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The Crystal and Molecular Structure of Iodomethylnitrosylbis(triphenylphosphine)iridium, $IrI(CH_3)(NO)(P(C_6H_5)_3)_2$

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The structure of iodomethylnitrosylbis(triphenylphosphine)iridium, $IrI(CH_3)(NO)(P(C_6H_5)_3)_2$, has been determined from three-dimensional X-ray data collected by counter methods. The compound crystallizes in the space group C_{2h}^6-$I2/a$ of the monoclinic system with four molecules in a unit cell of dimensions $a = 16.011$ (11) Å, $b = 9.817$ (9) Å, $c = 22.445$ (16) Å, $\beta = 105.2$ (2)°. The observed and calculated densities are 1.74 (±0.02) and 1.73 g/cm,^{3} respectively. Least-squares refinement of the structure has led to a final value of the conventional R factor (on F) of 0.033 for the 1304 independent reflections having $F^2 > 3\sigma(F^2)$. There is a crystallographic twofold axis imposed on the molecule. The immediate coordination around the iridium is approximately square pyramidal with the nitrogen atom of the nitrosyl group occupying the apical position and the other ligands lying in the basal plane. The twofold axis leads to a disorder of the mutually trans iodo and methyl ligands and also to a disorder of the nitrosyl group. Despite this disorder an iridium–nitrogen–oxygen bond angle of 120 (2)° may be derived from the data. Therefore this complex provides another example of the nitrosyl ligand coordinated as NO^- to a transition metal. Important bond lengths in the molecule are as follows: Ir–N, 1.91 (2) Å; Ir–P, 2.348 (3) Å; Ir–I, 2.726 (2) Å; Ir–C, 2.05 (4) Å; N–O, 1.23 (2) Å. This compound provides the first example of a five-coordinate complex in which a methyl group is trans to another ligand. The iridium–iodine bond length is approximately 0.06 Å longer than that found in related complexes, which is indicative of the trans bond weakening effect of the methyl group.

Introduction

The structures of the square-pyramidal complexes $[IrX(NO)(CO)(P(C_6H_5)_3)_2][BF_4]$ (X = Cl[2] or I[3]) and $IrCl_2(NO)(P(C_6H_5)_3)_2$[4] have been determined and have provided examples of the nitrosyl ligand coordinated formally as NO^-. This type of geometry is characterized by an Ir–N–O bond angle of approximately 120°, which contrasts with the approximately 180° bond angle found for complexes where the ligand is coordinated formally as NO^+.[5] We have determined the structure of $IrI(CH_3)(NO)(P(C_6H_5)_3)_2$, which is closely related to the compounds mentioned above, in order to evaluate the effect of the strong electron-releasing methyl group on the metal–nitrosyl geometry and on the coordination around the iridium atom. This compound was prepared by Reed and Roper[6] from the oxidative addition reaction of methyl iodide with the tetrahedral iridium(−I) complex $Ir(NO)(P(C_6H_5)_3)_3$.[7] It was noted by these authors[6] that the iodo ligand in $IrI(CH_3)(NO)(P(C_6H_5)_3)_2$ is very labile and they ascribed this to the strong trans effect of the methyl group. We were interested to see if this lability was a result of a long Ir–I bond resulting from the trans bond weakening effect of the methyl group. This is particularly pertinent because although there is evidence for bond lengthening of the trans bond by alkyl and aryl groups in octahedral complexes,[8] there is no structural evidence for the effect in five-coordinate complexes.

Collection and Reduction of Intensity Data

Brown, well-formed crystals of $IrI(CH_3)(NO)(P(C_6H_5)_3)_2$ were kindly supplied by Dr. Roper. On the basis of Weissenberg and precession photography using Cu Kα radiation we established that the crystals belong to the monoclinic system. The extinctions observed, $h + k + l = 2n + 1$ for hkl and $h = 2n + 1$ for $h0l$, suggest the space groups C_{2h}^6-$I2/a$ or C_s^4-Ia. On the basis of optical goniometry, the eight crystal faces were identified as belonging to the forms $\{\bar{1}10\}$, $\{100\}$, and $\{001\}$. The lattice constants at 23°, which were determined from a least-squares refinement of the setting angles of 12 strong reflections which had been centered on a Picker four-circle automatic diffractometer[9] using Mo Kα_1 radiation (λ 0.70930 Å), are $a = 16.011$ (11), $b = 9.817$ (9) $c = 22.445$ (16) Å, $\beta = 105.2$ (2)°. The density calculated for four formula weights per unit cell is 1.73 g/cm^3, which agrees well with that of 1.74 (±0.02) g/cm^3 measured by the gradient tube method. With four formula weights per unit cell either a twofold axis or a center of symmetry is imposed on the molecule in the space group $I2/a$ but no symmetry is imposed in the noncentric space group Ia.

The mosaicity of the crystal was measured by means of the narrow-source, open-counter, ω-scan technique. The width at half-height for a typical strong reflection was found to be approximately 0.18°, which is acceptable.[10] The intensity data were collected as previously described[9] using a crystal of approximate dimensions 0.2 × 0.1 × 0.05 mm. The crystal was mounted on the diffractometer with the $[\bar{2}12]$ reciprocal lattice vector roughly coincident with the spindle axis.

For data collection Mo Kα radiation was used and the diffracted beams were filtered through 3.0 mils of niobium foil. The intensities were measured by the θ–2θ technique at a takeoff angle of 1.5°. At this angle the intensity of a reflection was about 80% of the maximum value as a function of takeoff angle. A receiving counter aperture 4 × 4 mm was used and was positioned 30 cm from the crystal. A nonsymmetric scan range from −0.65 to +0.85° from the Kα_1 peak was used. Stationary-counter, stationary-crystal background counts of 10 sec were measured at each end of

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(1) (a) Northwestern University; (b) University of Canterbury.

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the scan. Attenuators were inserted automatically if the intensity of the diffracted beam exceeded about 7000 counts/sec during the scan; the attenuators used were Cu foils, whose thickness had been chosen to give attenuator factors of approximately 2.3. The pulse height analyzer was set for approximately a 90% window, centered on the Mo Kα peak.

The *hkl* and $\bar{h}\bar{k}\bar{l}$ members of the form $\{hkl\}$ having $2\theta < 41°$ were gathered; the intensities of a total of 3362 reflections were measured. The intensities of three standard reflections, measured after every 100 observations, remained essentially constant throughout the run showing only the deviations ±1%. There were very few reflections above background at values of $2\theta > 41°$.

All data processing was carried out as previously described.[9] The value of p was selected as 0.04. The values of I and $\sigma(I)$ were corrected for Lorentz and polarization effects. Of the 3362 reflections, 303 had intensities which were less than their standard deviations. The linear absorption coefficient for this compound using Mo Kα radiation is 52.2 cm^{-1}. The data were corrected for absorption[11] and the transmission coefficients ranged from 0.814 to 0.683.

No significant variations in F^2 among possibly nonequivalent *hkl* and $\bar{h}\bar{k}\bar{l}$ reflections were observed; therefore the space group was assumed to be $I2/a$ and the data were averaged to give 1711 independent reflections.

Solution and Refinement

In the least-squares refinements[11] the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes, respectively, and where the weight w is $4F_o^2/\sigma^2(F_o^2)$. The agreement factors R_1 and R_2 are defined as $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w \cdot F_o^2)^{1/2}$. The scattering factors used for P, N, C, and O were taken from the usual tabulation,[12] and those for Ir and I were calculated by Cromer and Waber.[13] The hydrogen scattering factors were those of Stewart, *et al.*[14] The effects of anomalous dispersion were taken into account in the structure factor calculations.[15] The values of $\Delta f'$ and $\Delta f''$ for Ir, P, and I were those given by Cromer.[16]

The structure of the compound $IrCl_2(NO)(P(C_6H_5)_3)_2$, which crystallizes in the same space group and has cell constants almost identical with those of $IrI(CH_3)(NO)(P(C_6H_5)_3)_2$, had been solved previously.[4] The coordinates of the atoms are also very similar for the two compounds. The procedure for solving the structure of $IrI(CH_3)(NO)(P(C_6H_5)_3)_2$ is so similar to that previously described for $IrCl_2(NO)(P(C_6H_5)_3)_2$ that only the differences will be emphasized here. The iridium and iodine atoms were located from a three-dimensional Patterson function and the remaining nonhydrogen atoms were located from subsequent difference Fourier syntheses. The assumption of the space group $I2/a$ requires that the molecule possess C_2 symmetry and that the iodine, methyl carbon, and oxygen atoms be disordered. Although the methyl group and iodine atom are disordered, the difference Fourier synthesis indicated that the carbon and iodine atoms were sufficiently resolved to permit individual refinement in the least-squares program. The phenyl ring carbon atoms were refined as rigid groups of D_{6h} symmetry with d(C–H) = 1.390 Å, as previously described.[17,18] The agreement factors with all nonhydrogen atoms included with isotropic thermal parameters were $R_1 = 0.048$ and $R_2 = 0.058$ for the 1304 reflections which had $F^2 > 3\sigma(F^2)$. Addition of variable anisotropic thermal parameters for the nongroup atoms and individual isotropic thermal parameters for the group atoms led to the agreement factors $R_1 = 0.041$ and $R_2 = 0.051$ after one cycle of least-squares refinement. A difference Fourier synthesis at this point revealed the positions of the phenyl and methyl hydrogen atoms. These positions were idealized (d(C–H) = 1.08 Å, ∠HCH = 109.5° for methyl). The fixed contributions of these hydrogen atoms to F_c were included in subsequent cycles of refinement (B = 4.0 Å^2). The refinement converged to give the final agreement factors $R_1 = 0.03260$ and $R_2 = 0.03882$. (These agreement factors are given to more than the usual number of figures to facilitate comparison of various models.) The location of the hydrogen atoms supports the assumption of the space group $I2/a$.

Examination of the thermal ellipsoids and N–O bond length (1.04 (2) Å) suggested at this point that the nitrogen atom of the nitrosyl group might also be disordered about the twofold axis in a manner similar to that observed for $IrCl_2(NO)(P(C_6H_5)_3)_2$.[4] This disorder was treated as previously described by considering the nitrosyl group as a diatomic group with two orientation angles, three positional parameters, and a variable N–O distance. The nitrogen atom was assigned an isotropic thermal parameter and the oxygen was refined anisotropically. This refinement converged to give the agreement factors $R_1 = 0.03261$ and $R_2 = 0.03882$, an N–O bond length of 1.23 (2) Å, and an Ir–N–O bond angle of 120 (2)°.

A final difference Fourier synthesis over the asymmetric unit showed no peaks of height greater than 0.84 (6) e$^-$/Å^3, which is approximately 15% the height of an average carbon atom peak in earlier difference syntheses.

Inspection of the data showed that no correction for secondary extinction was necessary, and a comparison of $\Sigma w(|F_o| - |F_c|)^2$ as a function of $|F_o|$, Miller indices, and the scattering angle showed only a slight dependence on $|F_o|$ and scattering angle. Thus the relative weighting scheme is a reasonable one. The error of an observation of unit weight is 1.08 electrons. Of the 407 reflections omitted from the refinement for which $F_o^2 < 3\sigma(F_o)^2$ none had $|F_o^2 - F_c^2| > 3\sigma(F_o^2)$.

The final least-squares parameters are given in Table I along with the standard deviations of these parameters as derived from the inverse matrix. The positional parameters of the ring carbon atoms and the nitrosyl group which may be derived from the data in Table I

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(11) In addition to various local programs, the programs used in this structure determination were local modifications of Hamilton's GONO9 absorption correction program, Busing and Levy's ORFFE function and error program, Johnson's ORTEP thermal ellipsoid plotting program, and Zalkin's FORDAP program. Our local least-squares program NUCLS in its nongroup form closely resembles the Busing–Levy ORFLS program.

(12) J. A. Ibers in "International Tables of X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, Table 3.3.1.A.

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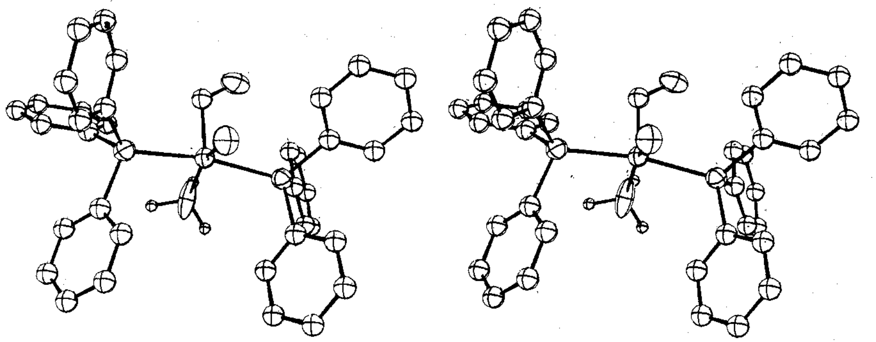

Figure 1.—A stereoscopic view of the molecule $IrI(CH_3)(NO)(P(C_6H_5)_3)_2$. Hydrogen atoms on the phenyl groups have been omitted for the sake of clarity. Also the disorder in the molecule as a result of the crystallographically imposed twofold axis is not illustrated.

TABLE I

POSITIONAL, THERMAL, AND GROUP PARAMETERS FOR $IrI(CH_3)(NO)(P(C_6H_5)_3)_2$

Atom	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ir	1/4	0.22068 (7)[b]	0	0.00310 (3)	0.00738 (9)	0.00143 (2)	0	0.00053 (2)	0
I	0.3731 (2)	0.1616 (3)	−0.0600 (1)	0.0043 (1)	0.0124 (3)	0.0020 (1)	0.0008 (1)	0.0011 (1)	−0.0004 (1)
P	0.3569 (2)	0.1981 (3)	0.0937 (1)	0.0032 (1)	0.0078 (4)	0.0018 (1)	−0.0001 (2)	0.0005 (1)	0.0002 (1)
C	0.1612 (27)	0.1594 (50)	0.0458 (18)	0.0064 (29)	0.0304 (70)	0.0012 (10)	0.0017 (36)	−0.0000 (12)	−0.0027 (18)
Group	x_0[c]	y_0	z_0	δ	ϵ	η			
NO	0.2621 (12)	0.4523 (13)	0.0088 (8)	0.814 (23)	0	−0.568 (23)			
R1	0.5471 (4)	0.2933 (6)	0.0886 (2)	0.379 (5)	−3.234 (5)	−0.313 (5)			
R2	0.3396 (4)	0.3696 (6)	0.2125 (3)	−1.952 (5)	−2.843 (5)	2.049 (5)			
R3	0.3666 (3)	−0.1197 (6)	0.1326 (3)	3.084 (7)	−2.391 (5)	−1.750 (7)			

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Standard deviations of the least significant figures are given in parentheses here and in subsequent tables. [c] x_0, y_0, and z_0 are the fractional coordinates of the rigid-group centers. The angles δ, ϵ, and η (in radians) have been defined previously.[17,18]

TABLE IIa

DERIVED PARAMETERS FOR GROUP CARBON ATOMS[a]

	x	y	z	B, Å^2
		Ring 1		
R1C1	0.4666 (4)	0.2471 (7)	0.0925 (4)	3.7 (2)
R1C2	0.5356 (5)	0.1567 (6)	0.1009 (4)	4.4 (3)
R1C3	0.6160 (4)	0.2029 (8)	0.0970 (4)	5.9 (3)
R1C4	0.6275 (4)	0.3394 (9)	0.0847 (4)	5.5 (3)
R1C5	0.5586 (6)	0.4298 (6)	0.0763 (4)	6.1 (3)
R1C6	0.4781 (5)	0.3836 (7)	0.0802 (4)	6.3 (3)
		Ring 2		
R2C1	0.3461 (5)	0.2953 (8)	0.1612 (3)	3.7 (2)
R2C2	0.2737 (4)	0.3760 (8)	0.1581 (3)	3.9 (2)
R2C3	0.2673 (5)	0.4503 (8)	0.2094 (4)	5.2 (3)
R2C4	0.3332 (6)	0.4439 (9)	0.2638 (3)	6.3 (3)
R2C5	0.4055 (5)	0.3632 (10)	0.2669 (3)	7.2 (4)
R2C6	0.4120 (4)	0.2889 (9)	0.2156 (4)	6.0 (3)
		Ring 3		
R3C1	0.3636 (5)	0.0180 (6)	0.1177 (4)	3.6 (2)
R3C2	0.3761 (5)	−0.0784 (9)	0.0755 (3)	5.9 (3)
R3C3	0.3791 (6)	−0.2161 (8)	0.0904 (4)	7.0 (3)
R3C4	0.3695 (6)	−0.2574 (5)	0.1475 (4)	6.0 (3)
R3C5	0.3570 (6)	−0.1611 (8)	0.1897 (3)	6.3 (3)
R3C6	0.3540 (5)	−0.0234 (8)	0.1748 (3)	5.0 (3)

[a] C1 is attached to P; other carbon atoms are numbered in succession so that C4 is para to C1.

TABLE IIb

DERIVED PARAMETERS FOR NITROSYL GROUP ATOMS

Atom	x	y	z	B, Å^2
N	0.2391 (16)	0.4140 (18)	−0.0102 (11)	2.9 (5)
O	0.2850 (11)	0.4905 (14)	0.0278 (8)	*a*

[a] Oxygen anisotropic thermal parameters: β_{11}, 0.0065 (12); β_{22}, 0.0070 (23); β_{33}, 0.0032 (6); β_{12}, −0.0002 (12); β_{13}, 0.0016 (16); β_{23}, −0.0005 (9).

TABLE IIc

PARAMETERS FOR THE HYDROGEN ATOMS

	x	y	z
		Methyl Group	
H1	0.124	0.079	0.023
H2	0.197	0.129	0.093
H3	0.121	0.247	0.050
		Ring 1	
H2[a]	0.527	0.051	0.110
H3	0.670	0.133	0.103
H4	0.690	0.375	0.082
H5	0.568	0.536	0.067
H6	0.425	0.454	0.074
		Ring 2	
H2	0.223	0.381	0.116
H3	0.211	0.513	0.207
H4	0.328	0.502	0.304
H5	0.457	0.358	0.309
H6	0.468	0.226	0.218
		Ring 3	
H2	0.362	−0.046	0.031
H3	0.389	−0.291	0.058
H4	0.372	−0.364	0.159
H5	0.350	−0.193	0.234
H6	0.344	0.052	0.208

[a] Atom H*n* is attached to carbon atom C*n*.

are presented in Tables IIa and IIb. The idealized positions of the hydrogen atoms are given in Table IIc. The final values of $10|F_o|$ and $10|F_c|$ (in electrons) are given in Table III; only the 1304 reflections which were used in the refinement are included in Table III.

Results and Discussion

The crystal structure consists of loosely packed monomeric units of $IrI(CH_3)(NO)(P(C_6H_5)_3)_2$. In Figure 1 a stereoscopic view of the overall molecular geometry is shown and in Figure 2 only the inner coordination sphere about the iridium atom is shown. Principal intermolecular distances and angles and their standard deviations are given in Table IV. The standard devia-

TABLE III

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES ($\times 10$) IN ELECTRONS FOR $IrI(CH_3)(NO)(P(C_6H_5)_3)_2$

H	K	FO	FC
*****	L =	0	*****
0	0		17171
0	2	4822	4499
0	4	1371	1313
1	1	5064	4859
1	3	1544	1584
1	5	576	664
2	0	3588	3447
2	2	1485	1511
2	4	1759	1750
2	6	536	550
3	1	2286	2259
3	3	1194	1189
3	5	1959	1963
3	7	715	769
4	0	2083	1983
4	4	1439	1556
4	6	1876	1956
4	8	660	685
5	1	1853	1882
5	3	1661	1641
5	5	1846	1841
5	7	1176	1170
6	0	1577	1540
6	2	1561	1618
6	4	1179	1171
6	6	1020	979
7	1	2297	2305
7	3	1005	1030
8	0	4509	4540
8	2	2710	2688
8	4	846	817
9	1	2611	2625
9	3	1359	1439
9	5	506	481
10	0	2727	2773
10	2	1649	1670
10	4	1120	1090
11	1	1468	1466
11	3	1346	1258
11	5	983	984
12	2	671	709
12	4	971	1027
13	1	755	805
13	3	847	791
13	5	923	923
14	2	854	846
15	1	657	679
*****	L =	1	*****
-15	2	518	456
-13	4	464	383
-12	5	704	796
-11	4	772	741
-11	6	1165	1189
-10	3	801	803
-10	5	1403	1491
-10	7	1002	1018
-9	2	808	848
-9	4	1600	1655
-9	6	1440	1395
-8	1	885	929
-8	3	1671	1665
-8	5	1492	1524
-8	7	895	930
-7	2	1403	1363
-7	4	1938	1952
-7	6	788	826
-6	1	991	959
-6	3	1181	1193
-6	5	1056	1039
-6	7	1020	1093
-5	2	497	463
-5	4	688	730
-5	6	1318	1294
-5	8	1374	1355
-4	1	2003	1902
-4	5	1078	1078
-4	7	1364	1377
-4	9	1159	1180
-3	2	1572	1476
-3	4	804	829
-3	6	1619	1598
-3	8	1768	1821
-2	1	352	238
-2	3	483	466
-2	5	1629	1732
-2	7	1655	1683
-2	9	1163	1105
-1	2	421	387
-1	4	2892	2743
-1	6	1812	1723
-1	8	1065	1032
0	1	1757	1609
0	3	3498	3463
0	5	3002	2863
0	7	1340	1238
0	9	622	629
1	2	3233	3169
1	4	2735	2850
1	6	1385	1436
1	8	711	698
2	1	478	406
2	3	2216	2223
2	5	1271	1343
2	7	1286	1343
2	9	849	870
3	2	793	779
3	4	1096	1030
3	6	1397	1458
3	8	1206	1179
4	1	1864	1875
4	3	735	704
4	5	448	535
4	7	1425	1529
4	9	1149	1106
5	2	1215	1172
5	6	1453	1451
5	8	1535	1559
6	3	668	650
6	5	1149	1181
6	7	1122	1184
7	2	1202	1131
7	4	1623	1691
7	6	1199	1212
7	8	838	805
8	1	1533	1556
8	3	1883	1896
8	5	1949	1980
8	7	994	1014
9	2	1412	1492
9	4	1957	1934
9	6	1082	1113
10	1	673	603
10	3	1256	1270
10	5	1089	1147
11	2	497	502
11	4	463	526
11	6	831	793
*****	L =	2	*****
-15	1	1255	1254
-14	0	1566	1525
-14	2	1231	1162
-13	1	1071	1127
-13	3	921	933
-13	5	702	682
-12	0	1068	1040
-12	2	1148	1141
-12	4	1098	1177
-11	1	1372	1350
-11	3	1328	1315
-11	5	1059	1027
-10	0	1977	1956
-10	2	1356	1441
-10	4	1295	1318
-10	6	1019	1002
-9	1	2219	2115
-9	3	1195	1250
-9	5	578	534
-8	0	2473	2563
-8	2	1795	1817
-7	1	2454	2530
-7	3	833	912
-6	0	1964	1969
-6	2	1820	1831
-6	4	745	861
-6	6	453	458
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-2	3	1861	1924
-2	5	1670	1680
-2	7	803	795
-1	2	1220	1335
-1	4	1580	1584
-1	6	1490	1446
-1	8	881	967
0	3	910	862
0	5	1830	1843
0	7	1636	1586
1	2	882	862
1	4	807	818
1	6	1297	1367
1	8	1302	1417
2	5	744	787
2	7	1334	1328
3	4	723	686
3	6	786	809
4	3	624	656
4	5	634	706
4	7	458	401
5	2	1108	1050
5	4	927	901
5	6	910	888
6	1	721	704
6	3	999	1076
6	5	1075	1130
7	2	814	809
7	4	934	938
7	6	1004	1013
8	3	501	496
8	5	1162	1081
9	4	665	545
*****	L =	12	*****
-14	2	515	532
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-11	3	1292	1312
-10	0	2664	2649
-10	2	1941	1916
-10	4	865	866
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-8	0	1410	1479
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-8	4	962	964
-7	3	1051	1089
-7	5	1101	1090
-7	7	574	628
-6	2	829	806
-6	4	1541	1585
-6	6	1509	1467
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-5	5	1258	1227
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1	5	1189	1219
1	7	664	692
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2	4	1370	1388
2	6	1217	1221
3	1	1078	1061
3	3	1218	1139
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3	7	616	612
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4	2	1297	1238
4	4	689	716
4	6	685	685
5	1	1961	2001
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6	0	2061	2057
6	2	1376	1398
7	1	1706	1714
7	3	930	973
8	0	1645	1633
8	2	1467	1416
8	4	871	815
9	1	1036	1004
9	3	1088	1057
10	0	792	818
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*****	L =	13	*****
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-8	3	693	707
-8	5	775	763
-8	7	934	985
-7	6	974	945
-6	3	378	323
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-5	6	1165	1153
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-4	5	1303	1424
-4	7	888	895
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-3	4	1585	1622
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-2	7	987	914
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-1	4	2027	1982
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0	7	1070	1086
1	6	961	983
2	3	589	455
2	7	1002	1057
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5	2	855	753
5	4	996	1040
5	6	943	968
6	3	1565	1518
6	5	1284	1257
7	2	1011	947
7	4	1353	1386
8	3	837	768
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-13	3	901	850
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-11	3	928	921
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-10	2	1373	1432
-9	1	1787	1751
-9	3	589	607
-8	0	1510	1500
-8	2	958	1009
-8	4	517	484
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-7	3	955	938
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-6	0	1305	1303
-6	2	855	781
-6	4	1390	1400
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-2	2	2424	2446
-2	4	865	835
-1	1	2921	2977
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0	6	484	589
1	1	828	792
1	3	915	915
1	5	965	971
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3	3	725	838
3	5	1528	1512
4	0	930	984
4	2	831	837
4	4	1213	1142
4	6	703	684
5	1	1559	1567
5	3	1061	1083
6	0	2137	2115
6	2	1555	1478
6	4	699	659
7	1	1899	1895
7	3	1075	1098
8	0	1569	1541
8	2	1319	1356
9	1	797	873
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-10	5	705	812
-9	2	861	782
-9	4	1121	1124
-8	1	438	444
-8	3	941	906
-8	5	698	745
-7	4	718	812
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-5	4	618	590
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-4	3	494	499
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-4	7	1235	1243
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-2	3	1548	1633
-2	5	1039	1049
-2	7	718	736
-1	2	980	992
-1	4	1509	1547
-1	6	818	782
0	3	1022	1048
0	5	794	846
1	4	700	737
1	6	762	755
2	5	802	765
3	6	811	811
4	5	853	851
5	2	610	570
5	4	750	792
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6	3	1044	1064
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-11	1	558	535
-11	3	754	658
-10	0	1286	1351
-10	2	808	815
-9	1	1487	1482
-9	3	780	746
-8	0	1872	1834
-8	2	1165	1115
-8	4	601	572
-7	1	1824	1931
-7	3	1183	1269
-7	5	631	690
-6	0	1405	1436
-6	2	1375	1363
-6	4	1169	1130
-6	6	496	417
-5	1	1063	1083
-5	3	1311	1286
-5	5	1115	1133
-4	0	919	914
-4	2	1455	1453
-4	4	1372	1420
-4	6	956	986
-3	1	1296	1194
-3	3	1269	1256
-3	5	867	938
-2	0	1856	1838
-2	2	1617	1687
-2	4	703	724
-1	1	1698	1734
-1	3	849	803
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0	2	922	889
1	1	1242	1297
1	3	1035	1085
2	0	985	1019
2	2	1190	1117
2	4	1124	1052
3	1	907	890
3	3	1357	1272
3	5	1050	1034
4	0	935	884
4	2	1350	1345
4	4	1129	1121
5	1	1099	1034
5	3	1069	1063
6	0	1202	1198
6	2	1221	1254
7	1	1269	1288
*****	L =	17	*****
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-9	4	712	655
-8	3	1133	1083
-8	5	961	890
-7	2	1114	1167
-7	4	1306	1315
-6	3	1031	936
-6	5	1125	1068
-5	4	761	782
-5	6	1073	1112
-4	5	791	749
-3	6	945	885
-2	5	661	755
-1	2	747	563
-1	4	708	757
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0	3	876	914
0	5	903	825
1	2	1021	1108
1	4	901	895
2	3	487	448
2	5	922	901
3	4	622	568
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-10	2	542	486
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-9	3	815	857
-8	0	1781	1781
-8	2	1322	1348
-8	4	631	648
-7	1	2163	2191
-7	3	1061	998
-6	0	1765	1729
-6	2	1625	1714
-5	1	1115	1007
-5	3	1082	1062
-5	5	710	724
-4	0	616	680
-4	2	900	1007
-4	4	1008	1069
-3	1	560	399
-3	3	1033	1070
-3	5	1035	986
-2	0	664	751
-2	2	616	621
-2	4	790	760
-1	1	1136	1170
-1	3	774	726
0	0	1772	1684
0	2	1272	1214
0	4	501	480
1	1	2226	2182
1	3	865	937
2	0	1910	1827
2	2	1506	1487
2	4	600	629
3	1	1127	1168
3	3	873	856
4	0	788	784
4	2	932	947
5	1	482	503
*****	L =	19	*****
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-7	2	1078	1016
-7	4	1230	1242
-6	1	476	406
-6	3	1229	1207
-5	4	864	823
0	3	889	915
1	4	1175	1154
2	3	1194	1145
*****	L =	20	*****
-10	0	594	558
-9	1	1037	970
-8	0	1591	1650
-8	2	1310	1346
-7	1	1620	1620
-7	3	651	654
-6	0	1591	1593
-6	2	1083	1143
-5	1	1125	1145
-5	3	759	770
-4	0	984	899
-4	2	586	567
-4	4	783	788
-3	1	710	703
-3	3	824	826
-2	0	665	654
-2	2	521	570
-2	4	854	818
-1	1	1028	953
-1	3	688	728
0	0	1385	1452
0	2	1286	1422
1	1	1591	1564
2	0	1362	1492
2	2	1176	1219
*****	L =	21	*****
-7	2	659	624
-6	1	532	480
*****	L =	22	*****
-5	1	1240	1248
-4	0	897	935

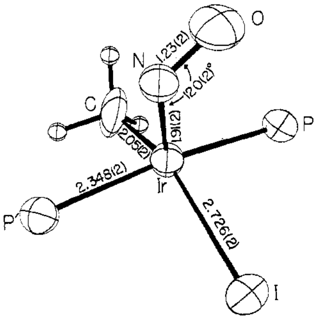

Figure 2.—Inner coordination sphere of $IrI(CH_3)(NO)(P(C_6H_5)_3)_2$. The 50% probability ellipsoids are shown.

tions of the bond lengths and angles involving the group atoms were calculated from the formulas of Ahmed and Cruickshank.[19] The root-mean-square amplitudes of vibration along the principal axis of thermal motion

TABLE IV

SELECTED DISTANCES AND ANGLES

Intramolecular distances, Å		Angles, deg	
Ir–I	2.726 (2)	Ir–N–O	120 (2)
Ir–P	2.348 (3)	N–Ir–P	103 (1)
Ir–C	2.05 (4)	N–Ir–P′	88 (1)
Ir–N	1.91 (2)	N–Ir–I	102 (1)
Ir–O	2.745 (15)	N–Ir–I′	102 (1)
P–P′[a]	4.675 (6)	P–Ir–P	169.2 (2)
I–I′	5.326 (5)	I–Ir–C	151 (1)
C–C′	3.92 (7)	P–Ir–I	88.3 (1)
N–O	1.23 (2)	P′–Ir–I	89.4 (1)
P–C	3.059 (42)	P–Ir–C	88 (1)
P–C′	3.091 (39)	P′–Ir–C	89 (1)
P–N	3.34 (3)	C–Ir–N	107 (2)
P–N′	2.98 (2)	R1C1–P–R2C1	100 (1)
I–N′	3.65 (2)	R1C1–P–R3C1	106 (1)
I–N	3.64 (2)	R2C1–P–R3C1	106 (1)
I–C	4.624 (38)		
I–P	3.545 (4)		
I–P′	3.578 (4)		
P–RC1 (av of 3)	1.836 (8)		

[a] The atom X′ is related to atom X by the twofold axis.

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(19) F. R. Ahmed and D. W. J. Cruickshank, *Acta Crystallogr.*, **6**, 385 (1953).

for the atoms which were refined anisotropically are given in Table V. The directions of the principal axes can be discerned at least approximately from the figures. The large anisotropy of the methyl carbon atom may possibly be the result of the iodine–methyl disorder.

TABLE V

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

Atom	Min	Intermed	Max
Ir	0.184 (1)	0.190 (1)	0.194 (1)
I	0.194 (4)	0.233 (3)	0.253 (3)
P	0.191 (5)	0.198 (5)	0.212 (4)
C	0.15 (7)	0.28 (6)	0.40 (5)
O	0.18 (4)	0.26 (3)	0.28 (3)

[a] Measured along the principal axes of the thermal ellipsoids.

The packing is largely dictated by intermolecular contacts between the bulky phosphine ligands. This can be seen by comparing this structure with that of $ReNCl_2(P(C_6H_5)_3)_2$, $OsCl_3(NH_3)(P(C_6H_5)_3)_2$, and $IrCl_2(NO)(P(C_6H_5)_3)_2$, which crystallize in the same space group, *I*2/*a*, with very similar cell dimensions (see Table VI in ref 4). The orientations of the phenyl rings in these compounds are only slightly different, and the volume per triphenylphosphine group for $IrI(CH_3)(NO)(P(C_6H_5)_3)_2$, 426 $Å^3$, is only slightly larger than those found for the other complexes (404–412 $Å^3$).

There is a crystallographic twofold axis imposed on the molecule which results in the disorder of the methyl group and iodine atom and of the nitrosyl group. The disorder of the nitrosyl group is very similar to that observed previously for $IrCl_2(NO)(P(C_6H_5)_3)_2$[4] and results in the displacement of the nitrogen atom approximately 0.25 Å from the twofold axis.

In the compound $IrI(CH_3)(NO)(P(C_6H_5)_3)_2$ the geometry around the iridium atom is approximately square pyramidal and the Ir–N–O bond angle is 120 (2)°. Therefore the geometry closely resembles that found for the other iridium NO^- complexes which have been studied.[1-4] This complex provides another example of the nitrosyl ligand coordinating formally to iridium(III) as NO^-.

The Ir–N bond length in this complex (1.91 (2) Å) is similar to that found for the other iridium NO^- complexes (that is, 1.97 (1) Å for $[IrCl(NO)(CO)(P(C_6H_5)_3)_2][BF_4]$,[2] 1.94 (2) Å for $IrCl_2(NO)(P(C_6H_5)_3)_2$,[4] and 1.89 (3) Å for $[IrI(NO)(CO)(P(C_6H_5)_3)_2][BF_4]$[3]) and quite different from the Ir–N bond lengths found for the NO^+ complexes ($Ir(NO)(P(C_6H_5)_3)_3$[7], 1.67 (2) Å, and $[Ir_2O(NO)_2(P(C_6H_5)_3)_2][ClO_4]$,[20] 1.76 (2) Å). For the NO^- complexes the differences between the Ir–N bond lengths are of the same order as the standard deviations and therefore a discussion of electronic effects of the different basal ligands on these bond lengths would not be meaningful.

It has been suggested that the nitrosyl ligand will coordinate with an M–N–O bond angle of approximately 120° for certain iridium complexes if the electronic configuration $(d_{xy})^2(d_{xz})^2(d_{yz})^2(\pi^*(NO))^2$ (formally Ir(III) and NO^-) is of lower energy than the configuration $(d_{xy})^2(d_{xz})^2(d_{yz})^2(\pi^*(NO))^0(d_{z^2})^2$ (formally Ir(I) and NO^+).[4] With the two possible extreme formulations of NO^+ and NO^- one may rationalize the geometries of most nitrosyl complexes provided one accepts that deviations as large as 20° from 180° for NO^+ complexes can occur either because of asymmetric π interactions between the metal and the nitrosyl ligand or because of the steric requirements of the other ligands. Bond angles for NO^- complexes should not deviate from 120° as a result of asymmetric π-bonding effects because the NO^- ligand has only one π^* orbital.

The Ir–NO^- complexes studied in this laboratory and the cobalt complexes $[Co(NO)(NH_3)_5]Cl_2$[21] and $[CoCl(NO)(en)_2][ClO_4]$[22] (en = ethylenediamine) all have bond angles close to 120°. The complex $[RuCl(NO)_2(P(C_6H_5)_3)_2][PF_6]$[23] has an Ru–N–O angle of 135°, but this may result, as the authors have suggested, from the interaction of the two nitrosyl group oxygen atoms.

The bonding in certain nitrosyl complexes is difficult to rationalize within the formal framework of NO^+ and NO^- coordination. For example, how is the complex $[Ir(NO)_2(P(C_6H_5)_3)_2][ClO_4]$,[24] which has an Ir–N–O bond angle of 164 (1)° and a very distorted tetrahedral geometry around the metal (N–Ir–N = 154.2 (7)°), best formulated? A structural study of the isoelectronic complex $Pt(CO)_2[P(C_6H_5)(C_2H_5)_2]_2$ has shown that the geometry around the platinum atom is very close to tetrahedral and the Pt–C–O bond angle is almost linear.[25] Because these two complexes are so similar, the large distortions for the iridium complex cannot result from steric repulsions and must arise from electronic factors. These large distortions from the ideal for the Ir–N–O and N–Ir–N angles cannot be explained in terms of coordination as NO^+ or NO^-, which are extreme formulations and do not take into account the influence of the metal on ligand orbitals. Further, rationalization of this intermediate type of geometry in terms of coordination as NO would also be a simplification and in addition spin coupling would have to be invoked for this type of complex to explain the observed diamagnetism.

Table VI compares some of the important bond lengths and angles for three closely related square-pyramidal iodotriphenylphosphine complexes. It is interesting that the metal–phosphorus bond lengths are

TABLE VI

IMPORTANT BOND DISTANCES AND ANGLES FOR SOME SQUARE-PYRAMIDAL TRIPHENYLPHOSPHINE COMPLEXES $MBAI(P(C_6H_5)_3)_2$ (M = Rh, Ir; B = BASAL LIGAND = I, CO, CH_3; A = AXIAL LIGAND = NO, CH_3)

	$[IrI(NO)(CO)(P(C_6H_5)_3)_2][BF_4]$[a]	$IrI(CH_3)(NO)(P(C_6H_5)_3)_2$[b]	$RhI_2(CH_3)(P(C_6H_5)_3)_2$[c]
M	Ir	Ir	Rh
A	NO	NO	CH_3
B	CO	CH_3	I
M–I, Å	2.666 (3)	2.726 (2)	2.643 (3)
M–N, Å	1.89 (3)	1.91 (2)	
M–C (methyl), Å		2.05 (4)	2.083 (7)
M–P, Å	2.36 (1)	2.348 (3)	2.350 (4)
P–M–P, deg	168.2 (3)	169.2 (2)	167.69 (5)
I–M–B, deg	158 (1)	151 (1)	169.69 (2)
M–N–O, deg	125 (3)	120 (2)	

[a] Reference 3. [b] Present work. [c] A. C. Skapski, personal communication.

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(20) P. Carty, A. Walker, M. Mathew, and G. J. Palenik, *Chem. Commun.*, 1374 (1969).

(21) C. S. Pratt, B. A. Coyle, and J. A. Ibers, submitted for publication.

(22) D. A. Snyder and D. L. Weaver, *Chem. Commun.*, 1425 (1969).

(23) C. G. Pierpont, D. G. van der Veer, W. Durland, and R. Eisenberg, *J. Amer. Chem. Soc.*, **92**, 4760 (1970).

(24) D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, **9**, 1105 (1970).

(25) P. L. Bellon, private communication.

very similar for the three compounds, as are the P–M–P bond angles. The I–M–B bond angles (M = Rh or Ir; B = basal ligand) show a wider variation for the three compounds (151–170°). We have noted previously that the phosphine ligands are less sensitive to the steric requirements of the axial ligand in square-pyramidal complexes. The Ir–C(methyl) and Rh–C(methyl) bond lengths are also very similar. Other Ir–C distances which have been reported are 2.16 (2) Å for $IrCl_2[(C_6H_5(CHCH_2CO)C_6H_5)][(CH_3)_2SO]_2$,[26] 2.10 (2) Å for $[IrCl_2(CH_3)(CO)_2]_2$,[27] and 2.05 (2) Å for $IrI_2(COOCH_3)(CO)(bipy)$ (bipy = 2,2′-bipyridine).[28] The average of these bond lengths (2.10 (2) Å) is larger than that found for the present iridium–nitrosyl complex. However it must be remembered that the standard deviation on the Ir–C bond length in this complex is rather large, 0.04 Å, because of the disorder of the iodine atom with the methyl group. Table VI also shows that the Ir–I bond length is 0.06 Å longer for $IrI(CH_3)(NO)(P(C_6H_5)_3)_2$ than for $[IrI(NO)(CO)(P(C_6H_5)_3)_2][BF_4]$. In the latter complex the Ir–I bond length is very similar to those found for the trans iodine atoms in $IrI_2(COOCH_3)(CO)(bipy)$, 2.672 (2) and 2.684 (2) Å.[28] We think that the lengthening of the Ir–I bond length for the methyl–iodo complex is a result of the trans bond weakening effect of the methyl group which is trans to the iodo ligand. Similar bond lengthening effects have been observed for halide ligands trans to alkyl and aryl groups in square-planar and octahedral complexes of the platinum metals, but this is the first reported example of a square-pyramidal complex where bond lengthening from an alkyl group has been observed. Unfortunately none of the square-planar and octahedral complexes[8,29] studied previously had an iodo ligand trans to the alkyl or aryl group, and therefore no direct comparison of the relative lengthenings for four-, five-, and six-coordinate complexes can be made. For octahedral complexes, where a chloride ligand is trans to the alkyl group, a lengthening of approximately 0.15–0.19 Å is observed compared with the metal–chlorine bond length found for two trans chloride ligands.[8,29] In the octahedral complex $PtBr_3[(CH_3)_2AsC_6H_4C_2H_3][(CH_3)_2AsC_6H_4C_2H_3OC_2H_5]$[30] the Pt–Br bond trans to the alkyl group is 0.10 Å longer than the average of the two trans Pt–Br bonds. Therefore on the basis of the limited data available a lengthening of the Ir–I bond by 0.06 Å for $IrI(CH_3)(NO)(P(C_6H_5)_3)_2$ seems quite reasonable.

It has been shown that the square-planar and octahedral complexes which show the greatest trans bond weakening effects are those which have a ligand (L) with good σ-donor properties and weak π-accepting properties trans to a ligand (X) which is a poor σ donor and π acceptor. Gray and Langford[31] and Mason and his coworkers[29,32] have argued, on the basis of simple molecular orbital considerations, that the σ orbital of the less electronegative ligand L overlaps more effectively than the X σ orbital with the metal σ orbital. This leads to a strengthening of the M–L bond at the expense of the M–X bond. These calculations lead to the following bond weakening order for the ligands L: $Si \simeq H, C \approx P > Cl > N > O$, which qualitatively agrees with the observed Pt–Cl bond lengthening for a series of square-planar platinum(II) complexes. Similar arguments would suggest that for a given ligand, L, the M–X (X = Cl, Br, or I) bond would be weakened more for the more electronegative ligands, *i.e.*, $\delta(M\text{–}Cl) > \delta(M\text{–}Br) > \delta(M\text{–}I)$, where $\delta(M\text{–}X)$ is the difference in bond lengths between X trans to L and X trans to X. Therefore the fact that the Ir–I bond length is only 0.06 Å longer than anticipated may be rationalized within the framework of current theories. Another factor which may diminish the weakening of the Ir–I bond by the methyl group is the fact that the C–Ir–I bond angle is 151 (1)°. The molecular orbital description given above suggests that the bond weakening effect will be at a maximum when the L–M–X angle is 180° (because the ligands are competing for the same σ orbital) and will be zero when the L–M–X angle is 90° (when the ligands overlap with two orthogonal pσ orbitals). It is interesting to note that for the complex $RhI_2(CH_3)(P(C_6H_5)_3)_2$ where the methyl ligand occupies the apical position of the square pyramid and the C–Rh–I bond angle is 95.16 (1)°, the Rh–I bond length is no longer than anticipated.[33] In fact, it is 0.01 Å shorter than that found for $RhI(C_2F_5)(C_5H_5)(CO)$ (Rh–I = 2.653 (3) Å).[34]

Reed and Roper[6] noted that the iodo ligand in $IrI(CH_3)(NO)(P(C_6H_5)_3)_2$ was labile to nucleophilic attack and suggested that it might be a result of the trans bond weakening effect of the methyl group. The structural evidence presented above verifies their suggestion.

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