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Computational, Spectroscopic, and Crystallographic Determination of the Molecular Structures of CO Adducts of Vaska-Type Complexes *trans*-$IrL_2(CO)_2X$

Faraj Abu-Hasanayn, Thomas J. Emge, John A. Maguire,
Karsten Krogh-Jespersen,* and Alan S. Goldman*

*Department of Chemistry, Rutgers-The State University of New Jersey,
New Brunswick, New Jersey 08903*

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Summary: The products of CO addition to Vaska-type complexes, trans-Ir(PH_3)$_2$(CO)$_2$X (X = Cl, I), have been calculated by use of ab initio electronic structure methods with effective core potentials on all non-hydrogen atoms and basis sets of double-ζ plus polarization function quality. The calculated trigonal-bipyramidal structure of Ir(PH_3)$_2$(CO)$_2$Cl differs significantly from the results of a previous crystallographic structure determination of Ir(PPh_3)$_2$(CO)$_2$Cl for which significant disorder and crystal decomposition during data collection were reported. In particular, the calculated OC−Ir−CO angle (133−138°) is significantly greater than the reported crystallographic value (121°). Results of a crystallographic (X = I, 131°) and IR spectroscopic (X = Cl, 132°; I, 133°) reinvestigation are in good agreement with the calculations. The origin of the distortion from idealized trigonal-bipyramidal geometry is briefly discussed.

Vaska's complex and many of its derivatives (*trans*-IrL_2(CO)X, **1-X**, L = phosphine, X^- = two-electron donor) reversibly bind CO (eq 1);[1] they are thus among

$$\underset{\textbf{1-X}}{trans\text{-}IrL_2(CO)X} + CO \rightleftharpoons \underset{\textbf{2-X}}{trans\text{-}IrL_2(CO)_2X} \text{ or } cis,cis\text{-}IrL_2(CO)_2X \quad (1)$$

the relatively small number of transition metal complexes that are isolable as both the unsaturated species and their corresponding CO adducts (**2-X**). Though this prototypical example of metal−carbonyl addition/dissociation provides an ideal system for the study of various aspects of such reactions, eq 1 has received much less attention, both experimental and theoretical, than its H_2-addition counterpart.[2,3] We have begun a comprehensive study of eq 1 based in part on ab initio MO calculations.[4] Our employed computational model (L = PH_3) successfully reproduces the geometry of **1-Cl** as compared with the reported crystal structure (L = PPh_3). However, our calculated geometry for **2-Cl** significantly differs in some respects from the reported crystal structure; in particular, the angle between the two carbonyl groups in **2-Cl** is reported to be 121°, while the calculated value lies between 133° and 138°, depending on the computational level. This discrepancy has led us to experimentally reinvestigate the molecular structure of **2-X**.

Computational Details

Ab initio electronic structure calculations[5] were carried out using the GAUSSIAN 92 series of programs.[6] Geometries of **1-X** and **2-X** (X = Cl, I) were optimized within appropriate C_{2v} symmetry constraints at the Hartree−Fock (HF)[7] and the Møller−Plesset second (MP2)[8] and third (MP3)[9] order perturbation theory levels. Effective core potentials and corresponding valence electron basis sets developed by Ermler, Christiansen and co-workers were employed for all non-hydrogen atoms.[10] The large core ECP-1 type potential was used for Ir (68 core electrons) and I (46 core electrons). Two basis sets were used. The regular, mostly double-ζ or better quality valence basis set was contracted as follows (3s, 3p, 4d) → [1, 1, 1/2, 1/2, 1, 1] for Ir, and (4s, 4p) → [3/1, 3/1] or (3s, 3p) → [2/2, 2/1] for all other non-hydrogen atoms; hydrogens on P were described by the STO-3G basis set.[11] A larger basis set included additional d-type polarization functions[12] on the equatorial ligands of **2-X** (the halogen and the two CO groups).

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Table 1. Crystallographic Details for 2-I

formula	$C_{44}H_{36}I IrO_2P_2$
mol wt	977.77
space group	*P*-1
temp (°C)	293(2)
a (Å)	12.287(1)
b (Å)	13.396(1)
c (Å)	13.503(1)
α (deg)	86.69(1)
β (deg)	73.93(1)
γ (deg)	62.93(1)
V (Å³)	1895.8(2)
Z	2
μ (cm⁻¹)	44.6
d_{calcd}	1.713
cryst dimens (mm)	0.54 × 0.28 × 0.26
reflcns measd	*h*, ±*k*, ±*l*
scan rate (deg min⁻¹)	2.4−16.5
2θ range (deg)	4−50
scan type	ω:θ
no. of reflcns measd	6878
no. of unique reflcns	6276
no. of reflcns used	6276
no. of parameters	589
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$ (%)	3.5
$R_w = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{0.5}$ (%)	6.8
$GOF = \{\sum[w(F_o^2 - F_c^2)^2]/(N_{obs} - N_{par})\}^{0.5}$	1.09

X-ray Crystallography

trans-$Ir(PPh_3)_2(CO)Cl$ was prepared according to published methods.[13] *trans*-$Ir(PPh_3)_2(CO)I$ was prepared from its chloride analog by metathesis with NaI and acetone.[14] A crystal of **2-I** was placed in a glass capillary, and X-ray data were collected on an Enraf-Nonius CAD-4 diffractometer (graphite monochromatized Mo Kα radiation, λ = 0.710 73 Å) at room temperature. Three intensity standard reflections were checked every hour and found not to vary significantly for the entire data set of 6878 reflections. The data were corrected for Lorentz effects, polarization, and absorption, the latter correction employing the numerical method found in SHELX76.[15] The structure was solved by use of the Patterson methods employed in SHELXS86[16] and refined by least-squares and Fourier techniques based upon F_{obs}^2 (SHELXL93).[17] The largest peak on the final difference Fourier map had an electron density of 1.8 e/Å³ and the lowest excursion was −1.6 e/Å³, both near the Ir atom. Crystallographic details are given in Table 1. Table 2 lists the positional parameters for the non-hydrogen atoms.

Table 2. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å² × 10³) for 2-I[a]

	x	*y*	*z*	*U*(eq)
Ir	1123(1)	2972(1)	2475(1)	31(1)
I	1239(1)	2811(1)	383(1)	45(1)
O(1′)	1507(88)	2387(15)	263(23)	163(44)
C(1′)	1471(61)	2564(11)	1076(14)	91(29)
O(1)	2475(11)	760(5)	3282(5)	51(2)
C(1)	1972(5)	1561(5)	2942(4)	42(1)
I′	2264(14)	1097(4)	3544(7)	66(3)
O(2)	−213(4)	5265(3)	3600(3)	70(1)
C(2)	277(5)	4406(5)	3162(3)	47(1)
P(1)	3009(1)	3136(1)	2033(1)	31(1)
P(2)	−779(1)	2834(1)	2932(1)	34(1)
C(3)	3667(4)	2981(4)	3125(3)	35(1)
C(4)	4972(5)	2510(5)	2981(4)	46(1)
C(5)	5452(6)	2372(5)	3818(4)	54(1)
C(6)	4645(6)	2730(6)	4791(5)	57(2)
C(7)	3366(7)	3203(6)	4943(5)	64(2)
C(8)	2863(5)	3329(5)	4123(4)	49(1)
C(9)	4328(4)	2095(4)	1041(3)	33(1)
C(10)	4973(5)	1002(5)	1276(4)	44(1)
C(11)	5986(5)	217(5)	544(5)	52(1)
C(12)	6359(5)	503(5)	−431(5)	54(1)
C(13)	5705(6)	1577(6)	−691(4)	58(2)
C(14)	4699(5)	2378(5)	41(4)	44(1)
C(15)	2887(4)	4475(4)	1548(3)	35(1)
C(16)	1915(5)	5167(5)	1127(5)	49(1)
C(17)	1894(7)	6135(5)	699(5)	61(2)
C(18)	2810(6)	6440(5)	714(5)	56(1)
C(19)	3766(6)	5770(5)	1136(4)	53(1)
C(20)	3806(5)	4794(5)	1551(4)	46(1)
C(21)	−2173(4)	4113(4)	2842(4)	39(1)
C(22)	−2071(5)	4874(5)	2120(4)	49(1)
C(23)	−3133(6)	5819(5)	2041(5)	60(2)
C(24)	−4318(6)	6027(6)	2671(5)	65(2)
C(25)	−4438(5)	5286(6)	3384(5)	59(2)
C(26)	−3368(5)	4340(5)	3469(5)	50(1)
C(27)	−810(5)	1744(4)	2205(4)	40(1)
C(28)	−1726(5)	1982(5)	1706(4)	48(1)
C(29)	−1753(7)	1120(6)	1202(5)	60(2)
C(30)	−879(7)	36(6)	1199(5)	62(2)
C(31)	28(7)	−206(6)	1684(6)	70(2)
C(32)	101(6)	635(5)	2183(5)	57(1)
C(33)	−1236(4)	2550(4)	4282(4)	42(1)
C(34)	−1365(7)	3286(6)	5037(4)	63(2)
C(35)	−1748(7)	3126(7)	6071(5)	74(2)
C(36)	−1974(7)	2250(7)	6363(5)	70(2)
C(37)	−1851(7)	1518(7)	5646(6)	75(2)
C(38)	−1487(6)	1662(6)	4607(5)	58(2)
C(39)	1995(14)	2098(9)	7406(7)	119(3)
C(40)	1283(13)	2033(9)	6862(8)	131(3)
C(41)	1744(12)	1276(9)	6068(8)	118(3)
C(42)	2958(13)	546(9)	5804(8)	125(3)
C(43)	3775(12)	567(9)	6336(9)	135(4)
C(44)	3334(13)	1346(9)	7143(8)	121(3)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

The $Ir(PPh_3)_2(CO)_2I$ complex, as shown in Figure 1, maintains a trigonal-bipyramidal (tbp) structure, with minor spatial disorder of the ligands in the equatorial $Ir(CO)_2I$ plane. This disorder was best modeled by placing the C1−O1 carbonyl group at the I atom site with partial occupancy and *vice versa* (site occupancy for C1′, O1′,and I′ converged to 7.9 ± 0.2%). Distance restraints for C1′, O1′, and I′ were applied (see below). For clarity, Figure 1 shows only the non-H atoms of the Ir complex and the major (92%) occupants of the two disordered sites. The C2−O2 carbonyl site and the two PPh_3 sites were completely ordered, and the geometries of the atoms within these ligands are as expected.

The crystal structure also contained one benzene molecule at 4.2 and 4.6 Å from O2 and O1, respectively (6.3 Å from Ir). The benzene solvate showed considerable positional disorder or thermal motion, which was modeled by anisotropic displacement parameters. The occupancy of the benzene molecule refined to 100 ± 1%. Anisotropic displacement parameters were refined for the non-hydrogen atoms of the Ir complex, except C1′ and O1′. The positional and isotropic displacement parameters of the H atoms on the two PPh_3 ligands were refined and yielded C−H distances in the range 0.73−1.18 Å and H−C−C angles in the range 113−126°. The H atoms on the benzene molecule were fixed to their calculated sp² geometries (C−H = 0.93 Å) and were

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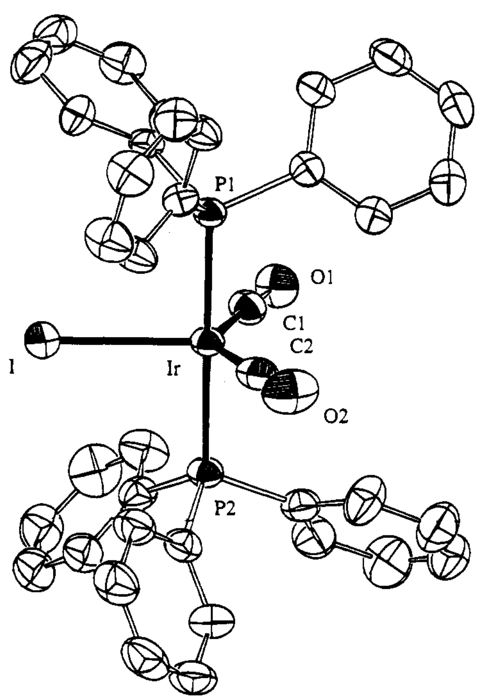

Figure 1. ORTEP diagram of *trans*-Ir$(PPh_3)_2(CO)_2$I; H atoms excluded.

assigned isotropic displacement parameters (U) of 1.2 times the equivalent isotropic U of the corresponding C atom.

The 51 distance and U_{ij} restraints applied during the full-matrix least-squares refinement (SHELXL93) were as follows: (i) the distances in column A (below) were restrained to be equal to the distances in column B with an effective standard deviation (Å) given in column C:

A	B	C
I′–Ir	I–Ir	0.002
I′⋯C1′	I⋯C1	0.005
I′⋯O1′	I⋯O1	0.007
I′⋯C2	I⋯C2	0.005
I′⋯O2	I⋯O2	0.007
C1′–Ir	C1–Ir	0.005
C1′–O1′	C1–O1	0.010
C1′⋯C2	C1⋯C2	0.010
C1′⋯O2	C1⋯O2	0.010
O1′⋯Ir	O1⋯Ir	0.007
O1′⋯C2	O1⋯C2	0.010
O1′⋯O2	O1⋯O2	0.010

(ii) the U_{ij} components of I′ and O1 were restrained to approximate isotropic behavior (with the corresponding isotropic U values free to vary), and the U_{ij} components of the nearly overlapping I and O1′ atoms and the I′ and O1 atoms were restrained to be the same with effective standard deviation 0.05 Å^2. (iii) The six C atoms of the benzene solvent molecule were restrained to be in a plane with an effective standard deviation of 0.02 Å, and the anisotropic displacement parameters of these C atoms were restrained to be equal to the anisotropic displacement parameters of the two C atoms to which they are bonded with an effective standard deviation of 0.01 Å^2 (e.g., "rigid-bond" restraints).

Results and Discussion

Previous crystallographic studies have shown that **1-Cl** and **2-Cl** (L = PPh_3) have square-planar[18] and trigonal-bipyramidal (tbp; axial phosphines) molecular structures,[19] respectively. Selected geometrical parameters for these two complexes are given in Table 3 along with the corresponding computed parameters (L = PH_3). Comparison between computed and crystallographic data shows that geometry optimization at the HF, MP2, or MP3 levels with the regular basis set accurately reproduces the geometry of **1-Cl**. Specifically, the computed Ir–Cl, Ir–P, Ir–C, and C–O bond distances in **1-Cl** (L = PH_3) at the MP3 level are 2.370, 2.323, 1.811, and 1.187 Å, respectively, in excellent agreement with the respective crystallographic values of 2.382, 2.330, 1.791, and 1.161 Å.

Table 3. Selected Crystallographic and Computed Bond Lengths (Å) and Angles (deg) for 1-X and 2-X

X	Ir–X	Ir–P	Ir–C	C–O	CIrC (θ)
trans-IrL_2(CO)X (**1-X**, Square Planar)					
crystallographic parameters (L = PPh_3)					
Cl[a]	2.382	2.330	1.791	1.161	
computed parameters (L = PH_3); MP3 level optimization					
Cl	2.370	2.323	1.811	1.187	
I	2.657	2.325	1.819	1.186	
trans-Ir$L_2(CO)_2$X (**2-X**, Trigonal Bipyramidal)					
crystallographic parameters (L = PPh_3)					
Cl[b]	2.37	2.33	2.04	1.14	120.9
I[c]	2.805(1)	2.337(1)	1.868(6)	1.13(1)	130.6(2)
computed parameters (L = PH_3); MP3 level optimization					
Cl	2.482	2.332	1.886	1.185	138.3
I	2.746	2.334	1.889	1.184	143.5
computed parameters (L = PH_3); MP2 level optimization[d]					
Cl	2.433	2.325	1.857	1.186	132.5
I	2.741	2.329	1.859	1.186	135.6

[a] Reference 18. No crystallographic study of **1-I** has been reported. [b] Reference 19. Due to disorder, error estimates are not given for parameters involving atoms in the equatorial plane. [c] This work. The given distances and angle are based upon the average of corresponding values of the major (92%) component (see text); values for the minor component are considered much less reliable. [d] With large basis set.

In **2-Cl**, the reported crystallographic Ir–P bond lengths are 2.322(7) and 2.341(7) Å in excellent agreement with the computed values of 2.325 (MP2, large basis set) or 2.332 Å (MP3, regular basis set). However, there are significant discrepancies between computed and crystallographic Ir–C, Ir–Cl, and C–O bond lengths in **2-Cl** (Table 3), including a difference of ca. 0.17 Å between the computed (1.86–1.88 Å) and reported (2.04 Å) Ir–C bond length. Additionally, and perhaps more significantly, a large discrepancy is found between crystallographic (121°) and computed values for the angle (θ) between the two equatorial carbonyl groups (138° at the HF level). Full geometry optimization of **2-Cl** at the MP2 level with the regular double-ζ basis set gives $\theta = 135°$. When the larger basis set is used for geometry optimization, θ is calculated as 135° and 133° at the HF and MP2 levels, respectively. Geometry optimization at the MP3 level with the regular double-ζ basis set gives $\theta = 138°$. The fact that θ is consistently large (relative to the nearly idealized tbp geometry of the reported structure) at all computational levels suggests that the discrepancy does not result from an inadequacy of the computational model. Rather, it may be attributed to 3-fold disorder in the location of the Cl and CO ligands and crystal decomposition reported for the crystallographic analysis of **2-Cl**. It should be noted

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Table 4. Selected Bond Lengths (Å) and Angles (deg) for 2-I

Ir−I	2.8052(4)	Ir−C(2)	1.867(6)	Ir−I′	2.802(2)
Ir−C(1)	1.868(6)	O(2)−C(2)	1.135(6)	Ir−C(1′)	1.874(8)
O(1)−C(1)	1.115(8)	Ir−P(1)	2.336(1)	O(1′)−C(1′)	1.12(1)
		Ir−P(2)	2.337(1)		

C(1)−Ir−C(2)	130.6(2)	C(1′)−Ir−C(2)	129.0(4)
C(1)−Ir−I	111.7(2)	C(1′)−Ir−I′	111.5(3)
C(2)−Ir−I	117.7(1)	C(2)−Ir−I′	119.3(2)
O(1)−C(1)−Ir	174.8(6)	O(1′)−C(1′)−Ir	171(6)
O(2)−C(2)−Ir	177.8(3)		
P(1)−Ir−I	90.94(3)	P(1)−Ir−I′	88.9(4)
P(2)−Ir−I	89.51(3)	P(2)−Ir−I′	91.5(4)
C(1)−Ir−P(1)	89.4(2)	C(1′)−Ir−P(1)	88(2)
C(1)−Ir−P(2)	91.1(2)	C(1′)−Ir−P(2)	93(2)
C(2)−Ir−P(1)	88.8(2)		
C(2)−Ir−P(2)	90.4(2)		
P(1)−Ir−P(2)	179.14(4)		

in this context that the structure of **2-Cl** was determined for purposes of comparison with the isoelectronic complexes $[IrX(CO)(NO)(PPh_3)_2]^+$, which revealed severely bent (ca. 125°) Ir−N−O angles. The conclusion reached, that the Ir−C−O angles of **2-Cl** are linear, was unaffected by the crystal decomposition and disorder (and is in agreement with the structure described below).

A new structure determination of **2-X** was undertaken. *trans*-$Ir(PPh_3)_2(CO)_2I$ was chosen for X-ray analysis in view of the disorder reported for **2-Cl** and because in the halide series of complexes, according to our computations, **2-X** loses CO least readily when X = I.[20] In the crystallographic study of **2-Cl**, decomposition during data collection, presumably due to CO loss, was reported to be a significant problem, but in our study of **2-I**, no signs of CO loss or other types of decomposition were observed. Selected geometrical parameters pertaining to the molecular structure of **2-I** are given in Tables 3 and 4, and an ORTEP diagram of **2-I** drawn with ellipsoids at the 50% probability level is given in Figure 1.

The molecular structure of **2-I**, like that of **2-Cl**, is found to have a trigonal-bipyramidal coordination sphere around Ir with the two PPh_3 ligands at the axial positions (P−Ir−P angle = 179.14(4)°). The value of θ was determined to be 130.6(2)° (for the major component[21]), somewhat smaller than the computed angle but, more importantly, clearly greater than the ideal tbp value of 120°.[22] Furthermore, the bond lengths in the equatorial plane are in good agreement with the calculations (Table 3); in particular the crystallographic Ir−C distance of **2-I** (1.87 Å) agrees well with the calculated values, in sharp contrast with the crystallographic value obtained for **2-Cl** (2.04 Å).

Additionally, the ratio of the intensities of the symmetric (I_{sym}) and antisymmetric ($I_{antisym}$) IR carbonyl stretch bands in a dicarbonyl complex can be related to the angle between the two carbonyls (θ) using eq 2.[23,24]

$$I_{sym}/I_{antisym} = \cot^2(\theta/2) \tag{2}$$

The measured carbonyl stretch frequencies (cm^{-1}) and corresponding extinction coefficients ($M^{-1}\ cm^{-1}$) for **2-X** (L = PPh_3; in toluene) are as follows: 1928 (3780) and 1978 (750) for X = Cl, and 1934 (3790) and 1988 (720) for X = I. Application of eq 2 gives values of 132° and 133° for θ, respectively, in excellent agreement with the values computed at the MP2 level using the large basis set, 133° (**2-Cl**) and 136° (**2-I**) (Table 3).

The angular distortion from tbp geometry found in **2-X** is computed to be present and of similar magnitude for a surprisingly wide range of substituents. When X = F, CN, H, and CH_3, for example, θ is computed (HF level) to be 132°, 132°, 136°, and 137°, respectively. Slightly distorted tbp structures were also found for the cationic complexes of **2-X**; when X^- = NH_3 or PH_3, for example, θ is computed to have a value of ca. 132° (HF). Only when X^- = CO is θ computed to be 120°. Experimentally, **2-H**[25] and **2-[C(O)OMe]**[26] (L = PPh_3 in both cases) are to our knowledge the only other crystallographically characterized d^8 tbp complexes with two equatorial CO ligands. Both complexes have one phosphine and the ligand X at the axial positions; thus, comparison with our calculations (both phosphines axial) is less direct. However, both structures do reveal a larger than ideal angle between the two equatorial carbonyls, 125.9(4)° (**2-H**) and 130.8(4)° (**2-[C(O)OMe]**), in spite of the presence of the bulky PPh_3 ligand in the equatorial planes.

The relatively small magnitude of the deviation of the C−Ir−C angle from ideal geometry makes its origin difficult to interpret in qualitative terms. One very simple (and speculative) interpretation involves maximizing the ability of the CO ligands to engage in π-backbonding. The conventional MO description of bonding assumes sp^2 hybridization in the equatorial plane and thus predicts a C−Ir−C angle of 120°. However, for each of the two equatorial d-orbitals to be of optimal orientation to interact with only one of the carbonyls requires the carbonyls to be positioned 135° apart. The driving force for each CO to interact with a different d-orbital may compensate for any loss of σ-overlap that may result from the increased C−Ir−C angle.

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Supplementary Material Available: Tables of intramolecular distances and angles, anisotropic displacement parameters, H atom parameters, torsion angles, and least-squares planes (13 pages). Ordering information is given on any current masthead page.

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[20] Computed and experimental substituent effects on the activation energy and thermodynamics of eq 1 will be presented elsewhere.

[21] The value of the C−Ir−C angle for the minor (7.9%) component, 129.0(4)°, is considered much less reliable.

[22] The C(1)−Ir−I and C(2)−Ir−I angles are 111.7° and 117.7°, respectively (Table 4). The difference presumably results from the phenyl groups "above" and "below" the C(2)−Ir−I moiety being canted so as to place an ortho-H between the ligands; the dihedral Ir−P−C−C angles are 22.3° and 30.2°, while those phenyl groups located above and below the C(1)−Ir−I grouping are not so directed (dihedral Ir−P−C−C angles are 73.4° and 56.2°).

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