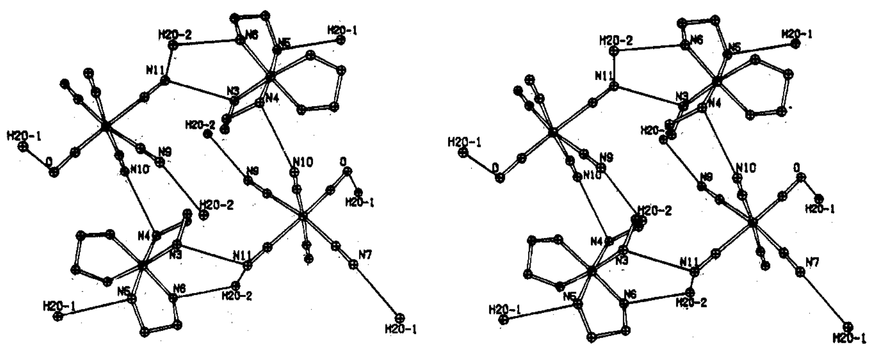

Figure 3.—Stereoscopic pair showing the hydrogen bonding and ionic packing in $[Co(en)_3][Cr(CN)_5(NO)]\cdot 2H_2O$ as viewed along the *b* axis. The horizontal axis is *a;* the vertical axis is *c*. For visual clarity only one layer of ions is shown. A second layer of ions can be generated by the twofold screw axes parallel to *b*. The hydrogen bonding between layers of ions can be inferred from Table VII. The identities of the unlabeled atoms can be determined by comparison to Figures 1 and 2.

array of alternating cations and anions. Layers of water molecules occur at $x \approx 0$ and $x \approx 0.5$ and probably account for the fact that the crystals grow as thin plates with the faces $\{100\}$ as the plate faces. The NO group, both H_2O molecules, all five CN ligands, and at least one H atom from each of the N atoms of the ethylenediamines are all involved in the network of hydrogen bonds (Table VII). The network of strong hydrogen bonds may also account for the slight deviations of the Cr–C–N and Cr–N–O groups from linearity. A stereoscopic view of the hydrogen-bonding scheme and ionic packing appears in Figure 3. For visual clarity only a portion of the unit cell is shown.

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The Structure of Hydridotetrakis(trifluorophosphine)cobalt(I), $CoH(PF_3)_4$

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The crystal structure of hydridotetrakis(trifluorophosphine)cobalt(I), $CoH(PF_3)_4$, has been determined from three-dimensional X-ray data collected by photographic methods at −125°. The material, as grown from the liquid phase, crystallizes in the monoclinic system, space group C_{2h}^6-$C2/c$, with four molecules in a cell of dimensions $a = 13.02$ (1), $b = 7.63$ (1), $c = 13.08$ (1) Å, and $\beta = 122.4$ (1)°. The calculated density is 2.49 g/cm^3. The structure has been solved by standard methods and refined by full-matrix least-squares methods to a final R factor on F of 0.11, based on 664 visually estimated intensities. The $CoH(PF_3)_4$ molecule is required crystallographically to possess C_2 symmetry. There is a distorted tetrahedron of PF_3 groups about the Co atom, the P–Co–P angles being 101.8 (3), 108.2 (2), 109.7 (2), and 118.0 (2)°. Various positions for the H atom, which was not located, are considered in terms of the distorted geometry of the molecule. A model is favored in which the H atom occupies an apical position of a distorted trigonal bipyramid. The Co–P distances average 2.052 (5) Å, indicative of considerably more multiple bonding than in metal–PR_3 bonds, where R is alkyl or aryl.

Introduction

The structure of $CoH(CO)_4$, and indeed of other simple carbonyl hydrides, has been the subject of study and contention for many years. A brief history of the subject has been given previously.[1] Ewens and Lister[2] deduced from electron diffraction studies of the gas that the CO groups are arranged approximately tetrahedrally about the central Co atom in $CoH(CO)_4$. (At that time it was assumed that the H atom was attached to one of the O atoms.) Eventually, spectroscopic studies[3] provided evidence that the H atom is bonded to the Co atom. The characteristic band initially identified as a Co–H stretching band[4,5] was later shown[6]

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to be a Co–H bending vibration. A tetrahedral model of $Co(CO)_4$, distorted to C_{3v} symmetry with the introduction of the H atom on the trigonal axis, was proposed.[3] Recently, broad-line nmr studies[7] have been interpreted in favor of a short Co–H distance of 1.42 Å. Such an interpretation is at variance with the wealth of diffraction evidence, collected over the last few years, which indicates that metal–hydrogen distances in transition metal hydride complexes are those expected for normal covalent bonds, *i.e.*, 1.6 Å or longer. In particular, the broad-line nmr results on $MnH(CO)_5$ of 1.42[8] and 1.44[9] Å for the Mn–H distance do not agree with the neutron diffraction value[10] of 1.601 (16) Å. It is now known that the interpretation of these broad-line nmr experiments is more complex than initially thought, and reliable details on the structures of these molecules are important in the reinterpretation of the nmr data. Thus details on the structure of $CoH(CO)_4$ are highly desirable, but the experimental conditions are made very difficult by the fact that the material decomposes on melting at −18°.

The analogous compound $CoH(PF_3)_4$ closely resembles $CoH(CO)_4$ in its chemical properties, but it is considerably more stable. The present X-ray diffraction study of $CoH(PF_3)_4$ was undertaken not only because of its obvious relation to the structure of $CoH(CO)_4$ but also for two additional reasons. First, although the chemistry of PF_3 complexes of transition metals has been systematically studied recently by Nixon,[11] Kruck,[12] and Clark[13] no structural information from diffraction studies is available.[13a] Because of the ability of PF_3 to function as a π-accepting ligand, the chemical properties of its transition metal complexes resemble those of carbonyl complexes more than aryl- or alkylphosphine complexes. This resemblance should also be evident in the structural details and in particular the shortening of the metal–PF_3 bond over the metal–PR_3 bond should provide a useful indication of the degree of multiple bonding. Second, of the approximately two dozen crystal structures of transition metal hydride complexes reported, only three neutron diffraction studies are available. The present compound contains a sufficiently small number of atoms to make it an attractive candidate for a neutron diffraction study following a successful X-ray study.

Experimental Section

Collection of X-Ray Data.—A sample of $CoH(PF_3)_4$ was generously supplied by Professor R. J. Clark. Portions of the pale yellow liquid were transferred to and sealed in 0.3-mm quartz capillaries.

Crystals were grown from the liquid (mp −51°) by passing a cold stream of nitrogen gas over a capillary mounted on a precession camera. A description of the low-temperature apparatus is given elsewhere.[14] Nineteen crystals were grown and examined by polarized light and by preliminary X-ray photographs. Of these, only three crystals were of sufficient quality to merit data collection. Various equipment failures aborted attempts to collect sufficient data from the first two of these crystals. A total of 1859 nonunique reflections were collected from the third crystal at $-125 \pm 6°$.

Preliminary precession photographs showed Laue symmetry $2/m$ and systematic extinctions for hkl, $h + k = 2n + 1$, and for $h0l$, $l = 2n + 1$, consistent with the space groups C_{2h}^6-$C2/c$ and C_s^4-Cc. The unit cell parameters at −125° are $a = 13.02$ (1), $b = 7.63$ (1), $c = 13.08$ (1) Å, and $\beta = 122.4$ (1)°, where the error estimates have been obtained from repeated measurements and where the wavelength of Mo Kα radiation has been taken as 0.7107 Å. For four molecules per unit cell, the calculated density is 2.49 ± 0.01 g cm^{-3}.

The (110) axis of the crystal was aligned with the spindle axis on a precession camera and a series of timed exposures of 11 reciprocal lattice layers ($hk0$; $h, h - 4, l$; $h, h - 2, l$; hhl; $h, h + 2, l$; $h, h + 4, l$; $h, h - 2l, l$; $h, h + l, l$; $h, h + 2l, l$; $h, h + 2l + 2, l$; $h, h + {}^4/_3l, l$) was taken using Zr-filtered Mo Kα radiation. Of the 1859 reflections observed, 1162 are nonequivalent in the noncentrosymmetric space group and 664 are nonequivalent in the centrosymmetric space group. Intensities were estimated visually against a calibrated strip. Lorentz–polarization corrections were applied;[15] no corrections for extinction effects or absorption were made. The linear absorption coefficient for $CoH(PF_3)_4$ is 23.6 cm^{-1} for Mo Kα radiation. The crystal was cylindrical with an estimated diameter of 0.3 mm and an estimated length of 0.6 mm. Thus with $\mu R = 0.35$ it is doubtful that the neglect of an absorption correction introduces errors greater than those of intensity estimation.

Determination and Refinement of the Structure.—The centric space group $C2/c$ was initially assumed. The data from the various layers were interscaled[15] through the use of the Hamilton–Rollett–Sparks algorithm.[16] The following weighting scheme was applied: $w = (5/|F|)^2$ for $I > 10$; $w = (I/(2|F|))^2$ for $I \leq 10$, where w is the weight, $|F|$ is the observed structure amplitude, and I is the raw intensity reading on a scale where a value of 2 is barely visible on the films. This weighting scheme was selected on the basis of a comparison of two independent sets of intensity measurements of the same reciprocal lattice layer. The intensity of a reflection common to more than one layer was obtained as a weighted average and a new weight was assigned to the averaged intensity on the basis of the weights and number of separate observations of this reflection. The agreement among separate observations of the same reflection was generally that expected for visual estimates of intensity. The goodness of fit, defined as the sum of the squares of the deviations from the weighted average divided by the number of reflections observed on more than one film, was 1.48.

The positions of the Co atom and one of the P atoms were located using a three-dimensional Patterson function.[15] Two cycles of least-squares refinement[15] resulted in an agreement factor $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.53$. Additional difference Fourier syntheses and least-squares cycles led to the location and refinement of the remaining nonhydrogen atoms. All of these atoms were refined anisotropically (78 variables) to a final R_1 factor of 0.112 and a weighted R factor or $R_2 = (\Sigma w(|F_o| -$

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[13a] NOTE ADDED IN PROOF.—Subsequent to submission of this paper, an electron diffraction study of $Ni(PF_3)_4$ and $Pt(PF_3)_4$ has appeared: J. G. Marriott, J. A. Salthouse, M. J. Ware, and J. M. Freeman, *Chem. Commun.*, 595 (1970).

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[15] Local modifications of the following programs for the CDC 6400 were used: Baur's LPFPRE Lorentz–polarization program, Hamilton's INSCALE data interscaling program, Zalkin's FORDAP Fourier program, the Busing–Levy ORFLS least-squares and ORFFE error function programs, and Johnson's ORTEP plotting program.

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TABLE I

VALUES OF $5|F_o|$ AND $5|F_c|$ (IN ELECTRONS) FOR $CoH(PF_3)_4$

K	L	FO	FC
***** H = 0 *****			
0	2	584	450
0	4	668	581
0	6	581	550
0	8	142	149
0	10	62	68
0	12	50	49
0	14	128	123
2	0	214	198
2	1	80	84
2	2	730	689
2	3	406	362
2	4	123	113
2	5	256	239
2	6	61	40
2	7	284	295
2	8	117	101
2	9	216	219
2	10	114	124
2	11	116	130
2	13	61	68
4	0	336	384
4	1	451	472
4	2	293	311
4	3	274	270
4	4	249	237
4	6	84	28
4	7	138	146
4	9	178	190
4	10	172	185
4	11	94	89
6	0	659	644
6	2	198	159
6	3	162	180
6	6	132	155
8	6	97	92
8	8	72	92
10	0	52	33
***** H = 1 *****			
1	-15	73	70
1	-14	50	51
1	-13	54	63
1	-11	107	110
1	-8	575	596
1	-7	155	142
1	-6	237	240
1	-5	439	432
1	-4	212	191
1	-3	153	146
1	-2	569	443
1	-1	776	615
1	0	333	291
1	1	1032	950
1	2	966	849
1	3	862	750
1	4	121	113
1	5	460	419
1	6	260	255
1	7	77	52
1	8	141	143
1	9	62	52
1	11	80	49
1	12	106	111
1	14	79	70
3	-13	61	18
3	-12	94	86
3	-11	60	49
3	-10	223	217
3	-9	98	97
3	-8	186	183
3	-7	274	260
3	-6	402	375
3	-5	67	64
3	-4	520	462
3	-3	85	33
3	-2	485	487
3	-1	348	369
3	0	194	207
3	1	350	332
3	2	538	558
3	4	110	115
3	6	117	116
3	7	125	127
3	8	316	337
3	10	194	202
3	11	63	46
3	12	65	74
5	-9	92	80
5	-8	288	322
5	-6	74	43
5	-5	217	196
5	-4	193	229
5	-3	254	284
5	-2	54	67
5	-1	113	139
5	0	54	53
5	1	570	587
5	2	434	563
5	3	211	230
5	4	180	208
5	5	200	218
5	6	123	132
5	9	85	74
5	10	72	37
7	-8	106	135
7	-6	83	71
7	-3	47	44
7	0	215	207
7	3	85	100
7	4	101	100
7	6	137	164
9	-4	90	94
9	0	53	51
9	5	66	54
***** H = 2 *****			
0	-16	89	113
0	-14	92	93
0	-10	120	115
0	-8	215	223
0	-6	828	777
0	-4	405	339
0	-2	1521	816
0	0	450	448
0	2	430	364
0	4	659	624
0	6	771	750
0	8	165	181
0	12	92	77
2	-14	50	51
2	-13	68	58
2	-12	91	72
2	-11	59	63
2	-10	115	133
2	-9	182	185
2	-8	356	327
2	-7	587	534
2	-6	140	124
2	-3	765	704
2	-2	535	616
2	-1	462	418
2	0	333	354
2	1	206	198
2	2	118	95
2	3	443	473
2	4	83	82
2	6	43	75
2	7	260	247
2	8	104	100
2	9	209	200
2	11	118	124
2	12	57	55
2	13	78	82
4	-14	63	46
4	-13	71	19
4	-12	132	131
4	-11	61	62
4	-10	141	145
4	-9	63	58
4	-7	426	382
4	-6	523	474
4	-5	583	516
4	-4	335	374
4	-3	296	292
4	-2	112	80
4	-1	41	24
4	0	351	383
4	1	151	153
4	2	331	377
4	4	90	92
4	5	101	97
4	7	67	65
4	8	191	204
4	9	177	174
4	10	64	61
4	11	62	55
6	-10	70	79
6	-8	80	100
6	-6	136	152
6	-5	61	59
6	-2	249	255
6	-1	84	90
6	0	260	251
6	1	153	177
6	4	304	299
6	5	131	156
6	6	216	231
6	7	71	57
8	-3	140	124
8	3	80	82
8	5	93	85
8	6	74	34
10	-4	90	74
10	0	46	34
***** H = 3 *****			
1	-15	98	87
1	-13	110	124
1	-12	63	24
1	-11	137	137
1	-10	208	215
1	-9	193	203
1	-8	322	333
1	-6	76	66
1	-5	196	175
1	-4	1008	792
1	-3	501	397
1	-2	1292	1089
1	0	313	344
1	1	700	733
1	2	190	182
1	3	185	140
1	4	136	114
1	5	329	328
1	6	166	144
1	7	217	211
1	8	140	150
1	9	69	68
1	10	178	165
1	12	80	77
3	-12	90	88
3	-10	80	82
3	-9	154	156
3	-8	158	167
3	-6	498	495
3	-5	244	242
3	-4	307	313
3	-3	402	424
3	-2	561	471
3	-1	124	139
3	0	387	413
3	1	54	70
3	2	111	126
3	3	66	55
3	4	158	163
3	5	109	117
3	6	51	39
3	8	286	286
3	9	49	37
3	12	73	73
5	-14	63	68
5	-13	66	68
5	-12	92	71
5	-11	130	130
5	-10	60	75
5	-8	84	87
5	-7	165	148
5	-5	117	89
5	-4	265	276
5	-3	58	12
5	-2	495	493
5	-1	228	229
5	0	317	323
5	1	294	323
5	2	156	153
5	3	252	265
5	4	59	42
5	5	193	202
5	6	79	86
5	7	196	186
5	8	141	131
5	9	65	61
5	10	62	56
7	-10	74	95
7	-4	120	115
7	-3	81	61
7	-2	221	227
7	0	37	37
7	1	74	89
7	2	84	93
7	3	98	76
7	4	149	170
7	5	94	103
7	6	72	68
7	10	85	62
9	-6	80	83
9	-3	190	155
9	0	81	74
***** H = 4 *****			
0	-16	72	63
0	-14	69	64
0	-12	160	166
0	-10	652	670
0	-8	182	150
0	-4	673	489
0	-2	118	88
0	0	173	189
0	2	628	656
0	4	780	762
0	6	292	284
0	8	90	104
0	10	223	217
2	-14	95	102
2	-12	100	111
2	-9	47	51
2	-8	423	379
2	-7	280	277
2	-6	135	123
2	-5	302	276
2	-4	410	349
2	-3	393	346
2	-2	77	67
2	-1	712	639
2	0	415	467
2	1	181	202
2	2	154	159
2	3	110	113
2	5	92	74
2	6	255	259
2	8	119	106
2	9	105	107
2	10	75	51
2	11	62	50
2	13	60	60
4	-14	79	77
4	-12	79	62
4	-11	94	80
4	-10	48	26
4	-9	101	80
4	-8	292	310
4	-7	374	330
4	-6	242	252
4	-5	42	50
4	-4	131	136
4	-3	334	327
4	-2	91	110
4	-1	369	422
4	0	506	536
4	1	76	82
4	2	86	90
4	5	158	150
4	6	214	215
4	7	49	53
4	8	114	126
4	10	47	22
6	-12	65	66
6	-11	64	64
6	-10	183	197
6	-9	75	62
6	-7	116	101
6	-5	64	52
6	-4	117	118
6	-3	127	114
6	-1	50	51
6	0	174	156
6	1	100	101
6	2	180	218
6	3	125	134
6	4	228	230
6	5	97	101
6	6	72	79
6	7	113	111
6	8	71	41
6	10	102	85
8	-9	55	39
8	-5	71	83
8	-4	72	125
8	-3	94	120
8	-2	146	132
8	0	38	25
8	3	102	99
8	5	73	56
8	6	52	45
8	9	64	53
***** H = 5 *****			
1	-13	64	85
1	-12	81	83
1	-11	171	188
1	-10	222	94
1	-9	411	422
1	-8	325	286
1	-7	312	281
1	-6	622	535
1	-4	552	401
1	-3	249	198
1	-2	839	663
1	-1	202	226
1	1	256	276
1	2	499	526
1	3	176	175
1	4	228	198
1	5	347	349
1	6	245	235
1	7	266	263
1	8	130	127
1	9	105	112
1	10	71	61
1	11	73	60
3	-10	103	147
3	-9	93	89
3	-8	205	216
3	-7	73	75
3	-6	43	46
3	-5	131	132
3	-4	116	116
3	-3	156	170
3	-2	337	338
3	0	372	428
3	3	128	127
3	4	66	61
3	6	102	117
3	8	69	33
5	-15	59	46
5	-14	48	56
5	-13	56	56
5	-11	95	78
5	-10	49	54
5	-9	285	228
5	-8	367	263
5	-7	142	117
5	-6	133	117
5	-5	125	126
5	-4	222	253
5	-2	82	69
5	-1	86	73
5	0	70	61
5	1	108	110
5	2	220	223
5	3	68	63
5	5	191	195
5	6	218	216
5	7	125	129
7	-12	76	67
7	-11	62	63
7	-10	102	88
7	-9	83	65
7	-6	94	89
7	-4	168	163
7	-2	97	73
7	-1	97	88
7	0	70	65
7	2	159	178
7	4	101	95
7	7	61	46
7	8	85	67
7	10	84	54
9	-3	82	105
9	-2	100	96
9	0	80	81
9	1	73	91
9	3	89	70
***** H = 6 *****			
0	-6	451	443
0	-4	462	357
0	-2	725	769
0	0	89	88
2	-13	65	75
2	-12	61	72
2	-11	101	97
2	-10	101	86
2	-8	203	193
2	-7	190	202
2	-6	39	33
2	-5	90	62
2	-3	505	517
2	-2	99	106
2	-1	384	450
2	1	316	331
2	2	138	151
2	3	255	277
2	4	132	127
2	5	127	119
2	6	169	166
2	7	96	61
2	10	72	65
4	-10	97	122
4	-8	178	242
4	-5	90	78
4	-4	140	153
4	-3	219	253
4	-2	387	444
4	-1	501	562
4	0	165	167
4	1	81	77
4	3	166	179
4	4	169	192
4	5	103	113
4	6	165	166
6	-12	90	89
6	-10	111	92
6	-9	100	108
6	-8	77	59
6	-7	59	61
6	-6	241	232
6	-5	106	109
6	-4	112	138
6	-2	188	203
6	-1	54	75
6	2	92	109
6	5	69	79
6	6	47	28
6	8	107	118
8	-8	98	69
8	-7	62	51
8	0	108	90
8	1	92	111
8	2	90	87
8	3	74	55
10	-2	86	100
***** H = 7 *****			
1	-6	218	189
1	-5	289	234
1	-4	197	151
1	-3	234	198
1	-2	146	154
1	0	712	729
1	3	55	48
3	-12	101	89
3	-10	136	159
3	-9	90	25
3	-8	55	80
3	-7	75	74
3	-6	51	77
3	-5	138	138
3	-4	87	27
3	-3	69	77
3	-2	566	592
3	-1	156	196
3	0	114	120
3	1	241	275
3	2	270	275
3	4	292	295
3	5	68	58
5	-11	59	70
5	-10	171	176
5	-9	178	185
5	-8	119	114
5	-7	142	153
5	-6	97	84
5	-5	171	181
5	-4	111	117
5	-3	215	208
5	-2	96	76
5	0	331	335
5	1	44	9
5	2	143	131
5	3	125	119
5	4	103	56
5	9	83	66
5	10	66	46
7	-12	64	61
7	-9	49	40
7	-7	76	76
7	-6	141	133
7	-5	83	87
7	-1	49	39
7	0	132	121
7	2	68	73
7	3	57	59
9	-1	104	84
9	1	113	104
***** H = 8 *****			
0	-8	689	649
0	-6	684	580
0	-4	278	239
0	0	435	446
0	4	84	74
2	-10	161	151
2	-5	94	89
2	-4	280	274
2	-2	130	120
2	0	248	245
2	3	234	233
2	5	142	145
4	-13	69	60
4	-11	92	80
4	-10	127	136
4	-8	75	76
4	-7	134	134
4	-6	61	13
4	-5	85	75
4	-4	230	276
4	-3	91	101
4	-2	156	162
4	0	68	75
4	1	131	184
4	2	191	208
4	3	186	198
4	4	128	133
4	5	71	70
6	-9	73	83
6	-8	143	199
6	-7	94	72
6	-6	173	190
6	-5	84	75
6	-4	60	65
6	-3	105	131
6	-2	70	81
6	0	165	144
6	1	78	50
6	6	96	77
8	-7	80	79
8	-4	58	51
8	-1	81	90
8	0	100	90
8	1	54	38
***** H = 9 *****			
1	-8	206	189
1	-6	152	138
1	-5	461	416
1	-4	333	333
1	-3	313	386
1	0	86	92
1	4	111	106
3	-12	147	160
3	-6	83	89
3	-5	141	137
3	0	78	80
3	3	74	61
5	-7	80	80
5	-6	161	194
5	-5	199	212
5	-4	246	284
5	-3	143	146
5	-1	78	40
5	1	123	122
5	2	90	83
5	4	72	44
5	6	71	71
7	-11	62	44
7	-8	96	116
7	-7	62	41
7	-6	62	45
7	-3	62	68
7	-2	88	88
7	0	92	86
***** H = 10 *****			
0	-4	365	407
0	0	65	63
2	-9	146	135
2	-8	135	115
2	-7	144	119
2	-6	190	169
2	-4	149	124
2	0	124	131
2	4	46	34
2	6	50	46
4	-14	80	44
4	-7	56	55
4	-6	159	151
4	-3	148	173
4	0	118	111
4	3	82	64
6	-12	62	60
6	-8	86	84
6	-4	98	100
6	-3	78	49
6	-2	172	196
6	-1	72	74
6	0	61	32
***** H = 11 *****			
1	-10	233	258
1	-6	75	59
1	0	75	74
3	-8	152	152
3	-6	218	229
3	0	115	110
3	4	45	30
5	-6	79	86
5	-3	80	90
5	0	134	122
7	-3	66	54
7	-2	115	78
***** H = 12 *****			
2	-14	81	70
2	-10	116	113
2	-7	123	130
2	-5	97	107
2	0	117	120
4	-8	108	126
4	-6	57	66
4	0	143	128
***** H = 13 *****			
1	-6	110	121
1	0	58	50
3	-12	53	42
3	-8	124	143
5	-8	77	26
5	-6	84	62
***** H = 14 *****			
0	0	170	121

TABLE II

FINAL ATOMIC PARAMETERS FOR $CoH(PF_3)_4$[a]

Atom	x	y	z	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Co	0	0.1477 (3)	$^1/_4$	83 (3)	135 (4)	68 (2)	0	16 (2)	0
P(1)	−0.1304 (3)	0.0095 (4)	0.1029 (3)	62 (3)	137 (5)	76 (3)	−13 (3)	26 (2)	−9 (3)
P(2)	−0.0816 (4)	0.3175 (4)	0.3072 (3)	83 (4)	165 (7)	88 (3)	−8 (3)	37 (3)	14 (4)
F(1,1)	−0.2681 (7)	0.0442 (12)	0.0477 (9)	64 (7)	242 (20)	148 (10)	−3 (8)	24 (8)	−34 (11)
F(1,2)	−0.1393 (9)	0.0210 (13)	−0.0182 (6)	144 (11)	271 (21)	70 (7)	−18 (12)	36 (7)	−6 (10)
F(1,3)	−0.1349 (8)	−0.1947 (9)	0.1102 (8)	120 (11)	155 (16)	114 (8)	−18 (8)	35 (8)	−12 (9)
F(2,1)	−0.0857 (9)	0.5172 (12)	0.2876 (10)	173 (12)	212 (19)	194 (12)	46 (12)	138 (10)	43 (13)
F(2,2)	−0.2188 (9)	0.2900 (14)	0.2581 (10)	91 (12)	432 (30)	154 (12)	−51 (12)	69 (10)	−46 (15)
F(2,3)	−0.0341 (10)	0.3238 (12)	0.4440 (7)	165 (14)	277 (23)	86 (8)	1 (11)	57 (9)	−22 (10)

[a] x, y, and z are in fractional coordinates. Thermal parameters are in the form: $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23}]$. The standard deviations of the least significant figures are given in parentheses here and in subsequent tables.

$|F_c|)^2/\Sigma wF_o^2)^{1/2}$ of 0.109, using the 664 observed reflections.

Atomic scattering factors for Co, P, and F were taken from the usual tabulation.[17] Anomalous dispersion effects were included in F_c;[18] the values of $\Delta f'$ and $\Delta f''$ for Co and P were those of Cromer.[19]

A final difference electron density map showed no significant features. The maximum residual electron density is 1.5 e$^-$ Å^{-3}. compared with 4.0 e$^-$ Å^{-3} for F atoms in a previous Fourier map. It is not surprising in view of the quality of the data and size of the unit cell that no reasonable position for the H atom could be assigned on the basis of the difference Fourier map. Table I lists values of $5|F_o|$ and $5|F_c|$ (in electrons) for the 664 reflections. The final atomic parameters are given in Table II.

Initially data collection was begun on a higher quality crystal grown from a different preparation of $CoH(PF_3)_4$, but this crystal was lost owing to experimental difficulties after two nets of data had been obtained. It is interesting that the 94 independent nonzero intensities collected from these two nets yield a value of R_1 of 0.17 when the structural parameters of Table II are employed and only the scale factors are varied. Under the rather extreme conditions of complete isotropic refinement (36 variables) R_1 is reduced to 0.10 and the derived parameters do not differ significantly from those given in Table II.

The possibility that the compound crystallizes in the noncentric space group *Cc* was considered. The data were interscaled again without the averaging of Friedel pairs. The structure found in *C*2/*c* was distorted slightly and refinement was initiated in *Cc*. Since *Cc* is a polar space group two enantiomorphic structures must be considered. Least-squares refinements gave values of R_1 and R_2 of 0.123 and 0.124 for one configuration compared with 0.121 and 0.120 for the other configuration. Using this same noncentric data set we find that the corresponding values of R_1 and R_2 for the centric solution are 0.126 and 0.130. Thus the improvement in agreement in the noncentric case is small.

The better noncentric structure had basically the same geometry as the centric structure, but the bond angles and rms amplitudes of vibration were greatly altered. The Co–P distances in the *Cc* structure varied from 1.98 to 2.15 Å; the P–F distances ranged from 1.41 to 1.68 Å. The thermal ellipsoids of some of the F atoms were physically unreasonable, although positive definite. In the last cycle of least-squares refinement there were

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[17] J. A. Ibers, "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962, Table 3.3.1 A.

[18] J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, **17**, 781 (1964).

[19] D. T. Cromer, *ibid.*, **18**, 17 (1965).

90 correlation coefficients greater than 0.50. If one assumes only random errors in the data and then applies the *R* factor ratio test,[20] then one can reject the hypothesis that the true space group is *Cc* at the 0.005 significance level. All of these facts suggest that the centric solution is the correct one.

Description of the Structure

Figure 1 shows a view of the $CoH(PF_3)_4$ molecule with the H atom omitted. A stereoscopic view of the unit cell is shown in Figure 2. All intermolecular distances are normal. The shortest interaction (3.0 Å) is between F atoms. Root-mean-square amplitudes of vibration are listed in Table III. The directions and shapes of the thermal ellipsoids (Figure 1) appear reasonable.

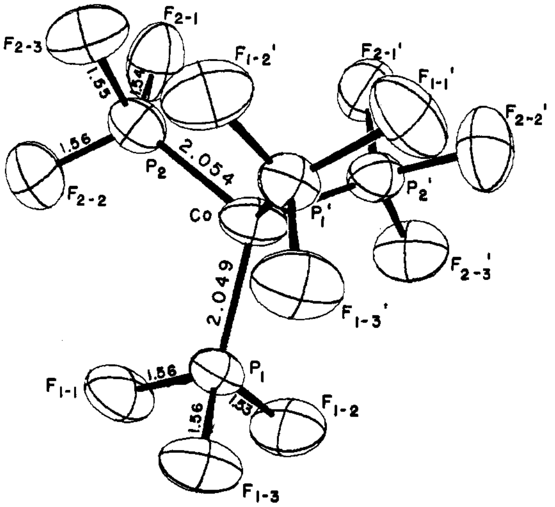

Figure 1.—A drawing of the $CoH(PF_3)_4$ molecule, with the H atom omitted. The 50% probability ellipsoids are shown.

TABLE III

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (Å)[a]

Atom	Min	Intermed	Max
Co	0.189 (3)	0.200 (3)	0.282 (5)
P(1)	0.180 (4)	0.211 (4)	0.243 (6)
P(2)	0.210 (5)	0.221 (5)	0.262 (6)
F(1,1)	0.20 (1)	0.26 (1)	0.36 (1)
F(1,2)	0.21 (1)	0.28 (1)	0.33 (1)
F(1,3)	0.21 (1)	0.25 (1)	0.33 (2)
F(2,1)	0.23 (1)	0.25 (1)	0.37 (1)
F(2,2)	0.22 (2)	0.30 (1)	0.37 (1)
F(2,3)	0.22 (1)	0.29 (1)	0.33 (2)

[a] Figure 1 provides an indication of the directions of these principal axes of vibration.

Interatomic distances and bond angles calculated from the final structure parameters are tabulated in Tables IV and V, respectively. The P atoms form a distorted tetrahedron around the Co atom. The P(1)–Co–P(1)′ angle is expanded to 118.0 (2)° from the tetrahedral angle of 109.5°; the P(2)–Co–P(2)′ angle is contracted to 101.8 (3)°. The fluorine atoms are arranged such that there is maximum F · · · F interaction along the edges of the tetrahedron and minimum interaction in the faces of the tetrahedron.

TABLE IV

INTERATOMIC DISTANCES (Å)

Atoms[a]	Distance	Atoms[a]	Distance
Co–P(1)	2.049 (4)	P(1)–P(1)′	3.513 (7)
Co–P(2)	2.054 (5)	P(1)–P(2)	3.354 (6)
Av Co–P[b]	2.052 (5)	P(1)–P(2)′	3.324 (6)
		P(2)–P(2)′	3.19 (1)
P(1)–F(1,1)	1.555 (9)		
P(1)–F(1,2)	1.529 (10)	F(1,1)–F(1,2)	2.27 (2)
P(1)–F(1,3)	1.564 (8)	F(1,1)–F(1,3)	2.34 (1)
P(2)–F(2,1)	1.542 (10)	F(1,2)–F(1,3)	2.33 (1)
P(2)–F(2,2)	1.555 (11)	F(2,1)–F(2,2)	2.33 (1)
P(2)–F(2,3)	1.550 (10)	F(2,1)–F(2,3)	2.31 (1)
		F(2,2)–F(2,3)	2.34 (1)
AvP–F	1.549 (12)	F(1,1)–F(2,2)	3.10 (1)
		F(1,2)-F(2,3)′	3.01 (1)
		F(1,3)–F(1,3)′	3.46 (2)
		F(2,1)–F(2,1)′	2.88 (2)

[a] Atoms with primes are related by twofold symmetry to the corresponding unprimed atoms. [b] A number in parentheses associated with an average quantity is the standard deviation of a single observation. This quantity is taken as the larger of that calculated from the inverse matrix for a single observation or from the range of values assumed to be from the same population. From these calculations we conclude that the individual estimates of error on the derived parameters are reasonable.

TABLE V

BOND ANGLES (DEG)

Atoms	Angle	Atoms	Angle
P(1)–Co–P(1)′	118.0 (2)	P(1)–Co–P(2)	109.7 (2)
P(2)–Co–P(2)′	101.8 (3)	P(1)′–Co-P(2)	108.2 (2)
Co–P(1)–F(1,1)	121.2 (4)	F(1,1)–P(1)–F(1,2)	94.6 (6)
Co–P(1)–F(1,2)	120.5 (4)	F(1,1)–P(1)–F(1,3)	97.3 (6)
Co–P(1)–F(1,3)	119.7 (3)	F(1,2)–P(1)–F(1,3)	97.8 (6)
Co–P(2)–F(2,1)	122.7 (5)	F(2,1)–P(2)–F(2,2)	97.8 (6)
Co–P(2)–F(2,2)	117.9 (4)	F(2,1–P(2)–F(2,3)	96.8 (6)
Co–P(2)–F(2,3)	118.4 (4)	F(2,2)–P(2)–F(2,3)	98.1 (7)
Av Co–P–F	120.7 (19)	Av F–P–F	97.1 (13)

The Hydrogen Atom.—The infrared and nmr spectra provide evidence for the existence of a Co–H bond in $CoH(PF_3)_4$. Bands[21] at 1973 and 1425 cm^{-1} in the ir spectra for $CoH(PF_3)_4$ and $CoD(PF_3)_4$, respectively, show the expected ratio of 1.384 and therefore are assigned to the frequencies of the Co–H and Co–D stretching vibrations. The nmr spectrum shows a large high-field chemical shift at τ 22.5,[22] which is characteristic of transition metal hydride complexes, *e.g.*, τ 20.7[4,23] for $CoH(CO)_4$. Thus the possibility of an F–H–F bond, *e.g.*, between F(2,1) and F(2,1)′, can be discounted.

The hydrogen atom was not detected in the final difference Fourier map. However, several chemically reasonable positions for the H atom can be eliminated on the basis of the arrangement of the other atoms in the molecule, thereby reducing the probable structural models to only one or two. The H atom may be considered either to be centered on an edge or centered in a face of the tetrahedron defined by the four P atoms surrounding the Co atom. The most reasonable tetrahedral edge on which to position the H atom is the

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[20] W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

[21] Th. Kruck, *Angew. Chem., Int. Ed. Engl.*, **6**, 53 (1967).

[22] Th. Kruck, W. Lang, and A. Engelmann, *ibid.*, **4**, 148 (1965).

[23] R. A. Friedel, I. Wender, S. L. Shufler, and H. W. Sternberg, *J. Amer. Chem. Soc.*, **77**, 3951 (1955).

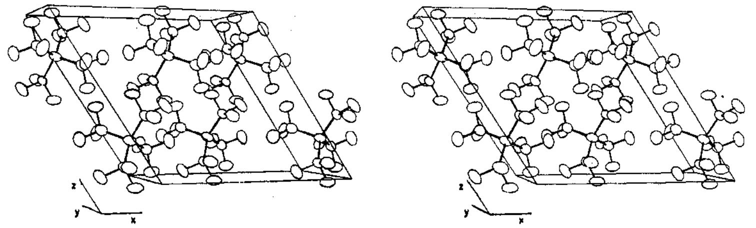

Figure 2.—A stereoscopic view of the unit cell of $CoH(PF_3)_4$.

one corresponding to the greatest P–Co–P angle, *viz.*, the P(1)–P(1)′ edge. Placing the H atom on the C_2 axis bisecting the P(1)–P(1)′ edge produces a distorted trigonal-bipyramidal molecule with the H atom in an equatorial position and the axial PF_3 groups displaced toward the H atom and the equatorial PF_3 groups displaced away from the H atom. If one assumes a Co–H distance of 1.60 Å, which is the Mn–H distance in $MnH(CO)_5$,[10] the H atom would be 1.84 Å from P(1) and 2.00 Å from F(1,3).

Alternatively, the H atom may be located in a tetrahedral face, thus implying a disordered crystal structure because of the crystallographic C_2 axis passing through the molecule. Both a twofold and a fourfold disorder are possible, but in either case an isolated molecule could be described as a distorted trigonal bipyramid with H axial and the adjacent equatorial PF_3 groups displaced toward the H atom. A twofold disordered structure may be described as having a statistical average of $^1/_2$ H in the P(1)–P(1)′–P(2) face (trans to P(2)′) and $^1/_2$ H in the P(1)–P(1)′–P(2)′ face (trans to P(2)). A second twofold disordered structure has $^1/_2$ H trans to P(1) and $^1/_2$ H trans to P(1)′. The fourfold disordered structure would have a statistical average of $^1/_4$ H in each of the four tetrahedral faces.

Table VI summarizes the P···H and F···H distances for various positions for the H atom.

TABLE VI

ALTERNATIVE POSITIONS FOR THE H ATOM IN $CoH(PF_3)_4$

Model	H position (1.6 Å from Co)	Av P···H distance, Å	Av F···H distance, Å	Trigonal-bipyramidal configu
1	P(1)–P(1)′ edge	1.84	2.00	H equatorial
2	Trans to P(1)	2.08	2.65	H axial, twofold disorder
3	Trans to P(2)	2.21	2.77	H axial, twofold disorder

On the basis of a minimization of nonbonded repulsions given in Table VI, we favor models 2 and 3 over model 1. This is in agreement with the observation, stated previously, that the maximum F···F interaction (Table IV) is along the edges of the tetrahedron and the minimum interaction is in the faces of the tetrahedron. (All of these intramolecular interactions exceed twice the van der Waals radius for F.) Such a choice is also consistent with the spectroscopic evidence for the structure of $CoH(CO)_4$. It is clearly not possible to choose among models 2 and 3 and a combination of these two models. For a molecule with H trans to P(2)′, the fractional coordinates of H (Co–H of 1.60 Å) are 0.0636, 0.0154, 0.2054. The equatorial PF_3 ligands are displaced toward the hydrogen atom such that the H–Co–P angles are 70, 72, and 78° for P(1), P(1)′, and P(2), respectively. The distance of the Co atom from the P(1)–P(1)′–P(2) plane is 0.59 Å. This type of displacement is generally observed in transition metal hydride complexes. Table VII summarizes these displacements and also the trans hydrogen–metal–ligand angles observed from X-ray structures of five-coordinate complexes, all of which are trigonal bipyramids (sometimes distorted) with an H atom in an axial position.

TABLE VII

FIVE-COORDINATE METAL HYDRIDE COMPLEXES

Compd ($P = P(C_6H_5)_3$)	Metal-to-plane distance, Å	Trans H–M–L angle, deg	Ref
$IrH(CO)_2P_2$	0.23	171	*a*
$CoH(N_2)P_3$	0.29 0.32	168 (4) 166 (4)	*b*
$RhH(CO)P_3$	0.36	170 (5)	*c*
$IrH(NO)P_3{}^+$	0.51	?	*d*
$CoH(PF_3)_4$	0.59	?	*e*
$RhHP_4$	0.70[f]	180[f]	*g*

[a] M. Ciechanowicz, A. C. Skapski, and P. G. H. Troughton, Collected Abstracts, VIIIth International Congress of Crystallography, Stony Brook, N. Y., 1969, p s172; *Acta Crystallogr.*, **22,** s172 (1969). [b] B. R. Davis, N. C. Payne, and J. A. Ibers, *Inorg. Chem.*, **8,** 2719 (1969). [c] S. J. La Placa and J. A. Ibers, *Acta Crystallogr.*, **18,** 511 (1965). [d] D. M. P. Mingos and J. A. Ibers, in preparation. [e] This work. [f] Assumes that the H atom is on the C_3 axis. [g] R. W. Baker and P. Pauling, *Chem. Commun.*, 1495 (1969).

The PF_3 Ligands.—PF_3 is generally considered to be a strong π-bonding ligand in transition metal complexes.[21] The highly electronegative F atoms lower the energy of the 3d orbitals of P and thereby increase the electron-accepting ability of the ligand. Thus PF_3 is comparable with CO in bonding character. The PF_3 ligand replaces CO in substitution reactions, but mixtures of intermediate and final substitution products are often obtained,[24] indicating a similarity in the nature of the metal–CO and metal–PF_3 bonds. Force constant calculations have suggested both $k_{M-P} > k_{M-C}$[25] and $k_{M-P} < k_{M-C}$.[26] The PF_3–metal complexes are thermally more stable than the corresponding CO complexes. Thus, $CoH(PF_3)_4$ decomposes at 250° in contrast to −18° for $CoH(CO)_4$.[21] A mass spectral study[27] of the series $CoH(CO)_x(PF_3)_{4-x}$, $x = 0–4$, has

(24) C. A. Udovich and R. J. Clark, *Inorg. Chem.*, **8,** 938 (1969).

(25) F. A. Cotton, *ibid.*, **3,** 702 (1964).

(26) A. Loutellier and M. Bigorgne, *Bull. Soc. Chim. Fr.*, 3186 (1965).

(27) F. E. Saalfeld, M. V. McDowell, S. K. Gondal, and A. G MacDiarmid, *J. Amer. Chem. Soc.*, **90,** 3684 (1968).

shown that the Co–CO and Co–PF_3 bond energies are essentially identical (56 ± 15 kcal/mol). Also, calculated heats of formation of the series of complexes imply similar bonding character for CO and PF_3 to Co.

Corresponding to these strong bonding abilities of PF_3 we find the $M-PF_3$ bond distance to be short compared with $M-PR_3$ where R is alkyl or aryl. The average Co–P distance in $CoH(PF_3)_4$ is 2.052 (5) Å. This is significantly shorter than $Co-PR_3$ distances that have been reported: $[Co(C_5H_5)P(C_6H_5)_2]_2$ (bridged P), 2.16 (1) Å;[28] $[Co(CO)_3P(n\text{-}C_4H_9)_3]_2$, 2.18 (2) Å;[29] $Co(C_3H_4CO_2C_6H_5)(CO)_2P(C_6H_5)_3$, 2.18 Å;[30] $CoH(N_2)\{P(C_6H_5)_3\}_3$, 2.19 (1) Å (av);[31] $Co\{P(C_6H_5)_2H\}_3Br_2$, 2.20 (2) Å (av);[32] $Co(C_9H_{11})_2\{P(C_2H_5)_2(C_6H_5)\}_2$, 2.23 (1) Å;[33] $Co_3CCH_3(CO)_8P(C_6H_5)_3$, 2.25 Å;[34] $Co(C_2HF_4)(CO)_3P(C_6H_5)_3$, 2.27 (1) Å.[35]

A similar contraction has been observed[36] for metal–fluoroalkyl bonds relative to metal–alkyl bonds. The contraction of *ca.* 0.07 Å for Co–C derivatives is considerably less than that observed above for the Co–P analogs.

The P–F bond distances in $CoH(PF_3)_4$ range from 1.52 (1) to 1.56 (1) Å, with an average of 1.55 (1) Å. These values are similar to the P–F distances (Å) obtained for the following compounds: $PF_3B_4F_6$ (1.51),[37] PF_3O (1.52),[38,39] PF_3S (1.53),[38,39] PF_5 (1.53 axial, 1.58 equatorial),[40] PF_3BH_3 (1.54),[41] PF_4CH_3 (1.54 axial, 1.61 equatorial),[42] $PF_3(CH_3)_2$ (1.55 equatorial, 1.64 axial),[42] PF_3 (1.57),[43] PF_2H (1.58),[44] PF_6^- (1.58).[45] (Structures reported before 1950 have been omitted from the tabulation.) The average F–P–F angle in $CoH(PF_3)_4$ is 97.1 (13)°, which compares favorably with 97.8 (2) for PF_3 itself.[43]

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The Crystal Structure and Absolute Configuration of D-β_2-(*SSS*)-(Triethylenetetramine-(*S*)-prolinato)cobalt(III) Tetrachlorozincate

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The crystal structure and absolute configuration of D-β_2-(*SSS*)-(triethylenetetramine-(*S*)-prolinato)cobalt(III) tetrachlorozincate, D-β_2-(*SSS*)-[Co(trien)((*S*)-Pro)]$ZnCl_4$, has been determined from three-dimensional X-ray data collected by counter methods. The compound crystallizes in space group $P2_1$ (C_2^2; no. 4), with a = 7.01 (1) Å, b = 15.58 (2) Å, c = 9.66 (1) Å, β = 109.9 (3)°, and Z = 2. Measured and calculated densities are, respectively, 1.76 (2) and 1.76 (1) g cm^{-3}. The structure has been refined by full-matrix least-squares techniques to a final residual R = 0.055 for 1694 independent nonzero reflections. The crystal is composed of discrete D-β_2-(*SSS*)-Co(trien)((*S*)-Pro)$^{2+}$ cations and $ZnCl_4^{2-}$ anions held together by hydrogen bonds and electrostatic forces. The coordination around cobalt is octahedral with the quadridentate trien ligand in the β configuration and the proline residue coordinated through the amino nitrogen and a carboxyl oxygen. Large angular distortions within the D-β_2-(*SSS*)-Co(trien)((*S*)-Pro)$^{2+}$ cation are shown to relieve steric crowding within the complex. A detailed comparison is made between this structure and that of the related complex cation L-β_2-(*RRS*)-Co(trien)((*S*)-Pro)$^+$.

Introduction

It was shown that the coordination of sarcosine in Co(en)$_2$sar^{2+} [1,2] and Co(trien)sar^{2+} (en = ethylenediamine, sar = *N*-methylglycine, trien = triethylenetetramine) is stereospecific with respect to the asymmetric *N*-methyl center.[3] For a given configuration

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