A correlation exists in the nitrogen- and sulfur-bridged iron carbonyls between the Fe–Fe and mean Fe–X (X = N, S) bond lengths, with a longer Fe–Fe bond associated with a shorter Fe–X bond. This relationship has previously been pointed out[32] for the sulfur-bridged compounds and is more clearly illustrated in the nitrogen-bridged series because of the larger bond length differences involved.

The first question which must be asked in any attempt to understand the basis of the long Fe–Fe and short Fe–N bonds in $[CH_3NFe(CO)_3]_2$ is whether these distances are simply a stereochemical consequence of the presence of the bond linking the two bridging nitrogen atoms or whether they stem from some other property of the bridging group. One possible approach to resolving this question is through structural analyses of other compounds having the same basic bridging configuration but different bridging ligands. Such studies are now in progress, and further discussion of this point will be reserved until their completion.

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The Structure of Chlorodicarbonylbis(triphenylphosphine)iridium(I)–Benzene, $IrCl(CO)_2(P(C_6H_5)_3)_2 \cdot C_6H_6$

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The structure of chlorodicarbonylbis(triphenylphosphine)iridium(I)–benzene, $IrCl(CO)_2(P(C_6H_5)_3)_2 \cdot C_6H_6$, has been determined from three-dimensional X-ray data collected by counter methods. The compound crystallizes with four formula units in space group C_{2h}^5-$P2_1/c$ of the monoclinic system in a cell of dimensions a = 18.019 (4) Å, b = 12.240 (4) Å, c = 18.237 (6) Å, and β = 102.51 (1)°. The measured density of 1.51 (1) g/cm³ agrees well with the calculated value of 1.50 g/cm³. The benzene molecule is well separated from the iridium atom. The coordination about iridium is that of a trigonal bipyramid, with *trans* phosphines at the apices. Partial disorder among the chlorine atom and carbonyl groups in the equatorial plane precludes a precise determination of all features of the molecular structure. Nevertheless, the fact that the coordination about iridium in this complex is very different from that in the isoelectronic $IrCl(CO)(NO)(P(C_6H_5)_3)_2^+$ cation has been established. The conventional R factor for the 1657 independent reflections above background is 0.093.

Introduction

We recently reported the preparation[1] and molecular structures[2,3] of the compounds $[IrX(CO)(NO)(P(C_6H_5)_3)_2][BF_4]$, where X = Cl and I. Both compounds were prepared by reaction of $NOBF_4$ with the parent d^8 complexes $IrX(CO)(P(C_6H_5)_3)_2$. In these compounds the coordination about iridium is that of a tetragonal pyramid, with *trans* phosphines, the halogen, and the carbonyl in the basal plane, and the nitrosyl group at the apex. The Ir–N–O linkage is bent, with an Ir–N–O angle of approximately 125°. These structure determinations represented the first well-authenticated cases of such a bent nitrosyl linkage in transition metal compounds.

As CO is isoelectronic with NO^+, we thought it would be of interest to examine the structure of the compound formed by addition of CO to the parent molecule. The results of such an examination are reported here.

Experimental Section

Preparation of the Crystal.—Vaska[4] has reported the preparation and characterization of the complex $IrCl(CO)_2(P(C_6H_5)_3)_2$ and on the basis of infrared evidence (ν_{CO} 1923, 1976 cm^{-1}) deduced a trigonal-bipyramidal structure, with *trans*-triphenylphosphine groups. The observed bands were assigned to the normal modes of vibration expected for a planar $IrCl(CO)_2$ fragment, with C_{2v} symmetry, and equivalent CO ligands.

Crystals suitable for data collection were prepared by an adaptation of Vaska's method. A deoxygenated, saturated solution of chlorocarbonylbis(triphenylphosphine)iridium(I) in benzene was prepared under dry nitrogen gas. Into the refluxing solution a stream of carbon monoxide was passed for 10 min; then the solution was allowed to cool under an atmosphere of carbon monoxide. Pale yellow crystals were formed, a Nujol mull of which showed absorption bands attributable to ν_{CO} at 1925 and 1975 cm^{-1}. Elemental analysis suggested the presence of a benzene molecule of crystallization. *Anal.*[5] Calcd for $IrC_{44}H_{36}O_2P_2Cl$ ($IrCl(CO)_2(P(C_6H_5)_3)_2 \cdot C_6H_6$): C, 59.62; H, 4.09. Found: C, 59.66; H, 3.98.

Collection and Reduction of the X-Ray Intensity Data.—An optical and X-ray analysis of the crystals showed monoclinic symmetry, Laue group 2/m. The systematic absences observed on Weissenberg photographs of the layers $h0l$ through $h2l$ and on precession photographs of the layers $0kl$, $1kl$, $hk0$, and $hk1$ are $h0l$ for l odd and $0k0$ for k odd. These absences are consistent with space group C_{2h}^5-$P2_1/c$. The unit cell dimensions, as established from a least-squares refinement of the setting angles of 13

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[1] D. J. Hodgson, N. C. Payne, J. A. McGinnety, R. G. Pearson, and J. A. Ibers, *J. Am. Chem. Soc.*, **90**, 4486 (1968).

[2] D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, **7**, 2345 (1968).

[3] D. J. Hodgson and J. A. Ibers, *ibid.*, **8**, 1282 (1969).

[4] L. Vaska, *Science*, **152**, 769 (1966).

[5] Analyses were performed by Miss Hilda Beck of this department.

high-angle reflections,[6] are $a = 18.019$ (4) Å, $b = 12.240$ (4) Å, $c = 18.237$ (6) Å, and $\beta = 102.51$ (1)° (Cu Kα_1 radiation, λ 1.5406 Å, at 22°). A density of 1.51 (1) g/cm^3, measured by flotation in a mixture of heptane and 1,1,2-trichloro-1,2,2-trifluoroethane, agrees well with the value of 1.50 g/cm^3 calculated for four formula units in the cell. Thus no crystallographic symmetry conditions need be imposed on the molecule.

Data were collected on a Picker four-circle automatic diffractometer by methods previously described.[6] Details are: prismatic crystal, with well-developed prismatic faces of the form $\{011\}$ and pinacoidal faces of the forms $\{100\}$ and $\{001\}$. Approximate crystal dimensions are 0.61 × 0.20 × 0.18 mm. The crystal was mounted in a capillary under nitrogen and oriented with its long dimension (010) approximately along the spindle axis. From the mosaicity check the average width at half-height was 0.15°. Data collection was by θ–2θ scan; the takeoff angle was 2.0°. Cu K$\bar{\alpha}$ radiation was filtered after diffraction through 0.5 mil of Ni. The counter aperture 4 mm × 4 mm was positioned 34 cm from the crystal. The scan range was -0.75 to $+1.0°$ in 2θ from the calculated 2θ position, the scan rate was 1 deg/min, and the background counts were 10 sec at each end of the scan range. Attenuators (Cu foil) were inserted automatically on intense peaks. The pulse height analyzer accepted a 90% window.

A total of 1696 reflections were examined within the sphere $\theta(\text{Cu K}\alpha_1) \leq 35°$. No further data were collected since significant crystal decomposition had occurred, as ascertained from the significant and variable decrease in intensity of four standard reflections. That this decrease was not the result of crystal movement was ascertained by periodic redeterminations of the crystal orientation matrix. Of the 1696 reflections measured, 1657 had $I > 2\sigma(I)$ and these were used in subsequent calculations.

The data were processed as previously described.[6] In the determination of $\sigma(I)$ a value of p of 0.04 was used. An absorption correction was applied;[7] transmission factors varied between 0.23 and 0.33, based on a linear absorption coefficient of 89.0 cm^{-1}.

Solution and Refinement of the Structure.—Initially the data were brought approximately to a common scale through the use of the average dropoff of intensity of the standard reflections. This was necessarily approximate, since the decrease in the standards ranged from 12.5 to 79%.

The structure was solved by normal heavy-atom techniques. A trial structure, including only the Ir and the two P atoms, led to values of R_1 and R_2 of 0.41 and 0.49, where $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2)^{1/2}$ and where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes with the weights w taken as $4F_o^2/\sigma^2(F_o^2)$. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$. Atomic scattering factors used are from the following sources: Ir, ref 8; other heavy atoms, ref 9; H, ref 10. Values of $\Delta f'$ and $\Delta f''$ for Ir, P, and Cl[11] were included in the calculated structure factors.[12] In subsequent refinements the phenyl rings and the benzene molecule were included as groups[13] (C–C = 1.392 Å, D_{6h} symmetry); the hydrogen atoms of these rings were included as fixed contributions to $|F_c|$ (C–H = 0.9 Å, $B = 5.0$ Å^2). In the refinements, the carbon atoms of the phenyl rings were allowed to vibrate with individual thermal parameters, while the atoms in the benzene molecule of crystallization were constrained to an overall group thermal parameter.

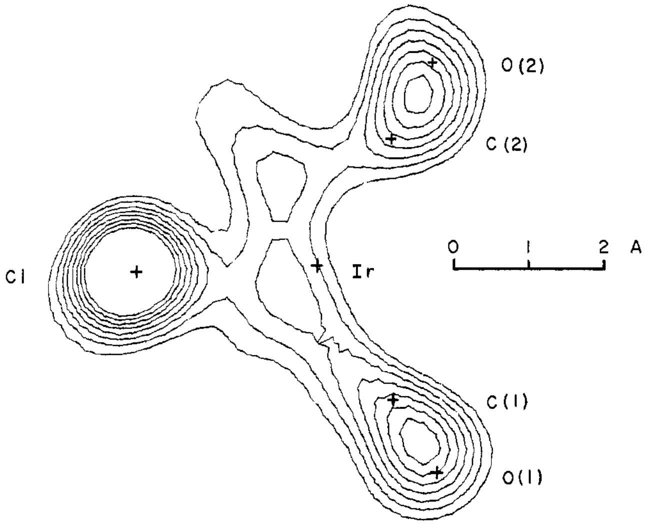

Figure 1.—Difference Fourier synthesis in the equatorial plane, showing the electron density of the Cl and CO ligands. Contours are drawn at intervals of 0.5 e$^-$/Å^3, from 1.0 to 5.0 e$^-$/Å^3. Final positions of the atoms in the equatorial plane are shown. The disordered atoms are not shown.

With only the Ir and the two P atoms allowed to vibrate anisotropically and all other atoms included and allowed to vibrate isotropically, the refinement converged to values of R_1 and R_2 of 0.15 and 0.19, respectively.

At this stage the scaling of the data was included in the least-squares refinement. In essence it was assumed that the scale factor k for reflection n could be written as $k = k_0 + a_1t_n + a_2t_n^2$, where t_n is the cumulative X-ray exposure of the crystal at the time the nth reflection was observed, and k_0, a_1, and a_2 were refined as variables. This method is described in greater detail elsewhere.[14] In applying this scaling procedure, the data were first reprocessed to remove the original decomposition correction. A subsequent refinement of the same model, with the inclusion of this scaling procedure, reduced the values of R_1 and R_2 to 0.089 and 0.095.

The final model showed clear evidence of disorder in the equatorial plane. The C–O bond lengths in the carbonyl groups were very short (0.9 Å) compared with values of 1.1–1.2 Å observed in analogous compounds. We have found this to be symptomatic of X/CO disorder in previous structures[15,16] so a difference Fourier synthesis was computed in the equatorial plane from a set of structure factors calculated omitting the contributions of the Cl and the two CO ligands. This synthesis is shown in Figure 1, and the lack of resolution of the C and O atoms is apparent.

A series of calculations was then made, in which the disorder was assumed to result in fractional chlorine atoms at the three equatorial sites Cl(1), Cl(2), and Cl(3) and fractional carbonyl ligands at the same sites, C(3) and O(3), C(1) and O(1), and C(2) and O(2), respectively. The necessary constraints among the derivatives were taken into account, and the multiplicity parameters of Cl(1) and C(1) were refined as variables in the final model, with the total ligand multiplicity at each site being constrained to 1.0. All disordered atoms had fixed positional and thermal parameters, which corresponded to mean Ir–Cl bond lengths of 2.41 Å, Ir–C lengths of 2.00 Å, and C–O lengths of 1.12 Å, with a linear Ir–C–O geometry. This model converged at $R_1 = R_2 = 0.093$, with a 0.67:0.14:0.19 disorder of the chlorine atom among the three sites (see Table II).

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(7) Programs used in this work include, in addition to various local programs for the CDC 6400, local modifications of W. C. Hamilton's GONO absorption correction program, Zalkin's FORDAP Fourier program, the Busing–Levy ORFFE error function program, and Johnson's ORTEP thermal ellipsoid plotting program.

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TABLE I

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (IN ELECTRONS) FOR $IrCl(CO)_2(P(C_6H_5)_3)_2 \cdot C_6H_6$

H	L	FO	FC
***** K = 0 *****			
0	2	421	476
0	4	266	257
0	6	206	188
0	8	198	196
0	10	97	97
1	-12	37	23
1	-10	6	6
1	-8	52	46
1	-6	85	71
1	-4	136	130
1	-2	100	101
1	0	140	162
1	2	135	126
1	4	13	19
1	6	26	27
1	8	86	76
1	10	75	80
1	12	12	24
2	-12	91	87
2	-10	119	119
2	-8	219	196
2	-6	274	277
2	-4	227	214
2	-2	421	429
2	0	333	380
2	2	289	294
2	4	190	189
2	6	233	230
2	8	166	172
2	10	70	64
2	12	51	36
3	-12	97	93
3	-10	131	149
3	-8	166	170
3	-6	167	140
3	-4	169	181
3	-2	232	219
3	0	264	294
3	2	190	215
3	4	163	206
3	6	262	243
3	8	139	125
3	12	19	12
4	-12	61	72
4	-10	97	90
4	-8	214	202
4	-6	162	135
4	-4	305	329
4	-2	41	46
4	0	104	115
4	2	22	15
4	4	104	120
4	6	42	49
4	8	82	80
4	10	78	75
5	-12	104	114
5	-10	160	188
5	-8	237	235
5	-6	232	229
5	-4	144	121
5	-2	266	271
5	0	208	240
5	2	164	169
5	4	144	184
5	6	179	160
5	8	106	103
5	10	67	67
6	-12	17	20
6	-10	29	25
6	-8	28	26
6	-6	14	18
6	-4	44	48
6	-2	4	8
6	0	7	13
6	2	52	49
6	4	37	47
6	6	43	57
6	8	36	26
6	10	9	1
7	-12	132	139
7	-10	194	195
7	-8	225	215
7	-6	183	175
7	-4	241	229
7	-2	321	341
7	0	250	261
7	2	146	153
7	4	68	92
7	6	105	97
7	8	88	80
8	-12	46	47
8	-10	78	92
8	-8	42	44
8	-6	75	70
8	-4	122	117
8	-2	164	150
8	0	59	65
8	2	85	72
8	4	8	16
8	6	76	50
8	8	87	72
9	-10	138	136
9	-8	170	166
9	-6	177	176
9	-4	134	142
9	-2	196	196
9	0	91	85
9	2	96	89
9	4	61	94
9	6	61	64
10	-10	169	172
10	-8	181	177
10	-6	147	156
10	-4	135	134
10	-2	177	178
10	0	93	90
10	2	74	77
10	4	59	69
10	6	81	62
11	-10	80	75
11	-8	61	61
11	-6	51	55
11	-4	58	54
11	-2	10	11
11	0	20	18
11	2	8	3
11	4	20	24
12	-8	149	148
12	-6	144	130
12	-4	143	134
12	-2	147	141
12	0	89	88
12	2	61	44
13	-6	26	17
13	-4	24	28
13	-2	9	9
13	0	45	50
***** K = 1 *****			
0	1	360	286
0	2	77	75
0	3	336	346
0	4	54	52
0	5	214	201
0	7	207	188
0	8	46	45
0	9	149	145
0	10	64	57
0	11	121	125
0	12	21	15
0	13	103	89
1	-13	32	16
1	-12	37	36
1	-11	32	24
1	-10	54	53
1	-9	19	23
1	-8	32	35
1	-7	64	63
1	-6	113	104
1	-5	126	110
1	-4	100	87
1	-3	116	95
1	-2	141	126
1	-1	45	48
1	0	87	73
1	1	49	50
1	2	126	132
1	3	18	9
1	4	87	79
1	5	39	37
1	6	69	72
1	7	70	57
1	8	44	47
1	9	48	43
1	10	37	36
1	11	33	35
1	12	34	31
2	-13	90	89
2	-12	19	18
2	-11	109	123
2	-10	21	20
2	-9	185	179
2	-8	38	37
2	-7	237	224
2	-6	44	44
2	-5	204	206
2	-4	62	63
2	-3	267	250
2	-2	47	38
2	-1	301	286
2	0	95	104
2	1	196	222
2	2	129	142
2	3	106	130
2	4	143	153
2	5	202	194
2	6	70	58
2	7	188	173
2	8	88	60
2	9	105	102
2	10	47	54
2	11	108	88
2	12	45	40
3	-13	97	80
3	-12	28	28
3	-11	66	67
3	-10	15	12
3	-9	160	160
3	-8	20	20
3	-7	226	219
3	-6	48	44
3	-5	212	210
3	-4	110	109
3	-3	125	125
3	-2	88	77
3	-1	234	212
3	0	9	7
3	1	108	146
3	2	190	217
3	3	123	149
3	4	21	25
3	5	101	108
3	6	10	12
3	7	86	84
3	8	7	4
3	9	100	96
3	10	25	20
3	11	56	61
3	12	16	16
4	-13	41	47
4	-12	24	25
4	-11	80	86
4	-10	8	7
4	-9	120	119
4	-8	22	23
4	-7	184	174
4	-6	63	67
4	-5	131	136
4	-4	64	60
4	-3	116	100
4	-2	58	53
4	-1	282	313
4	0	60	57
4	1	45	62
4	2	95	128
4	3	15	12
4	4	99	117
4	5	103	112
4	6	116	112
4	7	90	109
4	8	65	73
4	9	47	46
4	10	62	64
4	11	63	56
5	-13	117	113
5	-12	22	23
5	-11	114	134
5	-10	79	82
5	-9	189	193
5	-8	34	36
5	-7	254	252
5	-6	59	60
5	-5	171	161
5	-4	23	24
5	-3	204	217
5	-2	21	15
5	-1	274	288
5	0	170	177
5	1	152	198
5	2	12	18
5	3	153	203
5	4	16	15
5	5	150	176
5	6	41	54
5	7	140	153
5	8	11	11
5	9	86	98
5	11	92	87
6	-13	15	7
6	-12	25	30
6	-11	24	19
6	-10	56	58
6	-9	9	7
6	-8	78	77
6	-7	10	12
6	-6	57	56
6	-5	13	6
6	-4	100	87
6	-3	7	12
6	-2	11	7
6	-1	17	13
6	0	34	33
6	1	10	10
6	2	77	95
6	3	28	36
6	4	68	84
6	6	29	24
6	7	15	5
6	8	55	51
6	9	23	16
6	10	38	44
7	-12	41	42
7	-11	127	141
7	-10	30	31
7	-9	168	176
7	-8	5	3
7	-7	174	170
7	-6	13	14
7	-5	170	180
7	-4	63	72
7	-3	238	236
7	-2	13	9
7	-1	239	244
7	0	68	75
7	1	146	191
7	2	26	32
7	3	105	144
7	4	19	34
7	5	132	161
7	6	16	21
7	7	104	123
7	8	49	35
7	9	89	91
8	-12	65	66
8	-11	41	48
8	-10	57	61
8	-9	63	66
8	-8	47	51
8	-7	87	102
8	-6	56	59
8	-5	63	49
8	-4	11	21
8	-3	74	72
8	-2	65	61
8	-1	110	103
8	0	11	7
8	1	62	97
8	2	30	36
8	3	29	36
8	4	18	26
8	5	49	56
8	6	11	15
8	7	72	51
8	8	12	17
9	-11	88	92
9	-10	20	21
9	-9	123	119
9	-8	57	59
9	-7	96	102
9	-6	78	82
9	-5	115	123
9	-4	90	83
9	-3	159	165
9	-2	34	25
9	-1	158	154
9	0	106	98
9	1	72	87
9	2	48	69
9	3	64	101
9	4	27	27
9	5	62	78
9	6	38	27
9	7	67	65
10	-10	16	11
10	-9	118	117
10	-8	15	6
10	-7	124	125
10	-6	14	12
10	-5	102	106
10	-4	27	28
10	-3	113	111
10	-1	105	97
10	0	16	12
10	1	88	105
10	2	13	10
10	3	69	80
10	4	16	28
10	5	55	77
10	6	15	25
11	-9	49	48
11	-8	79	88
11	-7	34	35
11	-6	46	50
11	-5	41	40
11	-4	59	61
11	-3	80	90
11	-2	55	47
11	-1	51	49
11	0	74	75
11	1	23	26
11	2	38	45
11	3	22	29
11	4	15	22
11	5	19	24
12	-8	43	41
12	-7	100	92
12	-6	21	17
12	-5	112	103
12	-3	136	137
12	-2	20	22
12	-1	106	100
12	0	48	42
12	1	66	80
12	2	25	18
12	3	55	65
13	-5	8	6
13	-4	46	45
13	-3	10	12
13	-2	35	38
13	-1	18	21
13	0	30	29
***** K = 2 *****			
0	0	33	19
0	1	89	43
0	2	139	111
0	3	38	18
0	4	156	150
0	5	71	65
0	6	174	167
0	7	15	14
0	8	129	128
0	9	51	51
0	10	120	125
0	11	51	48
0	12	135	128
1	-13	90	94
1	-12	44	36
1	-11	95	98
1	-9	142	133
1	-8	34	39
1	-7	56	50
1	-6	138	127
1	-5	46	42
1	-4	85	70
1	-3	300	274
1	-2	168	139
1	-1	32	41
1	0	25	22
1	1	62	23
1	2	117	102
1	3	32	29
1	4	27	9
1	5	57	49
1	6	15	20
1	7	58	51
1	8	24	10
1	9	108	103
1	10	44	49
1	11	73	71
1	12	36	46
2	-13	12	6
2	-12	88	97
2	-11	15	9
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9	2	72	64
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9	4	71	60
10	-7	13	17
10	-6	72	77
10	-4	78	75
10	-3	18	13
10	-2	74	78
10	-1	23	18
10	0	58	55
10	1	8	6
10	2	63	49
11	-4	124	110
11	-3	26	33
11	-2	111	116
11	-1	24	25
***** K = 6 *****			
0	0	109	101
0	1	30	19
0	2	193	147
0	3	14	14
0	4	139	120
0	5	18	14
0	6	90	83
0	7	17	11
0	8	73	75
0	9	21	17
1	-10	15	18
1	-9	102	106
1	-8	23	22
1	-7	125	125
1	-5	157	160
1	-4	7	8
1	-3	151	155
1	-2	40	23
1	-1	210	180
1	0	7	9
1	1	183	155
1	2	49	47
1	3	196	180
1	4	83	57
1	5	220	193
1	6	62	59
1	7	146	123
1	8	26	30
1	9	105	90
2	-10	49	49
2	-9	46	49
2	-8	58	65
2	-7	44	50
2	-6	103	102
2	-5	59	56
2	-4	151	143
2	-3	84	83
2	-2	89	79
2	-1	109	100
2	0	87	85
2	1	98	77
2	2	91	74
2	3	96	78
2	4	72	69
2	5	70	67
2	6	40	46
2	7	24	25
2	8	53	45
2	9	35	29
3	-10	24	12
3	-9	87	84
3	-8	43	44
3	-7	113	118
3	-6	42	45
3	-5	112	118
3	-4	108	112
3	-3	111	104
3	-2	100	95
3	-1	136	134
3	0	49	55
3	1	180	140
3	2	105	86
3	3	126	110
3	4	108	85
3	5	130	120
3	6	90	86
3	7	116	102
3	8	73	67
4	-10	35	43
4	-9	82	79
4	-8	51	54
4	-7	127	134
4	-6	110	103
4	-5	138	145
4	-4	46	42
4	-3	113	124
4	-2	23	23
4	-1	178	166
4	0	38	37
4	1	166	139
4	2	32	30
4	3	134	118
4	4	33	36
4	5	104	92
4	6	17	19
4	7	97	73
5	-9	43	45
5	-8	64	66
5	-7	12	10
5	-6	103	108
5	-5	56	61
5	-4	133	120
5	-3	77	80
5	-2	95	100
5	-1	117	112
5	0	69	75
5	1	80	67
5	2	94	86
5	3	12	4
5	4	79	63
5	5	17	11
5	6	47	35
5	7	19	20
6	-9	131	136
6	-8	38	40
6	-7	131	139
6	-6	36	32
6	-5	152	151
6	-4	6	0
6	-3	173	170
6	-2	30	30
6	-1	191	187
6	1	144	133
6	2	17	16
6	3	86	86
6	4	24	18
6	5	88	77
6	6	13	5
7	-8	86	98
7	-7	20	18
7	-6	101	109
7	-5	8	3
7	-4	95	101
7	-3	14	15
7	-2	62	65
7	-1	21	27
7	0	59	45
7	1	30	25
7	2	80	82
7	3	18	11
7	4	47	46
7	5	20	12
8	-7	130	124
8	-6	38	38
8	-5	126	126
8	-4	61	60
8	-3	132	130
8	-2	58	55
8	-1	112	112
8	0	34	35
8	1	90	90
8	2	47	42
8	3	81	73
8	4	41	36
9	-6	60	60
9	-5	73	66
9	-4	44	48
9	-3	87	76
9	-2	30	31
9	-1	72	66
9	0	27	27
9	1	64	55
9	2	29	37
10	-3	74	71
10	-2	86	73
10	-1	74	71
***** K = 7 *****			
0	1	110	93
0	2	11	5
0	3	138	118
0	4	37	36
0	5	146	125
0	6	31	31
0	7	94	87
0	8	37	29
1	-8	58	49
1	-7	8	18
1	-6	67	67
1	-5	15	14
1	-4	53	60
1	-3	32	15
1	-2	62	73
1	-1	67	52
1	0	124	120
1	1	60	53
1	2	111	98
1	3	49	44
1	4	128	113
1	5	70	64
1	6	114	98
1	7	43	45
1	8	85	77
2	-8	65	67
2	-7	85	88
2	-6	52	56
2	-5	120	111
2	-4	26	34
2	-3	125	119
2	-2	64	42
2	-1	69	78
2	0	88	58
2	1	66	60
2	2	55	44
2	3	121	101
2	4	18	12
2	5	87	76
2	6	14	17
2	7	52	44
3	-8	47	41
3	-7	38	42
3	-6	29	30
3	-5	75	84
3	-4	42	59
3	-3	100	102
3	-2	35	33
3	-1	108	105
3	0	53	44
3	1	119	98
3	2	90	84
3	3	140	123
3	4	131	117
3	5	111	95
3	6	109	108
3	7	61	65
4	-8	100	102
4	-7	74	75
4	-6	78	84
4	-5	74	62
4	-4	74	71
4	-3	65	65
4	-2	74	67
4	-1	22	27
4	0	81	67
4	1	56	45
4	2	101	92
4	3	24	20
4	4	79	76
4	5	24	22
4	6	68	63
5	-8	9	9
5	-7	92	97
5	-6	6	5
5	-5	126	128
5	-4	39	40
5	-3	133	136
5	-2	52	52
5	-1	85	87
5	0	46	42
5	1	122	110
5	2	36	34
5	3	119	102
5	4	53	56
5	5	109	105
6	-6	76	72
6	-5	9	8
6	-4	99	94
6	-3	29	28
6	-2	103	103
6	-1	16	16
6	0	86	75
6	1	26	25
6	2	78	78
6	3	34	28
6	4	65	61
7	-6	11	8
7	-5	111	115
7	-4	9	5
7	-3	97	98
7	-2	13	14
7	-1	84	89
7	0	18	7
7	1	98	86
7	2	15	5
7	3	98	90
8	-4	57	63
8	-3	56	52
8	-2	69	70
8	-1	60	62
8	0	73	56
8	1	72	66
***** K = 8 *****			
0	0	94	86
0	2	122	103
0	3	13	8
0	4	132	106
0	5	12	6
0	6	115	108
1	-5	20	21
1	-4	25	23
1	-3	28	29
1	-2	50	46
1	-1	30	30
1	0	45	38
1	1	52	48
1	2	28	27
1	3	52	54
1	4	67	60
1	5	41	32
1	6	54	52
2	-6	82	82
2	-5	19	24
2	-4	63	65
2	-3	22	22
2	-2	56	53
2	-1	17	11
2	0	91	84
2	1	53	36
2	2	153	130
2	3	60	49
2	4	130	91
2	5	21	12
3	-6	39	42
3	-5	16	15
3	-4	60	62
3	-3	13	12
3	-2	92	78
3	-1	29	26
3	0	79	71
3	1	18	9
3	2	103	83
3	3	23	18
3	4	121	105
4	-5	23	25
4	-4	22	19
4	-3	24	22
4	-2	31	36
4	-1	34	35
4	0	62	54
4	1	29	22
4	2	74	66
4	3	40	34
4	4	39	33
5	-5	9	6
5	-4	62	59
5	-3	16	1
5	-2	79	78
5	-1	12	7
5	0	102	91
5	1	14	9
5	2	110	93
6	-3	14	16
6	-2	8	8
6	-1	25	29
6	0	12	3
***** K = 9 *****			
0	1	99	83
0	2	12	4
1	-2	12	12
1	-1	47	31
1	1	28	25
2	-1	75	68
2	0	29	30

We feel that the decomposition of the crystal has resulted in data which are not sufficiently accurate to warrant a more detailed description of the disordered atoms in the equatorial plane. It is, however, clear from the refinements of the disordered model and the difference Fourier map of the equatorial plane that the two carbonyl ligands are bonded in the usual linear fashion.

A statistical analysis of $|F_o|$ *vs.* $|F_c|$ showed no unusual trends. A total difference Fourier synthesis showed considerable residual density, 20 peaks being greater than 0.62 e$^-$/Å^3. Of these, five were associated with the solvent benzene molecule, which had a large group temperature factor. The remainder were in the region of the equatorial plane and probably resulted from

TABLE II

Atomic Positional and Thermal Parameters

Atom	x	y	z	$U(1,1)$[a]	$U(2,2)$	$U(3,3)$	$U(1,2)$	$U(1,3)$	$U(2,3)$
Ir	0.20836 (5)[b]	0.05640 (9)	−0.00149 (6)	0.057 (1)	0.045 (1)	0.055 (2)	0.003 (1)	0.016 (1)	0.001 (1)
P_1	0.1784 (4)	0.2614 (6)	0.4650 (4)	0.056 (5)	0.042 (6)	0.055 (6)	−0.003 (5)	0.003 (5)	−0.006 (5)
P_2	−0.2402 (3)	0.3745 (6)	0.4744 (4)	0.040 (5)	0.036 (5)	0.051 (5)	0.010 (5)	0.009 (5)	0.001 (2)

Constrained Atoms

Atom	x	y	z	B, Å^2	Multiplicity
Cl_1	0.1839	0.0084	−0.1304	9.0	0.68 (2)
Cl_2	0.1033	0.0419	0.0649	9.0	0.14 (2)
Cl_3	0.3324	0.1169	0.0630	9.0	0.18 (2)
C_1	0.1215	0.0444	0.0534	7.5	0.86 (2)
O_1	0.0727	0.0376	0.0841	8.5	0.86 (2)
C_2	0.3108	0.1063	0.0518	7.5	0.82 (2)
O_2	0.3685	0.1345	0.0817	8.5	0.82 (2)
C_3	0.1882	0.0167	−0.1081	7.5	0.32 (2)
O_3	0.1767	−0.0056	−0.1680	8.5	0.32 (2)

Group Parameters

Group	x_0[c]	y_0	z_0	δ	ϵ	η
PH-1	0.3169 (7)	0.3627 (11)	−0.0865 (7)	−0.073 (17)	−2.355 (13)	−0.804 (17)
PH-2	0.0363 (7)	0.2755 (9)	−0.1661 (7)	−0.629 (11)	2.525 (9)	−2.428 (11)
PH-3	0.1401 (6)	0.3868 (9)	0.0962 (6)	0.661 (11)	2.523 (11)	1.360 (11)
PH-4	0.1235 (7)	−0.2935 (10)	−0.0754 (6)	−2.190 (9)	2.804 (8)	−0.490 (9)
PH-5	0.2508 (5)	−0.2072 (11)	0.1953 (6)	2.880 (8)	2.923 (12)	1.765 (8)
PH-6	0.4075 (8)	−0.1878 (12)	0.0050 (8)	−2.964 (20)	−2.314 (13)	−2.590 (18)
PH-7	0.4549 (15)	0.4401 (20)	0.2205 (13)	−1.485 (53)	−2.564 (17)	2.864 (32)

[a] The form of the thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$, and $U_{ij} = \beta_{ij}/(2\pi^2 \mathbf{a}_i^* \cdot \mathbf{a}_j^*)$ (Å). [b] Numbers in parentheses given here and in other tables are estimated standard deviations in the least significant digits. [c] x_c, y_c, and z_c are the fractional coordinates of the ring center; δ, ϵ, and η (in radians) have been defined in ref 13.

the thermal and geometrical constraints imposed upon the atoms. No peak was so positioned as to suggest a nonlinear carbonyl group. An inspection of the intense low-order reflections showed that extinction could be neglected.

In Table I the values of $|F_o|$ and $|F_c|$ (in electrons) are given. The final nongroup atom positional, thermal, and multiplicity parameters are listed in Table II along with the group parameters. In Table III the group atom positional and thermal parameters are given.

Description of the Structure

The extensive anisotropic crystal decomposition and the disorder in the equatorial plane preclude the determination of accurate intramolecular distances. A selection of meaningful distances and angles is given in Table IV; those without estimated standard deviations were constrained in the refinement.

The over-all molecular geometry is trigonal bipyramidal, with *trans*-triphenylphosphine groups, as shown in Figure 2. The complex and the solvent molecule are discrete, the non-bonding intermolecular distances (including those of the hydrogen atoms) being greater than 2.48 Å.

The Ir–P distances of 2.341 (7) and 2.322 (7) Å are normal for compounds of this type. In the analogous molecular oxygen complex of $IrCl(CO)(P(C_6H_5)_3)_2$, which also has a *trans* arrangement of triphenylphosphine ligands, Ir–P distances of 2.38 (1) and 2.36 (1) Å were found.[15] In a preliminary report of the structure of the related complex $Ir(H)(CO)_2(P(C_6H_5)_3)_2$, in which the P atoms are *cis*, distances of 2.372 (2) and 2.377 (2) Å were reported.[17] The geometry of

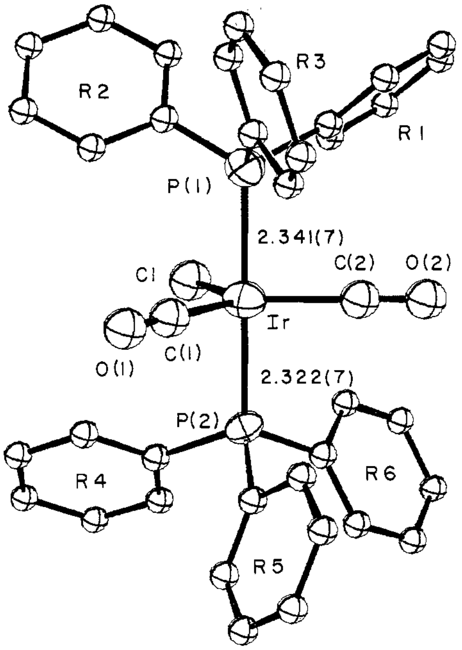

Figure 2.—Over-all view of the molecule. The vibrational ellipsoids of the Ir and P atoms are shown at the 50% probability level. The ellipsoids for all other atoms have been reduced arbitrarily for the sake of clarity.

the triphenylphosphine ligands in the present compound is also normal, the mean of the P–RC(1) dis-

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(17) M. Ciechanowicz, A. C. Skapski, and P. G. H. Troughton, "Collected Abstracts, Eighth International Congress of Crystallography," 1969, Paper XIV-44.

TABLE III

DERIVED GROUP ATOM PARAMETERS

Atom	*x*	*y*	*z*	*B*, Å²
		Ring 1		
C_1[a]	0.2592 (13)[b]	0.3106 (22)	−0.0601 (12)	3.9 (6)
C_2	0.2916 (10)	0.4062 (19)	−0.0258 (9)	8.2 (8)
C_3	0.3493 (15)	0.4583 (15)	−0.0521 (13)	8.7 (9)
C_4	0.3746 (13)	0.4148 (22)	−0.1129 (12)	6.9 (7)
C_5	0.3422 (10)	0.3192 (19)	−0.1473 (8)	7.3 (7)
C_6	0.2845 (14)	0.2671 (16)	−0.1209 (11)	6.5 (7)
		Ring 2		
C_1	0.1023 (8)	0.2597 (17)	−0.1112 (8)	3.7 (5)
C_2	0.1022 (8)	0.3328 (14)	−0.1698 (10)	6.4 (6)
C_3	0.0362 (9)	0.3485 (11)	−0.2247 (9)	4.2 (6)
C_4	−0.0297 (8)	0.2913 (17)	−0.2210 (9)	6.9 (6)
C_5	−0.0296 (9)	0.2182 (15)	−0.1624 (10)	7.1 (6)
C_6	0.0364 (10)	0.2024 (12)	−0.1075 (9)	6.2 (6)
		Ring 3		
C_1	0.1545 (11)	0.3211 (13)	0.0386 (9)	3.9 (6)
C_2	0.1130 (8)	0.4175 (13)	0.0217 (7)	3.2 (5)
C_3	0.0986 (10)	0.4831 (11)	0.0793 (10)	4.0 (6)
C_4	0.1256 (11)	0.4524 (14)	0.1538 (8)	5.1 (6)
C_5	0.1671 (9)	0.3561 (15)	0.1707 (7)	8.0 (7)
C_6	0.1816 (10)	0.2904 (12)	0.1131 (11)	5.0 (6)
		Ring 4		
C_1	0.1740 (8)	−0.2219 (13)	−0.0307 (8)	3.2 (6)
C_2	0.2015 (7)	−0.3118 (14)	−0.0637 (9)	3.3 (5)
C_3	0.1509 (9)	−0.3833 (11)	−0.1084 (9)	4.2 (5)
C_4	0.0729 (9)	−0.3650 (13)	−0.1201 (9)	6.4 (6)
C_5	0.0455 (7)	−0.2752 (15)	−0.0872 (9)	5.3 (6)
C_6	0.0960 (9)	−0.2036 (11)	−0.0425 (9)	3.9 (5)
		Ring 5		
C_1	0.2404 (8)	−0.1781 (16)	0.1201 (6)	3.8 (6)
C_2	0.2283 (7)	−0.2858 (13)	0.1396 (9)	4.5 (6)
C_3	0.2387 (8)	−0.3149 (12)	0.2149 (11)	6.3 (6)
C_4	0.2612 (9)	−0.2363 (18)	0.2706 (6)	6.7 (6)
C_5	0.2733 (8)	−0.1287 (15)	0.2510 (9)	7.6 (7)
C_6	0.2630 (8)	−0.0995 (11)	0.1758 (11)	6.5 (6)
		Ring 6		
C_1	0.3358 (10)	−0.1617 (27)	0.0167 (11)	5.1 (6)
C_2	0.3798 (10)	−0.2406 (20)	0.0613 (9)	7.1 (6)
C_3	0.4515 (13)	−0.2667 (21)	0.0496 (13)	9.0 (8)
C_4	0.4791 (11)	−0.2140 (30)	−0.0067 (14)	10.2 (10)
C_5	0.4351 (12)	−0.1351 (21)	−0.0513 (11)	11.9 (9)
C_6	0.3634 (14)	−0.1090 (19)	−0.0396 (12)	7.6 (7)
		Ring 7		
C_1	0.4732 (45)	0.3324 (27)	0.2069 (23)	18.4 (6)[c]
C_2	0.5213 (24)	0.3934 (56)	0.2621 (19)	
C_3	0.5029 (28)	0.5010 (43)	0.2757 (17)	
C_3	0.4365 (44)	0.5478 (27)	0.2341 (22)	
C_5	0.3885 (24)	0.4868 (54)	0.1788 (18)	
C_6	0.4068 (29)	0.3792 (42)	0.1652 (18)	

[a] Ring atoms are numbered sequentially, with C_1 attached to P. [b] The estimated standard deviations are derived from those of the group parameters; intra-ring distances are fixed at C–C = 1.392 Å. [c] The benzene molecule of crystallization was allotted an over-all group temperature factor.

TABLE IV

BOND DISTANCES AND BOND ANGLES

Atoms	Dist, Å	Atoms	Angles, deg
$Ir–P_1$	2.341 (7)	$P_1–Ir–P_2$	176.8 (2)
$Ir–P_2$	2.322 (7)	$P_1–Ir–Cl_1$	89.6
$Ir–Cl_1$	2.37[a]	$P_1–Ir–C_1$	92.2
$Ir–C_1$	2.04	$P_1–Ir–C_2$	88.4
$C_1–O_1$	1.14	$P_2–Ir–Cl_1$	87.6
		$P_2–Ir–C_1$	90.4
$P_1–R_1C_1$	1.84 (2)	$P_2–Ir–C_2$	91.7
$P_1–R_2C_1$	1.75 (2)		
$P_1–R_3C_1$	1.81 (2)	Ir–C–O	180.0
$P_2–R_4C_1$	1.83 (2)		
$P_2–R_5C_1$	1.84 (2)	$Cl_1–Ir–C_1$	118.2
$P_2–R_6C_1$	1.82 (3)	$Cl_1–Ir–C_2$	120.9
		$C_1–Ir–C_2$	120.9
		$R_1C_1–P_1–R_2C_1$	105 (1)
		$R_1C_1–P_1–R_3C_1$	104 (1)
		$R_2C_1–P_1–R_3C_1$	104 (1)
		$R_4C_1–P_2–R_5C_1$	100 (1)
		$R_4C_1–P_2–R_6C_1$	108 (1)
		$R_5C_1–P_2–R_6C_1$	101 (1)

[a] Since the positions of the Cl atom and of the C and O atoms of the carbonyl groups were derived from the electron density map and were not refined, no error estimates are given for bond distances or angles involving these atoms.

tances is 1.814 (14) Å, and the mean of the C(1)–P–C(1) angles is 104 (1)°.

We find the geometry of the inner coordination sphere to be that deduced from the infrared measurements. In spite of the crystal decomposition and the disorder in the equatorial plane, it is clearly evident that both carbonyl ligands are coordinated in a linear fashion. Hence we conclude, as might be expected, that whereas the amphoteric nature of the NO^+ ligand permits it to act as either a Lewis acid or a Lewis base, carbon monoxide coordinates preferentially as a Lewis base, with sp hybridization at the carbon atom and extensive multiple bonding between the metal and the ligand.

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