(14)	0.2173(28)	−0.1184(25)	0.0991(47)	9.5(10)
O(15)	0.0312(23)	−0.2779(21)	0.0927(38)	7.5(8)
O(16)	0.1157(24)	−0.1492(22)	−0.5808(42)	7.8(8)

TABLE 3 (*continued*)

Atom	x	y	z	B
O(17)	−0.0026(21)	−0.3917(19)	−0.6639(34)	6.6(7)
O(18)	−0.2232(26)	−0.1443(24)	−0.7607(44)	10.0(9)
O(19)	−0.2229(21)	−0.0067(19)	−0.4652(35)	6.6(7)
O(20)	−0.0304(20)	−0.0884(18)	0.0004(33)	6.2(6)
O(21)	0.0993(18)	−0.0057(16)	−0.2880(30)	5.1(6)
O(22)	−0.3761(19)	−0.4474(17)	−0.6916(32)	5.9(6)
O(23)	−0.1900(18)	−0.5075(17)	−0.2214(31)	5.2(6)
O(24)	−0.5220(19)	−0.4062(17)	−0.3568(32)	5.8(6)
O(25)	−0.1630(22)	−0.3642(20)	0.0489(37)	7.5(7)
O(26)	−0.2456(23)	−0.1051(20)	−0.0673(38)	7.5(8)
O(27)	−0.4901(22)	−0.2252(20)	−0.0998(37)	7.6(7)
O(28)	−0.3982(24)	−0.0464(22)	−0.4188(40)	7.7(8)
O(29)	−0.4549(47)	−0.2333(43)	−0.7660(80)	12.7(11)
O(30)	−0.6230(28)	−0.2044(26)	−0.4683(48)	10.4(10)
Bz(1)	−0.458	−0.0198	0.158	12.1(20)
Bz(2)	−0.548	−0.033	0.058	12.0(20)
Bz(3)	−0.585	−0.010	−0.098	11.7(19)

B. ANISOTROPIC THERMAL PARAMETERS[a] FOR COBALT ATOMS

Atom	$10^5\beta_{11}$	$10^5\beta_{22}$	$10^5\beta_{33}$	$10^5\beta_{12}$	$10^5\beta_{13}$	$10^5\beta_{23}$
Co(1)	428(27)	258(21)	871(67)	−210(38)	570(72)	6(61)
Co(2)	331(25)	382(22)	760(64)	−199(38)	352(66)	55(63)
Co(3)	543(30)	415(23)	476(61)	−295(42)	355(70)	−200(63)
Co(4)	443(27)	322(21)	652(60)	−145(38)	504(67)	194(58)
Co(5)	524(29)	237(20)	1021(69)	−221(38)	692(76)	−41(60)
Co(6)	394(26)	366(22)	810(63)	−280(38)	558(69)	59(61)
Co(7)	441(28)	419(24)	657(63)	−161(42)	590(71)	−10(65)
Co(8)	427(29)	499(26)	1011(73)	−187(44)	292(75)	350(74)

[a] Anisotropic thermal parameters for these atoms are given in part (B) of this Table. The anisotropic thermal parameter is defined as: $B=\exp[-(\beta_{11}\cdot h^2+\beta_{22}\cdot k^2+\beta_{33}\cdot l^2+\beta_{12}\cdot h\cdot k+\beta_{13}\cdot h\cdot l+\beta_{23}\cdot k\cdot l)]$.

Set 1, which has the highest consistency index, is the trivial solution (*i.e.*, all + phases) and was discarded. An F-map based on the 180 phased reflections from the solution of second highest consistency index (Set 2, $C=0.995$) showed no chemically sensible features, but an F-map based on the third highest solution (Set 11, $C=0.991$) immediately revealed the positions of all eight cobalt atoms.

The remaining 54 atoms of the $Co_8(CO)_{24}C_6$ molecule were immediately located from a difference-Fourier map based on all 2484 non-zero reflections and phased by the eight cobalt atoms ($R_F=45.9\%$). Using anisotropic thermal parameters for the cobalt atoms and isotropic thermal parameters for oxygen and carbon atoms, refinement of positional and thermal parameters converged in four cycles to a discrepancy index $R_F=11.2\%$. A second difference-Fourier synthesis at this stage revealed a benzene molecule of crystallization centered on 1/2, 0, 0. The empirical formula of the crystalline material was thus proven to be $Co_8(CO)_{24}C_6\cdot\frac{1}{2}C_6H_6$.

Refinement of the thermal parameters of the three independent benzene carbon atoms (using fixed positional parameters read from the Fourier map) along with all previously-refined parameters, led to convergence ($\Delta/\sigma < 0.10$) at $R_F=10.2\%$ for the

2484 independent non-zero reflections.

Observed and calculated structure factors are shown in Table 2; all atomic parameters are listed in Table 3, and the vibration ellipsoids for the cobalt atoms are defined in Table 4.

TABLE 4

DIRECTION COSINES FOR THE VIBRATION ELLIPSOIDS[a] OF THE COBALT ATOMS

Atom	B_{max} (dc's major axis)	B_{med} (dc's median axis)	B_{min} (dc's minor axis)
Co(1)	3.31 (0.737, −0.234, 0.170)	2.51 (−0.475, 0.051, 0.968)	2.37 (−0.480, −0.971, 0.185)
Co(2)	3.76 (−0.011, −0.966, 0.062)	2.58 (−0.903, −0.234, 0.771)	2.32
Co(3)	4.41 (−0.736, 0.431, 0.114)	4.27 (−0.676, −0.879, 0.454)	1.33 (−0.037, 0.204, 0.884)
Co(4)	3.42 (0.850, 0.504, 0.023)	3.22 (−0.376, 0.782, 0.225)	1.66 (−0.368, −0.366, 0.974)
Co(5)	3.99 (0.812, −0.069, 0.126)	2.97 (−0.545, −0.224, 0.990)	2.21 (0.209, 0.972, 0.062)
Co(6)	3.78 (0.347, −0.804, 0.006)	2.78 (0.516, 0.415, 0.495)	1.99 (−0.783, −0.426, 0.869)
Co(7)	4.25 (−0.295, −0.999, 0.165)	3.35 (0.846, −0.032, 0.072)	1.70 (−0.444, −0.004, 0.984)
Co(8)	5.13 (−0.084, 0.866, 0.322)	3.84 (−0.928, −0.452, 0.683)	2.70 (0.362, −0.214, 0.656)

[a] Direction cosines (dc's) are referred to the triclinic axes. Atomic vibration ellipsoids are defined in terms of the isotropic thermal parameter, B. The transformation to root-mean-square displacement is: $(\overline{U^2})^{\frac{1}{2}} = [B/(8\pi^2)]^{\frac{1}{2}}$.

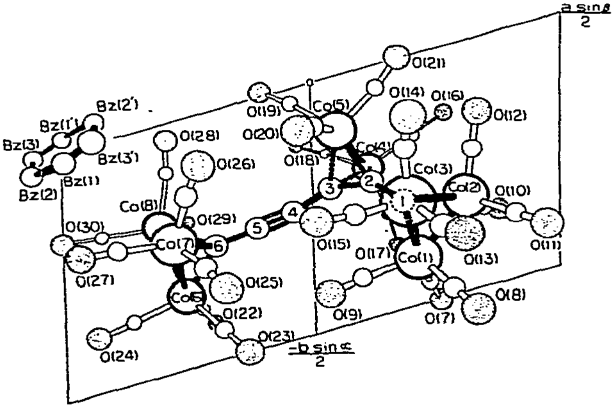

Fig. 2. Numbering of atoms for $Co_8(CO)_{24}C_6 \cdot \frac{1}{2}C_6H_6$. (Carbon atoms of the carbonyl groups are numbered similarly to their attached oxygens; carbon atoms of the diacetylene ligand are labelled with numbers only.)

The molecular structure

Bond distances are collected in Table 5 and bond angles are shown in Table 6. Important least-squares planes are shown in Table 7.

The $Co_8(CO)_{24}C_6$ molecule (see Fig. 2) can be formally described as a bis-

TABLE 5

INTRAMOLECULAR DISTANCES (Å) FOR $Co_8(CO)_{24}C_6 \cdot \frac{1}{2}C_6H_6$

(a). Cobalt–cobalt distances within Co_3C groups.			
Co(1)–Co(2)	2.467(6)	Co(6)–Co(7)	2.482(6)
Co(2)–Co(3)	2.460(6)	Co(7)–Co(8)	2.471(6)
Co(3)–Co(1)	2.477(6)	Co(8)–Co(6)	2.472(6)
		Average	2.472
(b). Cobalt–cobalt distance within $Co_2(CO)_6$ groups			
Co(4)–Co(5)	2.469(6)		
(c). Cobalt–carbon distances within Co_3C groups			
Co(1)–C(1)	1.944(27)	Co(6)–C(6)	1.906(32)
Co(2)–C(1)	1.918(27)	Co(7)–C(6)	1.935(32)
Co(3)–C(1)	1.912(28)	Co(8)–C(6)	1.970(32)
		Average	1.931
(d). Cobalt–C(acetylene) distances for $Co_2(CO)_6$ residue			
Co(4)–C(2)	2.023(28)	Co(5)–C(2)	2.014(28)
Co(4)–C(3)	1.965(32)	Co(5)–C(3)	1.994(32)
		Average	1.999
(e). Cobalt–carbonyl distances within $Co_3(CO)_9$ fragments			
Co(1)–C(7)	1.831(37)	Co(6)–C(22)	1.851(32)
Co(1)–C(8)	1.824(39)	Co(6)–C(23)	1.827(35)
Co(1)–C(9)	1.852(40)	Co(6)–C(24)	1.761(37)
Co(2)–C(10)	1.795(44)	Co(7)–C(25)	1.807(46)
Co(2)–C(11)	1.881(41)	Co(7)–C(26)	1.765(47)
Co(2)–C(12)	1.607(34)	Co(7)–C(27)	1.789(36)
Co(3)–C(13)	1.884(53)	Co(8)–C(28)	1.774(47)
Co(3)–C(14)	1.722(46)	Co(8)–C(29)	1.807(75)
Co(3)–C(15)	1.742(43)	Co(8)–C(30)	1.762(50)
		Average	1.793
(f). Cobalt–carbonyl distances within $Co_2(CO)_6$ fragment			
Co(4)–C(16)	1.737(44)	Co(5)–C(19)	1.881(44)
Co(4)–C(17)	1.766(34)	Co(5)–C(20)	1.842(40)
Co(4)–C(18)	2.004(51)	Co(5)–C(21)	1.787(41)
		Average	1.836
(g). Carbon–oxygen distances			
C(7)–O(7)	1.137(50)	C(19)–O(19)	1.091(54)
C(8)–O(8)	1.131(48)	C(20)–O(20)	1.126(50)
C(9)–O(9)	1.083(51)	C(21)–O(21)	1.204(49)
C(10)–O(10)	1.153(52)	C(22)–O(22)	1.114(43)
C(11)–O(11)	1.190(53)	C(23)–O(23)	1.139(45)
C(12)–O(12)	1.189(51)	C(24)–O(24)	1.185(47)
C(13)–O(13)	1.071(64)	C(25)–O(25)	1.210(58)

Continued

TABLE 5 (*Continued*)

C(14)–O(14)	1.096(63)	C(26)–O(26)	1.118(58)
C(15)–O(15)	1.173(56)	C(27)–O(27)	1.105(49)
C(16)–O(16)	1.216(58)	C(28)–O(28)	1.149(60)
C(17)–O(17)	1.173(46)	C(29)–O(29)	1.100(90)
C(18)–O(18)	1.089(65)	C(30)–O(30)	1.228(66)
		Average	1.145
(*h*). *Distances within the C_6/diacetylene residue*			
C(1)–C(2)	1.370(39)	C(4)–C(5)	1.199(43)
C(2)–C(3)	1.367(42)	C(5)–C(6)	1.361(44)
C(3)–C(4)	1.361(44)		
(*i*). *Distances within C_6H_6 of crystallization*[a]			
Bz(1)–Bz(2)	1.377	Bz(1′)–Bz(2′)	1.377
Bz(2)–Bz(3)	1.459	Bz(2′)–Bz(3′)	1.459
Bz(3)–Bz(1′)	1.278	Bz(3′)–Bz(1)	1.278
		Average	1.371

[a] The benzene of crystallization has a crystallographically required center of symmetry. Atoms related to the basic asymmetric unit by the relation $x'=-1-x$, $y'=-y$, $z'=-z$ are marked with a prime.

TABLE 6

BOND ANGLES, IN DEGREES, FOR $Co_8(CO)_{24}C_6\cdot\frac{1}{2}C_6H_6$

(*a*). *Angles within Co_3C tetrahedra*			
Co(3)–Co(1)–Co(2)	59.7(0.2)	Co(8)–Co(6)–Co(7)	59.8(0.2)
Co(1)–Co(2)–Co(3)	60.4(0.2)	Co(6)–Co(7)–Co(8)	59.9(0.2)
Co(2)–Co(3)–Co(1)	60.0(0.2)	Co(7)–Co(8)–Co(6)	60.3(0.2)
		Co–Co–Co(av.)	60.0
Co(2)–Co(1)–C(1)	49.9(0.8)	Co(7)–Co(6)–C(6)	50.3(1.0)
Co(3)–Co(1)–C(1)	49.5(0.8)	Co(8)–Co(6)–C(6)	51.5(1.0)
Co(1)–Co(2)–C(1)	50.8(0.8)	Co(6)–Co(7)–C(6)	49.2(1.0)
Co(3)–Co(2)–C(1)	49.9(0.8)	Co(8)–Co(7)–C(6)	51.4(1.0)
Co(1)–Co(3)–C(1)	50.6(0.8)	Co(6)–Co(8)–C(6)	49.2(0.9)
Co(2)–Co(3)–C(1)	50.2(0.8)	Co(7)–Co(8)–C(6)	50.1(0.9)
		Co–Co–C(av.)	50.2
Co(1)–C(1)–Co(2)	79.4(1.1)	Co(6)–C(6)–Co(7)	80.5(1.2)
Co(1)–C(1)–Co(3)	79.9(1.1)	Co(6)–C(6)–Co(8)	79.2(1.2)
Co(2)–C(1)–Co(3)	79.9(1.1)	Co(7)–C(6)–Co(8)	78.5(1.2)
		Co–C–Co(av.)	79.6
Co(1)–C(1)–C(2)	132.1(2.2)	Co(6)–C(6)–C(5)	139.4(2.5)
Co(2)–C(1)–C(2)	133.0(2.2)	Co(7)–C(6)–C(5)	128.8(2.5)
Co(3)–C(1)–C(2)	131.7(2.2)	Co(8)–C(6)–C(5)	128.5(2.4)
		Co–C–C(av.)	132.3
(*b*). *Angles within Co_2C_2 moiety*			
Co(5)–Co(4)–C(2)	52.1(0.8)	Co(4)–Co(5)–C(2)	52.5(0.1)
Co(5)–Co(4)–C(3)	52.0(1.0)	Co(4)–Co(5)–C(3)	50.9(0.9)
		Co–Co–C(av.)	51.9
Co(4)–C(2)–Co(5)	75.4(1.0)	Co(4)–C(3)–Co(5)	77.1(1.2)
		Co–C–Co(av.)	76.3

TABLE 6 (*continued*)

C(2)–Co(4)–C(3)	40.0(1.2)	C(2)–Co(5)–C(3)	39.9(1.2)
		C–Co–C(av.)	40.0
Co(4)–C(2)–C(3)	67.7(1.8)	Co(4)–C(3)–C(2)	72.3(1.8)
Co(5)–C(2)–C(3)	69.3(1.8)	Co(5)–C(3)–C(2)	70.8(1.8)
		Co–C–C(av.)	70.0
(*c*). *Diacetylene–cobalt–carbonyl angles for* $Co_3(CO)_9$ *groups*			
C(1)–Co(1)–C(7)	110.0(1.4)	C(6)–Co(6)–C(22)	111.8(1.1)
C(1)–Co(1)–C(9)	100.0(1.5)	C(6)–Co(6)–C(23)	99.1(1.5)
C(1)–Co(2)–C(10)	103.0(1.6)	C(6)–Co(7)–C(25)	101.1(1.8)
C(1)–Co(2)–C(12)	100.7(1.5)	C(6)–Co(7)–C(26)	100.6(1.8)
C(1)–Co(3)–C(14)	102.1(1.8)	C(6)–Co(8)–C(28)	99.1(1.8)
C(1)–Co(3)–C(15)	100.7(1.7)	C(6)–Co(8)–C(29)	102.7(2.6)
		C–Co–CO(equ.)	102.6
C(1)–Co(1)–C(8)	140.7(1.5)	C(6)–Co(6)–C(24)	142.4(1.6)
C(1)–Co(2)–C(11)	144.4(1.5)	C(6)–Co(7)–C(27)	148.3(1.5)
C(1)–Co(3)–C(13)	144.7(1.8)	C(6)–Co(8)–C(30)	141.9(1.9)
		C–Co–CO(ax.)	143.7
(*d*). *Diacetylene–cobalt–carbonyl angles for* $Co_2(CO)_6$ *group*			
C(2)–Co(4)–C(16)	106.0(1.7)	C(2)–Co(5)–C(20)	101.1(1.5)
C(2)–Co(4)–C(17)	100.5(1.4)	C(2)–Co(5)–C(21)	107.8(1.6)
C(3)–Co(4)–C(17)	100.6(1.5)	C(3)–Co(5)–C(19)	106.8(1.7)
C(3)–Co(4)–C(18)	104.6(1.8)	C(3)–Co(5)–C(20)	102.7(1.6)
		C–Co–C(equ.)	103.8
C(2)–Co(4)–C(18)	142.8(1.7)	C(2)–Co(5)–C(19)	144.7(1.6)
C(3)–Co(4)–C(16)	142.1(1.8)	C(3)–Co(5)–C(21)	143.2(1.6)
		C–Co–C(ax.)	143.2
(*e*). *Cobalt–cobalt–carbonyl angles for* $Co_3(CO)_9$ *groups*			
Co(2)–Co(1)–C(7)	101.4(1.2)	Co(7)–Co(6)–C(22)	149.9(1.5)
Co(2)–Co(1)–C(8)	99.0(1.2)	Co(7)–Co(6)–C(23)	97.0(1.1)
Co(2)–Co(1)–C(9)	148.7(1.3)	Co(7)–Co(6)–C(24)	96.7(1.2)
Co(3)–Co(1)–C(7)	157.7(1.2)	Co(8)–Co(6)–C(22)	94.0(1.5)
Co(3)–Co(1)–C(8)	96.7(1.2)	Co(8)–Co(6)–C(23)	149.7(1.1)
Co(3)–Co(1)–C(9)	95.8(1.2)	Co(8)–Co(6)–C(24)	99.4(1.2)
Co(1)–Co(2)–C(10)	94.7(1.4)	Co(6)–Co(7)–C(25)	96.7(1.5)
Co(1)–Co(2)–C(11)	101.7(1.3)	Co(6)–Co(7)–C(26)	149.7(1.6)
Co(1)–Co(2)–C(12)	151.4(1.3)	Co(6)–Co(7)–C(27)	106.8(1.2)
Co(3)–Co(2)–C(10)	150.6(1.4)	Co(8)–Co(7)–C(25)	151.1(1.5)
Co(3)–Co(2)–C(11)	99.2(1.3)	Co(8)–Co(7)–C(26)	101.2(1.5)
Co(3)–Co(2)–C(12)	101.8(1.3)	Co(8)–Co(7)–C(27)	100.7(1.2)
Co(1)–Co(3)–C(13)	98.9(1.6)	Co(6)–Co(8)–C(28)	147.3(1.5)
Co(1)–Co(3)–C(14)	151.4(1.6)	Co(6)–Co(8)–C(29)	95.2(2.4)
Co(1)–Co(3)–C(15)	95.8(1.4)	Co(6)–Co(8)–C(30)	99.2(1.6)
Co(2)–Co(3)–C(13)	102.1(1.6)	Co(7)–Co(8)–C(28)	94.7(1.5)
Co(2)–Co(3)–C(14)	97.4(1.5)	Co(7)–Co(8)–C(29)	150.9(2.4)
Co(2)–Co(3)–C(15)	149.4(1.4)	Co(7)–Co(8)–C(30)	98.7(1.6)
(*f*). *Cobalt–cobalt–carbonyl angles for* $Co_2(CO)_6$ *group*			
Co(5)–Co(4)–C(16)	96.5(1.5)	Co(4)–Co(5)–C(19)	100.6(1.4)
Co(5)–Co(4)–C(17)	150.3(1.7)	Co(4)–Co(5)–C(20)	151.4(1.3)
Co(5)–Co(4)–C(18)	100.6(1.5)	Co(4)–Co(5)–C(21)	98.2(1.3)

TABLE 6 *(continued)*

(g). Carbonyl–cobalt–carbonyl angles			
C(7)–Co(1)–C(8)	98.1(1.7)	C(19)–Co(5)–C(20)	97.8(1.8)
C(8)–Co(1)–C(9)	103.3(1.7)	C(20)–Co(5)–C(21)	100.9(1.8)
C(9)–Co(1)–C(7)	96.9(1.7)	C(21)–Co(5)–C(19)	97.5(1.9)
C(10)–Co(2)–C(11)	101.2(1.9)	C(22)–Co(6)–C(23)	100.7(1.4)
C(11)–Co(2)–C(12)	103.2(1.8)	C(23)–Co(6)–C(24)	102.9(1.6)
C(12)–Co(2)–C(10)	93.9(1.9)	C(24)–Co(6)–C(22)	102.7(1.5)
C(13)–Co(3)–C(14)	103.2(2.2)	C(25)–Co(7)–C(26)	91.7(2.1)
C(14)–Co(3)–C(15)	98.1(2.1)	C(26)–Co(7)–C(27)	99.6(1.9)
C(15)–Co(3)–C(13)	99.8(2.2)	C(27)–Co(7)–C(25)	102.5(1.9)
C(16)–Co(4)–C(17)	103.0(1.9)	C(28)–Co(8)–C(29)	100.7(2.8)
C(17)–Co(4)–C(18)	97.3(1.8)	C(29)–Co(8)–C(30)	100.7(2.9)
C(18)–Co(4)–C(16)	101.3(2.1)	C(30)–Co(8)–C(28)	105.6(2.2)
(h). Cobalt–carbon–oxygen angles			
Co(1)–C(7)–O(7)	172.8(3.5)	Co(5)–C(19)–O(19)	168.6(4.0)
Co(1)–C(8)–O(8)	175.9(3.5)	Co(5)–C(20)–O(20)	168.8(3.6)
Co(1)–C(9)–O(9)	177.2(3.8)	Co(5)–C(21)–O(21)	172.0(3.5)
Co(2)–C(10)–O(10)	174.9(3.8)	Co(6)–C(22)–O(22)	172.3(3.8)
Co(2)–C(11)–O(11)	177.6(3.7)	Co(6)–C(23)–O(23)	173.1(3.2)
Co(2)–C(12)–O(12)	175.4(3.4)	Co(6)–C(24)–O(24)	179.0(3.3)
Co(3)–C(13)–O(13)	172.1(4.9)	Co(7)–C(25)–O(25)	171.7(4.0)
Co(3)–C(14)–O(14)	169.2(4.5)	Co(7)–C(26)–O(26)	168.5(4.3)
Co(3)–C(15)–O(15)	176.4(3.9)	Co(7)–C(27)–O(27)	169.9(3.5)
Co(4)–C(16)–O(16)	178.3(4.0)	Co(8)–C(28)–O(28)	175.4(4.3)
Co(4)–C(17)–O(17)	174.7(3.2)	Co(8)–C(29)–O(29)	157.6(7.3)
Co(4)–C(18)–O(18)	168.5(4.7)	Co(8)–C(30)–O(30)	177.2(4.5)
		Co–C–O(av.)	172.4
(i). Angles within diacetylene ligand			
C(1)–C(2)–C(3)	140.2(2.8)	C(3)–C(4)–C(5)	172.1(3.4)
C(2)–C(3)–C(4)	148.0(3.1)	C(4)–C(5)–C(6)	175.1(3.4)
(j). Angles within benzene molecule (cyclically)			
Bz(3′)–Bz(1)–Bz(2)	113.6	Bz(3)–Bz(1′)–Bz(2′)	113.6
Bz(1)–Bz(2)–Bz(3)	118.9	Bz(1′)–Bz(2′)–Bz(3′)	118.9
Bz(2)–Bz(3)–Bz(1′)	127.5	Bz(2′)–Bz(3′)–Bz(1)	127.5
		Bz–Bz–Bz(av.)	120.0

(tricobalt nonacarbonyl)/dicobalt hexacarbonyl derivative of 2,4-hexadiyne. The terminal carbon atoms of the completely unsaturated C_6 ligand, C(1) and C(6), are each symmetrically coordinated by three Co–C σ-bonds to a basal triangular $Co_3(CO)_9$ cluster, and one acetylene linkage, C(2)–C(3), is bonded to a $Co_2(CO)_6$ moiety*. The second linkage, C(4)–C(5), remains uncoordinated. The formation of $Co_8(CO)_{24}C_6$

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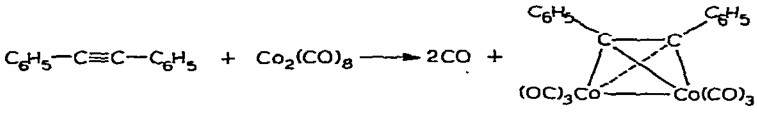
* Reactions of dicobalt octacarbonyl with acetylenes are well-known[13], and the structure of the diphenylacetylene/dicobalt octacarbonyl reaction product, $Co_2(CO)_6[C_2(C_6H_5)_2]$, (III), has been determined[14].



(III)

TABLE 7

IMPORTANT PLANES FOR $Co_8(CO)_{24}C_6 \cdot \frac{1}{2}C_6H_6$ (IN CARTESIAN COORDINATES[a])

I: Co(1), Co(2), Co(3)
$0.6549X - 0.4417Y + 0.6131Z = 3.6385$
II: Co(6), Co(7), Co(8)
$-0.9504X - 0.2972Y + 0.0909Z = 5.3947$
III: Diacetylene ligand
$-0.3339X + 0.6261Y + 0.7045Z = -4.5615$
[Deviations: C(1) −0.02 Å, C(2) +0.08 Å, C(3) +0.00 Å, C(4) −0.08 Å, C(5) −0.06 Å, C(6) +0.08 Å]
IV: Benzene molecule
$-0.5599X + 0.7908Y + 0.2469Z = 2.5421$
[Deviations: Bz(1) +0.007 Å, Bz(2) −0.007 Å, Bz(3) +0.008 Å, Bz(1′) −0.007 Å, Bz(2′) +0.007 Å, Bz(3′) −0.008 Å.]

[a] Cartesian coordinates (X, Y, Z) are related to the triclinic cell coordinates (x, y, z) by:
$X = x \cdot a \cdot \sin\gamma + z \cdot c \cdot (\cos\beta - \cos\alpha \cdot \cos\gamma)/\sin\gamma$
$Y = y \cdot b + x \cdot a \cdot \cos\gamma + z \cdot c \cdot \cos\alpha$
$Z = z \cdot c \cdot [(1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha \cdot \cos\beta \cdot \cos\gamma)/\sin^2\gamma]^{\frac{1}{2}}$

(I) in the reaction of hexachlorocyclopropane and dicobalt octacarbonyl thus involves opening of the C_3 ring and linkage of two such C_3 units via a C–C bond. The precise nature of this novel transformation is not understood at the present time.

Cobalt–cobalt bond lengths range from 2.460(6)–2.482(6) Å (average = 2.472 Å) within the $Co_3(CO)_9$ moieties, with the metal–metal bond length in the $Co_2(CO)_6$ residue being 2.469 (6) Å. These distances are in excellent agreement with the values of 2.47 Å in $Co_2(CO)_6[C_2(C_6H_5)_2]$[14], 2.46 Å in $[Co_3(CO)_9C]_2C{=}O$[15,16], 2.495 Å in $Co_3(CO)_{10}BH_2N(C_2H_5)_3$[17], 2.461 Å in $Co_5(CO)_{15}C_3H$[18], 2.485 Å in $Co_6(CO)_{18}C_4$[18], 2.467 Å in $Co_3(CO)_9CCH_3$[19], and with other observed Co–Co distances listed by Sutton and Dahl[19].

In all respects, the $Co_3(CO)_9C$ units of this complex, with approximate C_{3v} symmetry, are identical with the structures already reported for other derivatives of (tricobalt nonacarbonyl)methane[15,16,17,19]. Each cobalt atom (d^9) attains the desired rare gas (Kr) configuration by donation of two electrons from each of the three carbonyl groups to which it is coordinated, and one electron each from the apical carbon atom and the two remaining cobalt atoms within the triangular array.

The cobalt–(apical carbon) bond lengths range from 1.912(28)–1.970(32) Å (average 1.931 Å), in excellent agreement with bond distances of 1.92 Å in $[Co_3(CO)_9C]_2C{=}O$[15,16], 1.90(2) Å in $Co_3(CO)_9CCH_3$[19], and 1.92(1) Å in $Co_3(CO)_{10}BH_2N(C_2H_5)_3$[17].

Average bond angles within the tetrahedral Co_3C frameworks are: Co–Co–Co = 60.0°, Co–Co–C = 50.2°, and Co–C–Co = 79.6°. The Co–C(1)–C(2) angles range from 131.7(2.2) to 133.0(2.2) and Co–C(6)–C(5) angles range from 128.5(2.4) to 139.4(2.5)°, indicating that within the limits of experimental error, both C(1) and C(6) have environments of C_{3v} symmetry. All the above angular values are in good agreement with those reported in references 16, 17, and 19.

Average cobalt–carbonyl and carbon–oxygen distances (for all 24 carbonyl ligands) are 1.145 Å and 1.809 Å, respectively. No significant differences are observed between bond lengths in axial [(C(8)O(8), C(11)O(11), C(13)O(13), C(24)O(24), C(27)O(27), C(30)O(30)] and equatorial carbonyl groups within the $Co_3(CO)_9C$ units. The Co–C–O bond angles average 172.4°.

Within the $Co_2(CO)_6C_2$ portion of the $Co_8(CO)_{24}C_6$ molecule, the structural features are very similar to those reported for $Co_2(CO)_6[C_2(C_6H_5)_2]$[14] or $Co_2(CO)_6[C_6F_6]$[20,21]. The Co–Co bond makes an angle of ~89° with the C(2)–C(3) bond, with cobalt–carbon distances ranging from 1.965(32) to 2.023(28) Å, averaging 1.999 Å, as compared to the average Co–C distance of 1.96 Å in $Co_2(CO)_6[C_2(C_6H_5)_2]$[14] and 1.92 Å in $Co_2(CO)_6[C_6F_6]$[20–21]. The carbon–carbon distance within the π-bonded acetylene group, C(2)–C(3), is 1.367(42) Å as compared to 1.37 Å* in $Co_2(CO)_6[C_2(C_6H_5)_2]$ and 1.36(3) in $Co_2(CO)_6[C_6F_6]$.

Carbon–carbon distances within the present diacetylene ligand are: C(1)–C(2) = 1.370(39) Å, C(2)–C(3) = 1.367(42) Å, C(3)–C(4) = 1.361(44) Å, C(4)–C(5) = 1.199(43) Å and C(5)–C(6) = 1.361(43) Å. The free acetylene linkage, C(4)–C(5), is significantly shorter than the other carbon–carbon bonds, and is in excellent agreement with the accepted value of 1.204(2) Å for a C≡C triple bond[22].

Angles within the diacetylene ligand are: C(1)–C(2)–C(3) = 140.2(2.8)°, C(2)–C(3)–C(4) = 148.0(3.2)°, C(3)–C(4)–C(5) = 172.1(3.4)° and C(4)–C(5)–C(6) = 175.1(3.4)°. Clearly, atoms C(3), C(4), C(5) and C(6) are essentially colinear, as expected with an uncoordinated triple bond between atoms C(4) and C(5). There is, however, *cis*-bending of the substituents on the coordinated acetylene, C(2)–C(3). Values for the bond angles C(1)–C(2)–C(3) and C(2)–C(3)–C(4) agree well with those of 137° and 139° in the diphenylacetylene complex, $Co_2(CO)_6[C_2(C_6H_5)_2]$[14].

The $Co_2(CO)_6$-to-acetylene bonding is best considered in terms of a combination of ligand π-electron → metal forward donation and metal *d*-electron → ligand π* back-donation. The bonding and *cis*-bending of metal-coordinated acetylenes have been considered in detail by a number of previous authors[23–26], and will not be discussed further here. It may be noted, however, that each cobalt atom of the $Co_2(CO)_6$ moiety may formally achieve a rare gas configuration by receiving two electrons from each of the three carbonyl groups to which it is bonded, one electron from the other cobalt atom, and two electrons from the C(2)–C(3) triple bond.

Intermolecular contacts

The packing of $Co_8(CO)_{24}C_6$ and C_6H_6 molecules within the unit cell is shown in Fig. 3. Intermolecular contacts to 3.3 Å are collected in Table 8.

EPILOGUE

After the presence of the uncoordinated C≡C bond in (I) had been recognized, an attempt was made to convert it also to its $Co_2(CO)_6$ derivative [*i.e.*, $Co_{10}(CO)_{30}C_6$] by reaction with further dicobalt octacarbonyl. However, no reaction was observed and one must conclude that this C≡C linkage is too hindered to permit further attack by $Co_2(CO)_8$. The structure of (I) as shown in Fig. 2 bears this out. It is of interest to note that *both* C≡C bonds of 2,4-hexadiyne and 1,4-diphenyl-1,3-butadiyne were found to react with dicobalt octacarbonyl, giving complexes of type $[Co_2(CO)_6]_2(RC_2–C_2R)$[27–30]

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* Originally reported[14] as 1.46 Å, but later refined to a value of 1.37 Å (personal communication by W. G. Sly to L. F. Dahl, 1963).

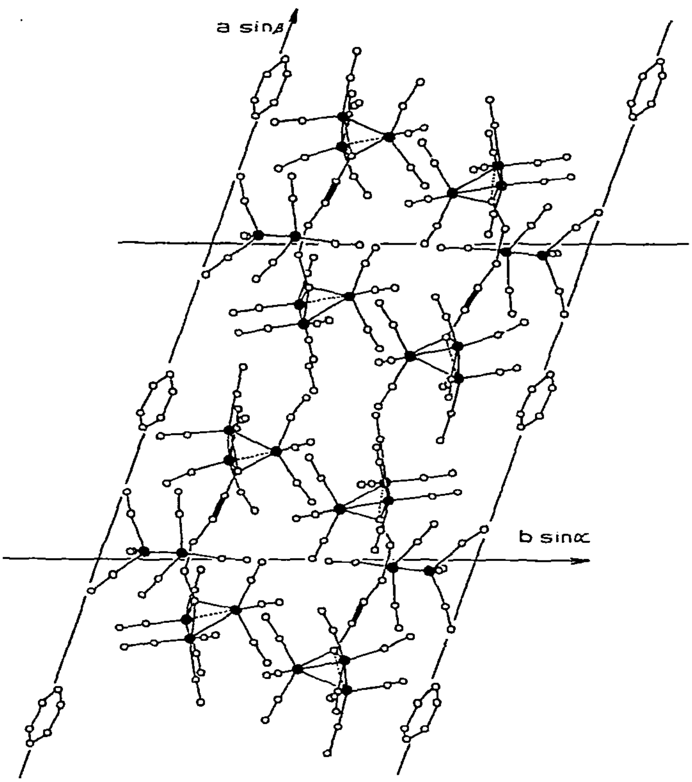

Fig. 3. Packing diagram for $Co_8(CO)_{24}C_6 \cdot \frac{1}{2}C_6H_6$.

In conclusion, it should be pointed out that it has recently been reported[18] that the reaction of chloromethylidynetricobalt nonacarbonyl with *mesitylene* gives cobalt carbonyl complexes in which the $Co_3(CO)_9C$ unit has been retained [*e.g.*, $Co_6(CO)_{18}C_4$] and, in some cases, those which also have a $Co_2(CO)_6$ group coordinated to an acetylene linkage. Among the latter class of products is $Co_8(CO)_{24}C_6$.

EXPERIMENTAL

Reaction of dicobalt octacarbonyl with hexachlorocyclopropane

A solution of 14.05 g (41.0 mmol) of dicobalt octacarbonyl (Strem Chemicals, Inc.) in 60 ml of dry THF was prepared under nitrogen in a 300-ml three-necked flask equipped with a magnetic stirring unit and a pressure-equalizing dropping funnel. To this solution was added 10.2 g (41.0 mmol) of hexachlorocyclopropane[4] in 65 ml of THF during the course of 5 min. A slow evolution of gas occurred at room temperature. Gas evolution became vigorous when the reaction mixture was heated to 40°. After it had been stirred at 40° for 5 h, the reaction mixture was kept at room temperature for 10 h.

Filtration served to remove 8.40 g of blue solid, which after being dried overnight at 100° (1 mm) gave 4.77 g of anhydrous cobalt(II) chloride.

The filtrate was evaporated at reduced pressure, leaving a solid residue which was extracted with two 500-ml portions of boiling hexane and 50 ml of hot THF. A

TABLE 8

INTERMOLECULAR CONSTANTS (TO 3.3 Å) FOR $Co_8(CO)_{24}C_6 \cdot \frac{1}{2}C_6H_6$

Atom	Atom	Transformation			Dist. (Å)
O(17)...O(25)		x	y	$-1+z$	2.86
O(11)...O(11)		$1-x$	$-1-y$	$-z$	2.92
O(11)...O(22)		$1+x$	y	$1+z$	3.02
O(18)...O(26)		x	y	$-1+z$	3.02
O(10)...O(23)		$-x$	$-1-y$	$-1-z$	3.05
O(27)...O(29)		x	y	$1+z$	3.09
C(28)...O(18)		x	y	$1+z$	3.10
O(8)...O(11)		$1-x$	$-1-y$	$-z$	3.13
O(8)...O(25)		$-x$	$-1-y$	$-z$	3.17
C(20)...O(20)		$-x$	$-y$	$-z$	3.19
O(9)...O(17)		$-x$	$-1-y$	$-1-z$	3.20
O(12)...O(27)		$1+x$	y	z	3.21
C(8)...O(25)		$-x$	$-1-y$	$-z$	3.22
C(8)...O(21)		$-x$	$-y$	$-1-z$	3.23
O(16)...O(19)		$-x$	$-y$	$-1-z$	3.27
O(20)...O(20)		$-x$	$-y$	$-z$	3.27
C(23)...O(8)		$-x$	$-1-y$	$-z$	3.28
Bz(3)...O(12)		$-x$	$-y$	$-z$	3.29
Bz(3)...O(18)		x	y	$1+z$	3.29
C(19)...O(16)		$-x$	$-y$	$-1-z$	3.30

brown powder, 2.5 g, remained undissolved. The combined extracts were cooled to 0°; 1.65 g of brown-black plates, (I), m.p. 131–133° (dec), crystallized. Filtration was followed by evaporation of the filtrate at reduced pressure and sublimation of the residue to give (at 25°, 0.1 mm) 3.70 g (14.8 mmol) of hexachlorocyclopropane, m.p. 101–103°. Crystallization of the nonvolatile residue from hexane gave another 0.20 g of (I). (Found: C, 29.52; Co, 38.29. $C_6Co_8(CO)_{24}$ calcd.: C, 29.64; Co, 38.78%.)

A solution containing 0.114 g of (I), 4 ml of conc. sulfuric acid and 30 ml of methanol was stirred at room temperature for 18 h and at 60° for 5 h. (I), 0.113 g, m.p. 132–133° dec. (sealed tube), was recovered on cooling.

Attempted reaction between $Co_8(CO)_{24}C_6$ and $Co_2(CO)_8$

To 1.4 g (4.1 mmol) of dicobalt octacarbonyl was added under nitrogen a solution of 0.40 g of $Co_8(CO)_{24}C_6$ in 25 ml of dry THF. No gas evolution was observed. The reaction mixture was heated at 60° for 18 h, during which time some gas was evolved. Evaporation of a small aliquot and infrared examination of the residue suggested that no reaction had occurred. The reaction mixture was poured into 200 ml of 10% sulfuric acid. After gas evolution had ceased, the mixture was extracted with 150 ml of ether. Evaporation of the ether extracts and crystallization of the residue from hexane at −20° gave 0.37 g (93% recovery) of (I), m.p. 129–131° dec. (sealed tube).

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