

Theoretical Study of the Structures of Electron-Deficient d^6 ML_5 Complexes. Importance of a π -Donating Ligand

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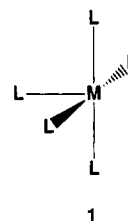
The structure of d^6 $Ir^{III}L_2ZZ'X$ complexes ($L = PH_3$; $Z, Z' = H^-, Me^-, Cl^-$; $X = H^-, Cl^-, NH_2^-, OR^-$ ($R = H, CH_3, CH_2F, CF_3$)) has been studied by ab initio pseudopotential calculations. In agreement with a previously published EHT study (Rachidi, I. E.-I.; Eisenstein, O.; Jean, Y. *New J. Chem.* 1990, 14, 671), it is shown that two structures are possible for a closed-shell state: a square-based pyramid (SP also called T) and a distorted trigonal bipyramid (dist-TBP also called Y) in which two ligands subtend an acute angle of about $70-80^\circ$. It is shown that the Y structure is favored when the ligand in the site trans to the acute angle is both a weak σ donor and a good π donor ($X = Cl^-, NH_2^-, OR^-$). These results are in full agreement with known experimental data: $Ir(PCy_3)_2ClH(C_5H_6)$ (2) and $Ir[N(SiMe_2CH_2P(Ph)_2)]RR'$ (3). The calculations also indicate that the structure of the recently synthesized $Ir(PCy_3)_2(OCH_2CF_3)H_2$ complex, 4b, in which the H centers could not be located in the X-ray data should be of the same Y type. We show that a partial metal-X π bond appears in the Y structure involving the lone pair of X and an empty metal orbital. This shortens the M-X bond significantly. When X is a single-faced donor ($X = NH_2^-, OR^-$), a preferred orientation of X is expected. Rotational barriers, calculated with $X = NH_2^-, OR^-$, have been shown to follow the electron-releasing ability of X. We show that the requirement of the metal for this electron donation from X is sufficient to stabilize the most sterically hindered isomer such as 4b. The fluxional behavior of the different complexes is discussed. The structure of the lowest triplet state, which is much higher in energy than the ground singlet state, is also determined in the case of the simplest complexes.

Introduction

Electron- and ligand-deficient transition-metal complexes are important intermediates in organometallic chemistry. They are usually highly reactive species and cannot be easily observed. However, the understanding of reaction paths can be improved by isolation and characterization of stabilized models of the reactive intermediates. In this context, d^6 ML_5 systems play a privileged role. They are key intermediates in numerous reactions since they derive from the d^6 octahedron by loss of one ligand, a typical first step in organometallic reactions. Despite their intrinsically high reactivity, many such complexes with a large range of metals and ligands have been stabilized, isolated, and structurally characterized in various reaction media.¹⁻⁸

These complexes usually contain ligands that have π -donating capability, which partially compensate for the electron deficiency at the metal and deactivate the complex toward an incoming reagent.⁶⁻⁸ They also frequently carry bulky protecting groups which hinder the approach of a reagent to the metal center.⁶⁻⁸ The most reactive of these complexes contain exclusively π -acceptor ligands ($M(CO)_5$; $M = Cr, Mo, W$) and can only be characterized in inert media (hydrocarbon glasses, rare-gas matrices, alkane and perfluoroalkane solvents).³⁻⁵

Until recently, all d^6 ML_5 complexes were known to have a square-pyramidal structure (SP), 1, in which the apical site was occupied by the ligand with the largest trans in-



fluence and the angles between transoid basal ligands ranged from 160° to 180° .⁶⁻⁸ In 1986, two independent groups reported a new type of structure for diamagnetic

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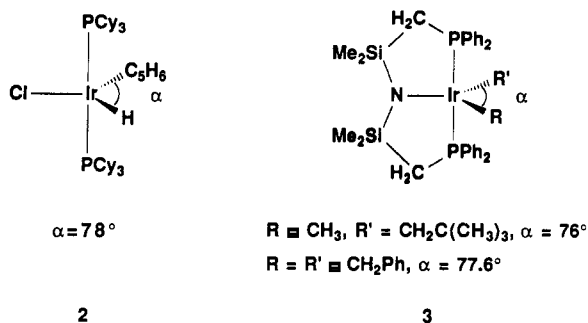
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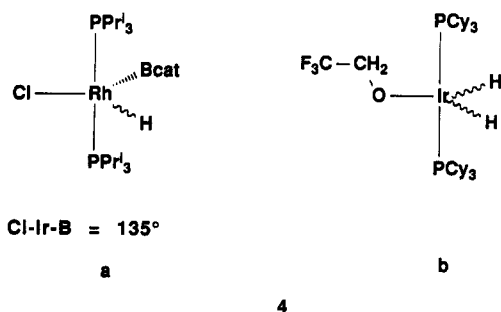
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Ir(III) complexes, **2** and **3**.⁹⁻¹⁰ This new structure is best



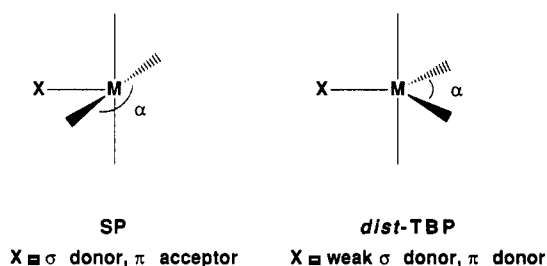
viewed as a highly distorted trigonal bipyramid (dist-TBP) in which two equatorial ligands are squeezed toward each other so that they subtend an angle α inferior to 80° . In these complexes the acute angle is opposite to a π -donating ligand. It should be noted that no steric factors can account for the presence of this acute angle. Fryzuk has shown that changing the nature of the R groups (alkyl, aryl, H) which subtend α in **3** does not alter the shape of the complex. Another complex **4a**, has just been reported.¹¹ Although the hydride ligand was not located by X-ray diffraction, the presence of a Cl-Rh-B angle of 135° suggests the dist-TBP structure. Other complexes have a related structure.¹²



In searching for stable electron-deficient polyhydride complexes, the diamagnetic complex $\text{Ir}(\text{OCH}_2\text{CF}_3)_2(\text{PCy}_3)_2$ (**4b**) was isolated.¹³ As in **4a**, the hydride ligands in **4b** could not be located. We suggest in this work that this complex also has a dist-TBP structure, with the H atoms subtending an acute angle. We will show how the unusual orientation of the OCH_2CF_3 ligand, which is sterically less favorable, helps to stabilize the dist-TBP structure. This result is in agreement with the earlier suggestion of Fryzuk concerning the complex $\text{Ir}[\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2]\text{H}_2$ in which the H could not be located in the X-ray diffraction.¹⁴

A considerable amount of theoretical work has been done on these $d^6 \text{ML}_5$ complexes. The presence of a partially filled set of degenerate orbitals results in a TBP geometry being stable for the triplet state and Jahn-Teller unstable for the singlet state.^{3b} All the reported structures are diamagnetic; hence, a TBP geometry is unlikely. The SP structure was shown to be favored at various levels of

calculations.^{3b,c,15-19} The possibility of a dist-TBP structure was mentioned by Morokuma et al. in their work on the mechanism of the Wilkinson catalyst.¹⁹ Thorn and Hoffmann proposed that a d^6 pentacoordinated strained metallacycle in which the C-M-C angle is around 70° may be stabilized by a π -donor ligand in the plane of the carbon chain.^{16c} A qualitative analysis based on EHT calculations was performed to determine the factors which favor dist-TBP over SP.²⁰ It was shown that an X ligand with strong σ -donating and π -accepting capabilities favors an SP structure, **5a**. In contrast, an X ligand with poor σ -donating and good π -donating capabilities could stabilize a dist-TBP structure in which X is trans to the acute angle, **5b**.



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The EHT calculations^{3c,20} have also indicated a facile transformation between dist-TBP and SP structures, which is in agreement with the fluxional behavior of these complexes in solution.²¹ The path for interconversion was shown not to go through a regular TBP structure (**6**, path 1) since it would involve a crossing between occupied and empty orbitals. The exchange process involves a circular route (**6**, path 2). A similar suggestion was done by Tatsumi and Hoffmann in the case of $d^8 \text{ML}_3$ complexes.²² It was, however, impossible to calculate the shape of the potential surface for the ML_5 complexes at the EHT level in a quantitative manner. The relative stabilities of all the dist-TBP and SP structures could not be determined accurately since some of them were found to be close in energy. It is thus necessary to use a higher level of calculations.

In this work, we describe the results of ab initio calculations for several $d^6 \text{Ir}^{\text{III}}\text{L}_2\text{ZZ}'\text{X}$ complexes in which L is a phosphine ligand (PH_3 for the calculations). The nature

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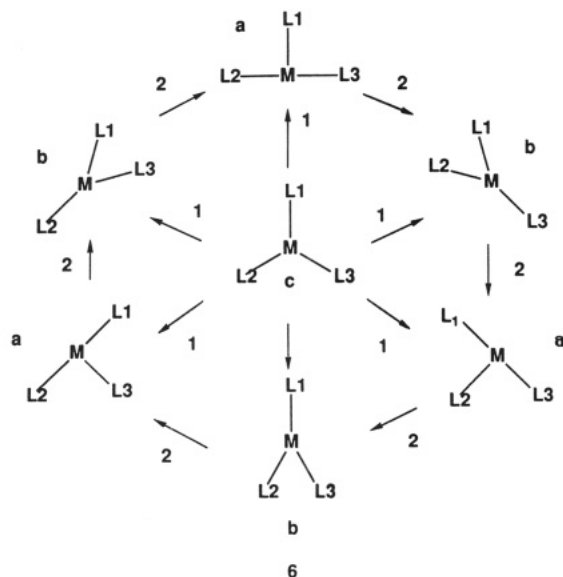
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of Z, Z' (H^- , CH_3^- , Cl^-) and X (Cl^- , NH_2^- , OH^- , OCH_3^- , OCH_2F^- , OCF_3^-) was changed to model the different experimental complexes. The energies of several possible structures of the singlet state were calculated. The structure of the lowest triplet state was also determined in the simplest systems ($Z = Z' = H^-$). The importance of a π donor and of a proper orientation of a single-faced π -donating group in stabilizing dist-TBP structures was also investigated.

For sake of simplicity, the PH_3 groups will often be left out of the drawings and SP and dist-TBP structures called T and Y, respectively. When substituents such as X are introduced in the complex, the notation T_X (Y_X) will be used to describe a T (Y) shape structure with ligand X opposite to the open site (acute angle).

Qualitative Analysis of the Geometries of $d^6 ML_5$ Complexes

Before presenting our results from the ab initio calculations, we need to briefly summarize the qualitative analysis.²⁰

The orbital pattern of TBP with all identical ligands is shown in Figure 1a. The e' set is only partially filled in a d^6 complex which leads to a Jahn-Teller-active system. Two types of distortion which lower the energy of one member of the e' set have been found to stabilize the singlet ground state of the complex. Opening the α angle (SP structure) lowers xy while closing α (dist-TBP structure) lowers $x^2 - y^2$. In contrast, the lowest triplet state is predicted to have a regular TBP geometry. The SP structure has been shown to be slightly more stable than dist-TBP for homoleptic complexes; in SP, xy can be fully nonbonding with respect to all σ ligands while, in dist-TBP, $x^2 - y^2$ always maintains some antibonding character with the σ ligands in the equatorial xy plane, particularly with the ligand trans to the acute angle. Similar results were found for the isolobal $d^8 ML_3$ complexes.²²

We have shown that the above picture is significantly modified by changing the nature of the ligands.²⁰ Ligands in the equatorial plane which stabilize xy and destabilize $x^2 - y^2$ favor SP; this is the case when X is a strong σ donor and a good π acceptor. Ligands which destabilize xy more than $x^2 - y^2$ favor dist-TBP; this is the case when X is a weak σ donor and a good π donor. The effect of such a π donor ligand ($X = D$) on the two orbitals, xy and $x^2 - y^2$, is indicated in Figure 1b. The role of the ligands perpendicular to the xy plane has been shown to be neg-

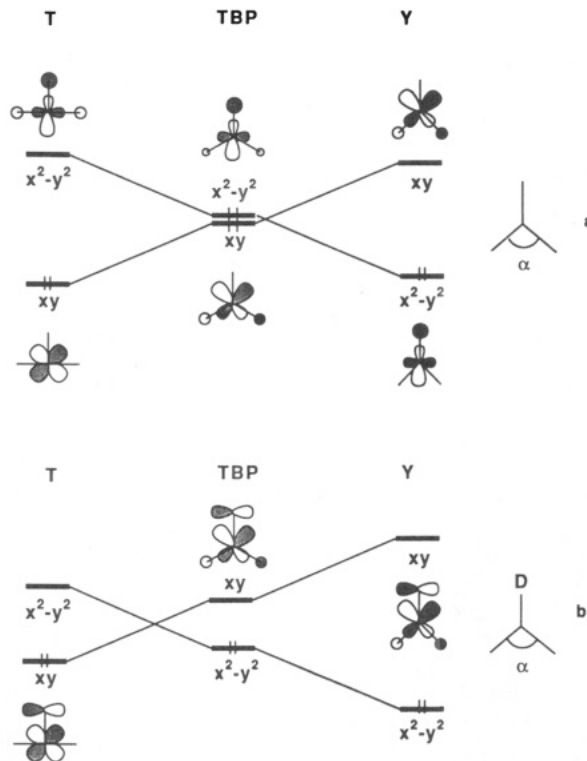


Figure 1. Energy diagram (T \rightarrow TBP \rightarrow Y) for (a) $Ir(PH_3)_2H_3$ and (b) $Ir(PH_3)_2H_2D$ with D = π donor.

ligible. A natural extension of this qualitative analysis can be done for the triplet state. Its geometry will also be modified by the nature of the ligands in the xy plane. The optimal energy of the triplet state will be when the two orbitals $x^2 - y^2$ and xy are degenerate (D_{3h} structure for identical ligands in the xy plane). In the case of a π -donor ligand, the degeneracy of $x^2 - y^2$ and xy does not occur for D_{3h} geometry but for a structure (pseudo-TBP) in which the α angle is larger than 120° (Figure 1b); i.e., the geometry of the pseudo-TBP shifts toward SP.

It is interesting to present an alternative point of view of the above analysis. The ML_4X system ($X = \pi$ donor) can be viewed as made of a C_{2v} $d^6 ML_4^+$ fragment and an X^- group or atom. The empty b_2 orbital of ML_4^+ stabilizes the ligand-occupied p orbital, making a partial M-X double bond, 7. This approach better illustrates that a shortening of the M-X bond is expected in a Y shape. If X was a single-face donor, a preferred orientation of X would also be observed.



Method of Calculations

An effective core potential (ECP) was used for Ir, Cl, and P. For Ir, the ECP of Hay and Wadt which includes the 5s and 5p electrons in the valence shell was chosen^{23a}

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Table I. Structures of Ir(PH₃)₂H₃, Distances (Å), Angles (deg), Geometry Optimizations (See Text), and Energies (kcal/mol) Relative to the Most Stable Structure within Each Method

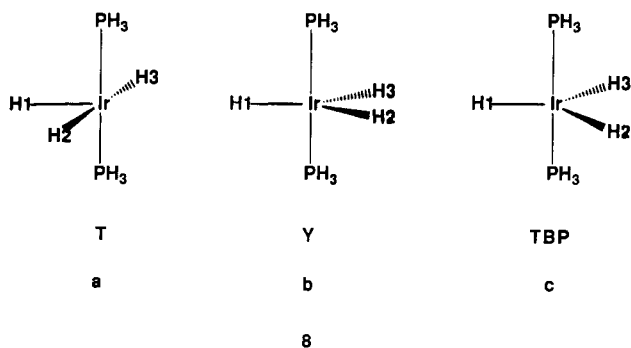
structure	Each Method				
	T	T	Y	Y	TBP
opt level	POPT	FOPT	POPT	FOPT	POPT
α	179.2	179.5	70.1	69.6	120.0
Ir-H1	1.55	1.54	1.76	1.75	1.68
Ir-H2(3)	1.69	1.69	1.59	1.59	1.68
Ir-P	2.40	2.37	2.39	2.34	2.40
P-H	1.40 ^a	1.42	1.40 ^a	1.41	1.40 ^a
H1-Ir-P	90.0 ^a	89.2	90.0	90.2	90.0 ^a
H-P-Ir	109.5 ^a	118.3 ^b	109.5 ^a	118.1 ^b	109.5 ^a
E(SCF)	0	0	4.0	4.1	22.4 (³ B ₂)
E(MCSCF)	0	0	3.6	3.8	27.6 (³ B ₂) 37.8 (¹ A ₁)

^a Frozen coordinate. ^b Average value.

with a (6s6p5d) Gaussian basis set contracted into (3111/3111/311) for the valence shell. For Cl and P, a (4s4p) Gaussian basis set, contracted into (31), with the ECP of Barthelat et al. (Cl)^{23b} and of Stevens and Basch (P)^{23c} was selected. For H, the (4s) contracted into a (31) basis set of Huzinaga was used for all H except those of PH₃ and the CH₃ group (Z = Z' = Me⁻) where a (4s/1s) basis set was chosen.^{23d} The basis set for all other atoms (C, N, O, F) is a split-valence 6-31G.^{23e}

Geometry optimization for triplet and singlet states was carried out at the RHF level with the HONDO 8 program.²⁴ The energies of the singlet-state structure were recalculated with 2 × 2 MCSCF using $x^2 - y^2$ and xy orbitals in the simplest model complexes (Z = Z' = H⁻). For Z and Z' different from H, the results are given at the RHF level. This approximation is reasonable since in both the T and Y structures the RHF configuration is about 95% of the total wave function. Two levels of geometry optimization were performed: POPT and FOPT. In POPT, (partial optimization) the phosphine ligands, modeled by PH₃, were kept perpendicular to the xy plane with a frozen internal geometry (P-H = 1.4 Å, H-P-H = 109.5°). All other structural parameters including the Ir-P distances were optimized by gradient method. In FOPT, a full structural optimization was allowed. On some of the more crucial complexes, the nature of the structure on the potential energy surface was established by calculating the Hessian matrix.

Ir(PH₃)₂H₃. The geometries of the ground singlet (¹A₁) and triplet (³B₂) states have been optimized with POPT, under C_{2v} symmetry constraint (structures 8a-c; Table I).



Two extrema are found for the singlet state, the T geometry being more stable than the Y one by 3.6 kcal/mol. The ab initio orbitals confirm the EHT analysis which has

- 1 T Structure
- 2 Y Structure
- 3 D_{3h} Structure
- 4 Outside the PES

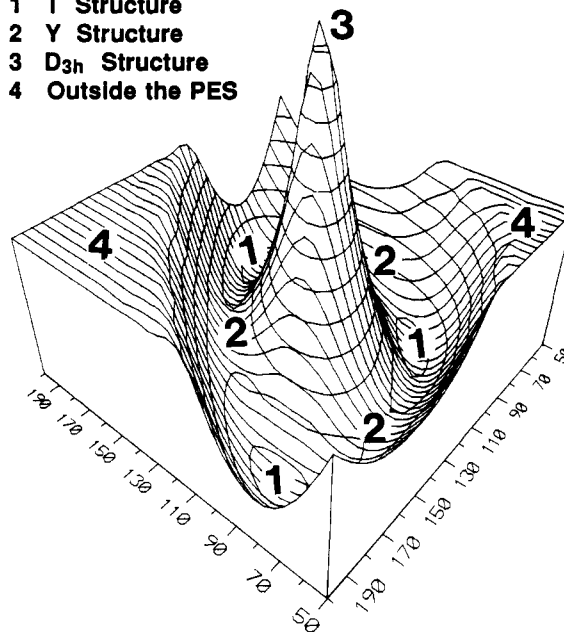


Figure 2. Potential energy surface at the RHF level for Ir(PH₃)₂H₃. The variables are two H-Ir-H angles; all other structural parameters have been optimized. The energy is given in kilocalories per mole. The energy region close to the D_{3h} structure is over-estimated by 3-5 kcal/mol. The first contour is 1 kcal/mol above the minimum, and the next contour lines are separated by 3 kcal/mol.

been described above. The greater stability of T over Y is due to the fact that $x^2 - y^2$ lies higher in energy than xy due to remaining Ir-H antibonding interaction in the first orbital (see Figure 1). The triplet state, ³B₂, of D_{3h} geometry (8c), is considerably higher in energy (27.6 kcal/mol). This accounts for the lack of observation of species like 8c. The ¹A₁ state, with the D_{3h} geometry, is even higher in energy (37.8 kcal/mol), a clear indication that the interconversion between 8a and 8b does not go through this structure and a natural consequence of the forbidden crossing of $x^2 - y^2$ and xy .

POPT and FOPT give similar geometries for structures T and Y which will allow the use of the less expensive POPT for larger and less symmetrical systems. This is why the highly energetic ³B₂ and ¹A₁ TBP species were not recalculated with FOPT. It is also to be noted that the RHF and the MCSCF calculations give very similar relative energies of T and Y geometries. The reason is that the RHF configuration makes up 95% of the 2 × 2 wave function in the T and Y structures. However, the use of FOPT is important for revealing the real nature of structure Y. As indicated by the Hessian matrix, the T geometry is the only real minimum while the Y geometry is a transition state to interconnect two T structures. The interconversion between the T structures is a facile process since it requires only 3.6 kcal/mole (path 2 in 6). The general feature of the potential energy surface, at the RHF level, is shown in Figure 2 where the variables are two angles in the IrH₃ plane, all other parameters being optimized at the RHF level. Therefore, the energy of the D_{3h} region is overestimated by 3-5 kcal/mol.

The apical Ir-P bond lengths are slightly longer than the experimental ones (2.40 Å vs 2.35-2.39 Å). Such lengthening has been commonly obtained in the calculation of metal-ligand bond length and has been attributed to the lack the correlation energy (notably in the presence of CO ligands).²⁵ Similar results are thus found for pure

(24) Dupuis, M.; Watts, J. D.; Villar, H. O.; Hurts, G. J. B. HONDO 8, I.B.M. Corporation, Scientific and Engineering Computations, Department 48B/MS 428.

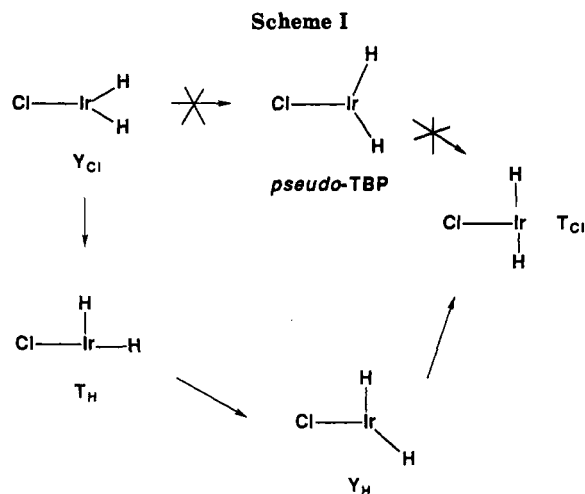


Table II. Structures of $Ir(PH_3)_2ClH_2$, Distances (Å), Angles (deg), Geometry Optimizations (See Text), and Energies (kcal/mol) Relative to the Most Stable Structure within Each Method

structure	T_{Cl}	T_{Cl}	Y_{Cl}	Y_{Cl}	pseudo-TBP
	POPT	FOPT	POPT	FOPT	POPT
opt level	177.1	177.2	73.6	73.4	142.5
α	177.1	177.2	73.6	73.4	142.5
Ir-Cl	2.40	2.40	2.51	2.49	2.57
Ir-H2(3)	1.69	1.68	1.56	1.56	1.67
Ir-P	2.41	2.39	2.41	2.39	2.41
P-H	1.40 ^a	1.41 ^b	1.40 ^a	1.42 ^b	1.40 ^a
Cl-Ir-P	90.0 ^a	87.4	90.0 ^a	90.0	90.0 ^a
H-P-Ir	109.5 ^a	117.1 ^b	109.5 ^a	117.5 ^b	109.5 ^a
$E(SCF)$	38.9	38.9	0	0	26.7 (³ B ₂)
$E(MCSCF)$	40.1	39.2	0	0	29.9 (³ B ₂) 53.9 (¹ A ₁)

^a Frozen coordinate. ^b Average value.

σ -donor ligands. However, in our case, we are mostly interested in comparing closely related structures, and the results are not affected by the lengthening of the apical bonds. Interestingly, the T and Y structures have very similar Ir-PH₃ bonding: Ir-P distances are equivalent, and the geometry for the PH₃ group is the same. The phosphines remain perpendicular to the IrH₃ plane in both the Y and T geometries. This result is not surprising for the Y structure and has been observed in compounds 2 and 3. However, it is less expected in the case of T where the angles between transoid basal ligands are often less than 180°. One might attribute this result to steric strain between the apical ligand of the square-based pyramid and the bulky basal ligands such as PCy₃ which are present in some of the experimental complexes.

The calculated Ir-H bond lengths differ considerably in the T and Y structures (see Table I). The shortest bond (1.54 Å) is calculated for the apical H1 center in structure T and is due to the absence of a trans ligand. The longest Ir-H bond (1.74 Å) is obtained for Ir-H1 in structure Y. The two other bond lengths are intermediate to those and are longer in T (1.69 Å) than in Y (1.59 Å). The long Ir-H1 bond in Y is due to the fact that the occupied $x^2 - y^2$ orbital is mostly antibonding with H1 while almost nonbonding with respect to H2 and H3.

$Ir(PH_3)_2ClZ_2$ ($Z = H^-, CH_3^-, Cl^-$). (a) $Ir(PH_3)_2ClH_2$. The complex $Ir(PH_3)_2ClH_2$ is our first model for the ex-

- 1 Y_{Cl} Structure
- 2 T_{Cl} Structure
- 3 T_H Structure
- 4 Pseudo- D_{3h} Structure
- 5 Outside the PES

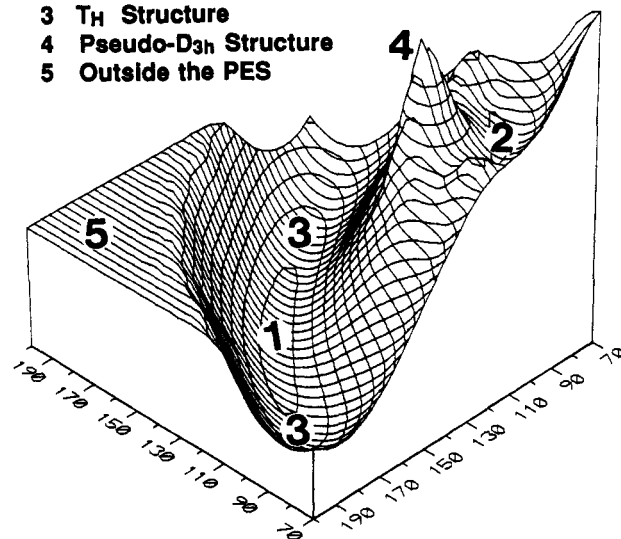
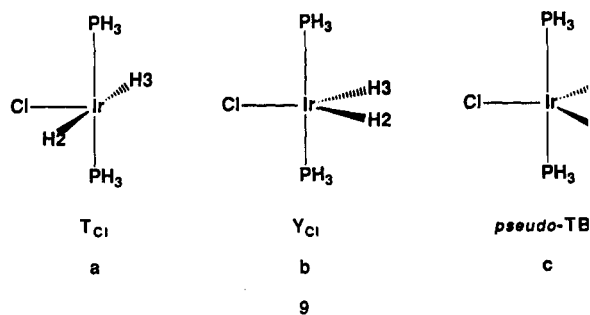


Figure 3. Potential energy surface at the RHF level for $Ir(PH_3)_2H_2Cl$. The variables are two Cl-Ir-H angles; all other structural parameters have been optimized. The energy is given in kilocalories per mole. The energy region close to the pseudo- D_{3h} structure is over-estimated by 3–5 kcal/mol. The first contour is 1 kcal/mol above the minimum, and the next contour lines are separated by 3 kcal/mol.

perimental complex 2. Two T structures (T_{Cl} and T_H) and two Y structures (Y_{Cl} and Y_H) are possible (Scheme I). T_{Cl} (9a) and Y_{Cl} (9b) can be calculated with C_{2v} constraint.



With POPT, Y_{Cl} is more stable than T_{Cl} by 40.1 kcal/mol (Table II) in good agreement with the qualitative analysis. FOPT gives equivalent results, T_{Cl} being 39.2 kcal/mol higher in energy than Y_{Cl} . The geometries of the two structures calculated from POPT and FOPT remain essentially identical (Table II). The Ir-Cl bond length is short in T_{Cl} (2.40 Å, FOPT) and long in Y_{Cl} (2.49 Å, FOPT), but the change in the Ir-Cl bond length is considerably less than that of Ir-H1 from T to Y in $Ir(PH_3)_2H_3$. This moderate lengthening of the Ir-Cl bond length is due to the appearance of a partial Ir-Cl π bond in the Y_{Cl} structure, which is not present in the T_{Cl} structure. In T_{Cl} the only factor responsible for the short Ir-Cl bond length is the lack of a ligand trans to Cl. The other geometrical parameters have a less remarkable behavior. The Ir-H2(3) bond lengths in $Ir(PH_3)_2ClH_2$ are very similar to those calculated for $Ir(PH_3)_2H_3$. The acute angle between the two H centers in Y_{Cl} is just a little larger than in the Y structure of $Ir(PH_3)_2H_3$.

Calculation of the Hessian matrix establishes that both T_{Cl} (9a) and Y_{Cl} (9b) are minima on the potential energy surface. Interconversion between the two structures avoids the pseudo-TBP geometry 9c (³B₂, 29.9 kcal/mol; ¹A₁ with the geometry of the ³B₂ state, 53.9 kcal/mol above Y_{Cl}).

(25) See for instance: Lüthi, H. P.; Siegbahn, P. E. M.; Almlöf, J. J. *Phys. Chem.* 1985, 89, 2156. Antolovic, D.; Davidson, E. R. *J. Chem. Phys.* 1988, 88, 4967. Antolovic, D.; Davidson, E. R. *J. Am. Chem. Soc.* 1987, 109, 5828. Dedieu, A.; Nakamura, S.; Sheldon, J. C. *Chem. Phys. Lett.* 1987, 141, 323. Dedieu, A.; Sakaki, S.; Strich, A.; Siegbahn, P. E. M. *Chem. Phys. Lett.* 1987, 133, 317.

Table III. Structures of $\text{Ir}(\text{PH}_3)_2\text{ClMe}_2$, Distances (Å), Angles (deg), and Energies (kcal/mol) (Geometry Optimization Performed Using POPT)

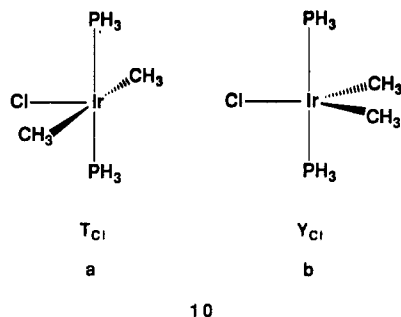
structure	T_{Cl}	Y_{Cl}	structure	T_{Cl}	Y_{Cl}
α	177.1	81.9	P-H	1.40 ^a	1.40 ^a
Ir-Cl	2.39	2.53	Cl-Ir-P	90.0 ^a	90.0 ^a
Ir-C2(3)	2.20	2.10	H-P-Ir	109.5 ^a	109.5 ^a
Ir-P	2.42	2.41	$E(\text{SCF})$	32.7	0

^a Frozen coordinate.

As expected, in this pseudo-TBP structure, the H-Ir-H angle is larger than 120° (142°). The general shape of the potential energy surface is shown in Figure 3 (RHF calculations). Like in the case of $\text{Ir}(\text{PH}_3)_2\text{H}_3$ (Figure 2) the variables are two angles in the IrClH_2 plane, all other parameters being optimized. One can see that T_{H} (H-Ir-H = 90°) and Y_{H} (Cl-Ir-H = 80° , 140°) are not singular points on the surface. T_{H} is very close in energy to the minimum, Y_{Cl} , while Y_{H} is just below T_{Cl} by 4.1 kcal/mol (RHF) or 3.6 kcal/mol (MCSCF). As expected from the Hammond principle, the geometry of the transition state for the transformation of Y_{Cl} into T_{Cl} is close to T_{Cl} (approximately Cl-Ir-H = 115° , 88°) and lies 1.5 kcal/mol (RHF) above T_{Cl} .

At this point, it is interesting to discuss the reactivity of the complex with an incoming nucleophile. The reactant can add to the metal only by approaching in a wide ligand-metal-ligand angle. Addition trans to Cl would involve approaching either the T_{Cl} or the Y_{H} structures, which are both very high in energy. The nucleophile would prefer to approach Y_{Cl} which is lower in energy. The precise structure of the transition structure is unknown, but it is reasonable to believe that the nucleophile distorts the reactant toward a T_{H} type structure¹⁹ which is close in energy to Y_{Cl} . This leads to an addition trans to H. This explains why no addition of an incoming ligand trans to Cl is experimentally observed in **2**.

(b) $\text{Ir}(\text{PH}_3)_2\text{ClMe}_2$ and $\text{Ir}(\text{PH}_3)_2\text{ClMeH}$. The calculations on $\text{Ir}(\text{PH}_3)_2\text{ClH}_2$ demonstrated that the angle between the two Ir-H bonds should be acute. However, no steric strain prevents the two H ligands from coming close together. This is thus a poor representation of experimental complexes where alkyl and aryl ligands subtend the acute angle. In order to verify to what extent the preference for a Y structure was influenced by the presence of steric hindrance, we calculated $\text{Ir}(\text{PH}_3)_2\text{ClMe}_2$ with C_{2v} constraint and POPT (Table III; 10). The optimized angle



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in the Y_{Cl} structure (**10b**) was found to be 81.9° , larger than that found with the H centers (73.6°). Nevertheless, it is clear that the Y structure is still quite favored. Y_{Cl} is more stable than T_{Cl} (**10a**) by 32.7 kcal/mol, a value close to that calculated in the case of $\text{Ir}(\text{PH}_3)_2\text{ClH}_2$ (38.9 kcal/mol). It thus appears that the shape of the potential energy surface is little affected by the presence of alkyl groups.

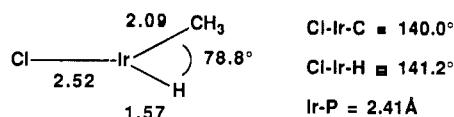
An intermediate situation, even closer to the experimental complex, is represented by $\text{Ir}(\text{PH}_3)_2\text{ClMeH}$ (**11**).

Table IV. Structures of $\text{Ir}(\text{PH}_3)_2\text{Cl}_2$, Distances (Å), Angles (deg), and Energies (kcal/mol) (Geometry Optimization Performed Using POPT)

structure	T	Y	structure	T	Y
α	160.4	89.2	P-H	1.40 ^a	1.40 ^a
Ir-Cl	2.35	2.42	Cl-Ir-P	90.0 ^a	90.0 ^a
Ir-Cl2(3)	2.39	2.45	H-P-Ir	109.5 ^a	109.5 ^a
Ir-P	2.41	2.42	$E(\text{SCF})$	0.0	4.2

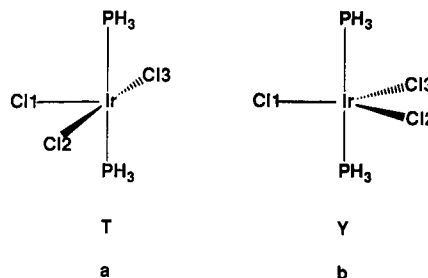
^a Frozen coordinate.

Using POPT, the angle between Ir-Me and Ir-H is calculated at 78.8° , a value very close to that observed experimentally in **2** (78°). The two structures, T_{H} and T_{Me} , are not minima on the potential energy surface and are calculated (by freezing the angles between ligands in the xy plane to idealized 90° and 180°) to be slightly higher in energy than Y_{Cl} .



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(c) $\text{Ir}(\text{PH}_3)_2(\text{Cl})_2$. The replacement of two Me groups by two Cl atoms ($Z = \text{Cl}^-$) leads to a drastic change in the shape of the potential energy surface. Using POPT, the T structure (**12a**) becomes more stable than the Y

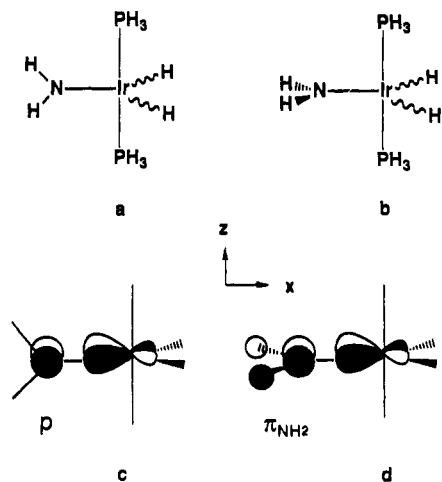


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structure (**12b**) by 4.2 kcal/mol (Table IV). The reason for the lower stability of the Y structure is a large four-electron repulsion between the Cl12 and Cl13 p lone pairs lying in the xy plane. This is an example where the electronic repulsion between lone pairs which is a part of the steric hindrance between the two centers diminishes the stability of the Y geometry. Interestingly, the steric hindrance seems to be larger in the case of two Cl ligands than in the case of two Me groups. This may be due to the fact that the lone pairs of the Cl ligands always point toward each other. This interaction also results in a general lengthening of the Ir-Cl bond lengths when compared to the $\text{Ir}(\text{PH}_3)_2\text{H}_2\text{Cl}$ case.

$\text{Ir}(\text{PH}_3)_2(\text{NH}_2)_2$ ($Z = \text{H}^-, \text{CH}_3^-$). The system $\text{Ir}(\text{PH}_3)_2(\text{NH}_2)_2$ ($Z = \text{H}^-, \text{CH}_3^-$) models the experimental complex **3** and carries one single-face π -donating ligand whose orientation should influence the T/Y energy difference. For convenience, the conformation with NH_2 perpendicular to the xy plane (**13a**) is called vertical (Y^v and T^v), and the conformation where NH_2 is lying in the xy plane (**13b**) is called horizontal (Y^h and T^h). In the experimental complex **3**, the vertical orientation is forced by the tridentate nature of the ligand.

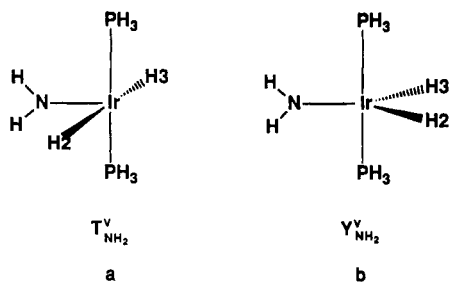
The qualitative analysis suggests that the Y structure should be favored by the presence of the nitrogen lone pair lying in the xy plane (i.e., vertical orientation of the NH_2 group) as shown in **13c**. This corresponds to the observed structure in **3**. In the other orientation, the π -donating



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orbital which is symmetry adapted to interact with the metal xy orbital is π_{NH_2} (13d), a less powerful π donor than the N lone pair. It is even questionable whether the structure with NH_2 lying in the xy plane would prefer to have a T or Y shape.

Let us first consider conformation 13a. Using POPT, in the ground singlet state, $Y^v_{NH_2}$ (14b) is a true minimum, as indicated by the Hessian matrix and is more stable than $T^v_{NH_2}$ (14a) by 42.8 kcal/mol (Table V). In $Y^v_{NH_2}$, the



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H–Ir–H angle value is 70.6° , a value close to that calculated for $Ir(PH_3)_2ClH_2$ (73.4°). This demonstrates the strong π -donating influence of the amido group in this orientation which is also the experimental one. In order to obtain further information on the shape of the potential energy barrier, the T^h_H structure (C_s), in which a hydride ligand is opposite to the empty site, was optimized (POPT and frozen angles in the xy plane). Such a structure is not a true minimum on the potential energy and is found to be 20.2 kcal/mol higher than $Y^v_{NH_2}$. It is thus lower in energy than the very disfavored $T^v_{NH_2}$. A similar ordering in the energy of the various Y and T structures was obtained for $Ir(PH_3)ClH_2$ (Scheme I). Finally, in the lowest triplet state, the H–Ir–H angle opens to 141° , as expected from the qualitative diagram given in Figure 1b. However, this state is calculated to be high in energy (41.9 kcal/mol above $Y^v_{NH_2}$). The 1A_1 state with this pseudo-TBP geometry is even higher at 61.8 kcal/mol.

Let us now rotate the NH_2 group by 90° (13b). We found that $Y^h_{NH_2}$ (15b) is 17.4 kcal/mol above $Y^v_{NH_2}$ (14b) in agreement with the weaker π -donating ability of the π_{NH_2} orbital. However, the corresponding $T^h_{NH_2}$ structure (15a) is found to be more stable than $T^v_{NH_2}$ (14b), although it is higher than the two preceding Y structures. The reasons for $T^h_{NH_2}$ being lower than $T^v_{NH_2}$ are not easy to identify. In both conformations, the N lone pair and π_{NH_2} overlap with the same two occupied d orbitals. However,

Table V. Structures of $Ir(PH_3)_2(NH_2)H_2$, Distances (Å), Angles (deg), and Energies (kcal/mol) (Geometry Optimization Performed Using POPT)^a

structure	$T^v_{NH_2}$	$Y^v_{NH_2}$	$T^h_{NH_2}$	$Y^h_{NH_2}$
α	177.2	70.6	177.4	69.6
Ir–N	2.02	2.02	2.00	2.15
Ir–H2(3)	1.70	1.60	1.68	1.59
Ir–P	2.41	2.41	2.41	2.41
N–H	0.99	1.00	0.99	1.00
P–H	1.40 ^b	1.40 ^b	1.40 ^b	1.40 ^b
N–Ir–P	90.0 ^b	90.0 ^b	90.0 ^b	90.0 ^b
H–N–Ir	122.8	125.7	121.4	124.3
H–P–Ir	109.5 ^b	109.5 ^b	109.5 ^b	109.5 ^b
E (SCF)	42.7	0.0	31.2	16.6
E (MCSCF)	42.8	0.0	32.4	17.4

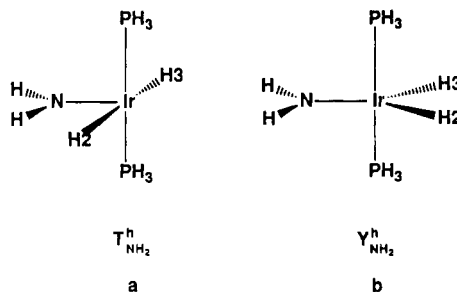
^a The pseudo-TBP structure was calculated in the (v) orientation: the main geometric features are Ir–N = 2.06 Å, Ir–H2(3) = 1.69 Å, and $\alpha = 141.0^\circ$. The energy of 3B_2 (relative to $Y^v_{NH_2}$) is 41.9 kcal/mol, and the energy of 1A_1 is 61.8 kcal/mol (MCSCF energy). $Y^v_{NH_2}$ is a true minimum as evidenced by calculation of the Hessian matrix. No equivalent calculations were done for the other structures which have been optimized with a symmetry constraint. ^b Frozen coordinate.

Table VI. Structures of $Ir(PH_3)_2(NH_2)Me_2$, Distances (Å), Angles (deg), and Energies (kcal/mol) (Geometry Optimization Performed Using POPT)

structure	$T^v_{NH_2}$	$Y^v_{NH_2}$	structure	$T^v_{NH_2}$	$Y^v_{NH_2}$
α	177.8	79.3	P–H	1.40 ^a	1.40 ^a
Ir–N	2.00	2.02	N–Ir–P	90.0 ^a	90.0 ^a
Ir–C2(3)	2.19	2.12	H–N–Ir	122.5	125.7
Ir–P	2.42	2.42	H–P–Ir	109.5 ^a	109.5 ^a
N–H	0.99	0.99	E (SCF)	35.4	0

^a Frozen coordinate.

these two structures are too high in energy to ever be observed experimentally.



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Although the rotation of the NH_2 group is not permitted in the experimental complex 3 because of the tridentate nature of the ligand, it is interesting to discuss the geometry of the conformers $Y^v_{NH_2}$ (14b) and $Y^h_{NH_2}$ (15b) in more detail since some the conclusions will be relevant in the next system to be discussed. In $Y^v_{NH_2}$, the nitrogen lone pair is stabilized by the empty xy orbital as shown in 13c. Meanwhile, in the same conformation, the π_{NH_2} orbital overlaps with the filled metal xz orbital which creates a four-electron destabilization which is weak because the overlap between π_{NH_2} and xz remains small. Rotating the NH_2 group by 90° induces a weaker stabilization since π_{NH_2} is now the electron-donating orbital (13d) and a larger four-electron destabilization since there is a larger overlap between the nitrogen p lone pair and xz . Because the partial double-bond character between N and Ir arises exclusively from an interaction with the empty metal xy orbital, it is clear that the π Ir–N bond character should be larger in $Y^v_{NH_2}$. This is why the Ir–N bond is significantly shorter in $Y^v_{NH_2}$ (2.02 Å) than in $Y^h_{NH_2}$ (2.15 Å). It also explains why the Ir–N bond distance is similar in both

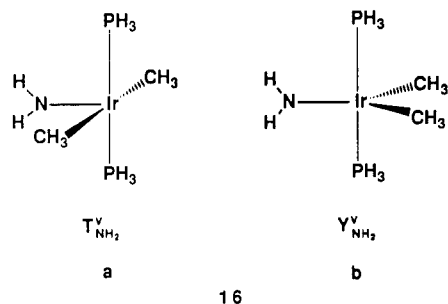
Table VII. Structures of Ir(PH₃)₂(OH)H₂, Distances (Å), Angles (deg), and Energies (kcal/mol) (Geometry Optimization Performed Using POPT)

structure	T _{OH} ^v	Y _{OH} ^v	T _{OH} ^h	Y _{OH} ^h
α	179.4	70.4	177.4	69.6
Ir-O	2.02	2.03	1.99	2.03
Ir-H ₂	1.72	1.59	1.69	1.58
Ir-H ₃	1.72	1.59	1.67	1.55
Ir-P ₁	2.42	2.40	2.41	2.41
Ir-P ₂	2.40	2.41	2.41	2.41
O-H	0.95	0.93	0.94	1.00
P-H	1.40 ^a	1.40 ^a	1.40 ^a	1.40 ^a
O-Ir-H ₂	90.3	144.8	91.9	147.2
O-Ir-P ₁	90.8	89.9	90.3	89.4
O-Ir-P ₂	88.2	89.4	90.3	89.4
H-O-Ir	114.6	124.5	114.0	124.3
H-P-Ir	109.5 ^a	109.5 ^a	109.5 ^a	109.5 ^a
E(SCF)	36.8	0	30.7	6.0

^a Frozen coordinate.

the Y^v and T^v structures (Table V). In a T-type geometry no Ir-N multiple bond is possible but the lack of a ligand trans to N shortens the Ir-N bond, whereas in a Y-type geometry an Ir-N π bond compensates the antibonding interaction between *x*² - *y*² and N. This contrasts with the case of Ir(PH₃)₂H₃ (8) where no multiple bonding between Ir and H was possible, and considerable elongation of the Ir-H bond was obtained in the Y structure. In Ir(P-H₃)₂(H)₂Cl a small lengthening of the Ir-Cl bond distance was calculated when Y_{Cl} and T_{Cl} were compared. This illustrates the weaker π-electron-donating ability of Cl.

In the experimental complex 3, the two alkyl groups subtend the acute angle. The replacement of the H ligands by Me groups has already been discussed in the case of Ir(PH₃)₂ClH₂, and it was shown to have little consequence. Similar results are obtained for Ir(PH₃)₂(NH₂)H₂ with POPT (Table VI). With two methyl groups on the metal center (16b) the acute Me-Ir-Me is calculated to be 79.3°,



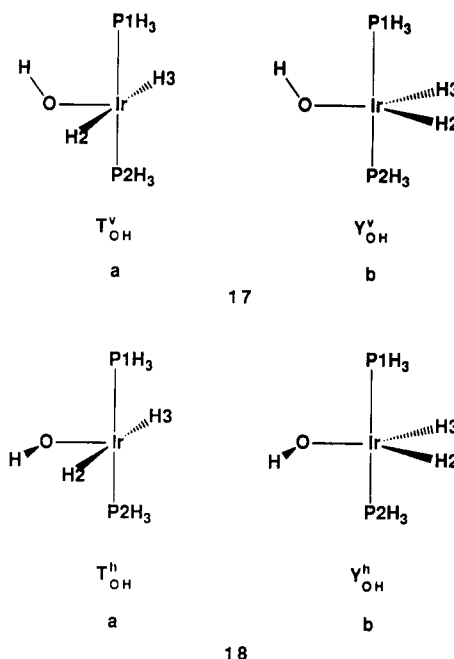
which reproduces well the experimental 77.6° value. It is clear that the presence of moderately bulky groups does not prevent the appearance of this Y-type structure; a slight widening of the α angle is the only consequence of the presence of alkyl groups. This point strongly supports the experimental observation made by Fryzuk according to which several alkyl- and aryl-substituted complexes analogous to 3 were suggested to have similar features based on NOE measurements. Since Y^v_{NH₂} with two methyl groups is calculated to be more stable than its T^v_{NH₂} analogue by 35.4 kcal/mol, the overall energy shape of the potential energy surface also resembles the unsubstituted case.

Ir(PH₃)₂(OR)H₂ (R = H, CH₃, CH₂F, CF₃). As we mentioned in the Introduction, the most striking aspect of Ir(PR₃)₂(OCH₂CF₃)H₂ (4b) is that the orientation of the OCH₂CF₃ group corresponds to the most sterically demanding arrangement since the O-C-C skeleton is coplanar with the bulky phosphine ligands.¹³ The steric hindrance is apparently reduced in this conformation by

Table VIII. Relative Energies (kcal/mol) at the RHF Level of Four Structures of Ir(PH₃)₂(OR)H₂, Distances (Å), and Angles (deg)

R	Y _{OH} ^v	Y _{OH} ^h	T _{OH} ^v	T _{OH} ^h
H	0	6.0	36.8	30.7
CH ₃	0	5.0	34.6	33.8
CH ₂ F	0	3.5	37.3	34.9
CF ₃	0	3.9	39.8	41.1

the large Ir-O-C angle (138.0°). The Ir-O bond length is also very short (2.032 Å), which is a mark of a multiple bond character.¹³ This is particularly interesting since an OCH₂CF₃ is not thought as a strong π-donating ligand. In order to study the influence of the nature and orientation of the OR group on the complex, we calculated first several possible structures using the simple system Ir(PH₃)₂(O-H)(H₂) (see 17 and 18). After establishing a preference



for a Y_{OH}^v (same notation as in the NH₂ case) type structure, we changed the nature of the alkoxide focusing our attention on the problem of the preferred orientation for the OR group (R = H, CH₃, CH₂F, CF₃) in a Y_{OR} structure. Since considerable steric strain between the OR group and the phosphine ligands is expected, we optimized the angle between the phosphine ligands and the *xy* plane with POPT.

The results are summarized in Table VII. With R = H, Y_{OH}^v is the most stable structure. Bringing the OH group into the *xy* plane (Y_{OH}^h) costs 6.0 kcal/mol. T_{OH}^v, which is not a minimum on the potential energy surface, is 9.6 kcal/mol above Y_{OH}^v while T_{OH}^v and T_{OH}^h are much higher in energy (36.8 and 30.7 kcal/mol above Y_{OH}^v, respectively).

It is thus quite clear that the preferred geometry of 4b is a Y-type structure, with the OR group eclipsing an Ir-P bond. However, the role of R remains to be studied. This was done by calculating two representative structures, Y_{OH}^v and T_{OH}^v (R = CH₃, CH₂F, CF₃). The relative energies are shown in Table VIII and do not vary much with R; the Y_{OH}^v structure is found to be more stable than the T_{OH}^v structure by some 35–40 kcal/mol, values which are similar to the R = H case (36.8 kcal/mol). This suggests that the shape of the potential energy surface is the same for all R and that the ordering between the several Y and T structures is similar to that calculated for R = H. We believe that other saturated R groups would give similar results. Ad-

Table IX. Main Structural Features of $Ir(PH_3)_2(OR)_2H_2$, Distances (Å), Angles (deg), and Energies (kcal/mol) (Geometry Optimization Done with POPT with Optimization of the Angle between Ir-PH₃ and the xy Plane)

R	CH ₃	CH ₃	CH ₂ F	CH ₂ F	CF ₃	CF ₃
structure	Y _{OH} ^v	Y _{OH} ^h	Y _{OH} ^v	Y _{OH} ^h	Y _{OH} ^v	Y _{OH} ^h
α	71.4	71.1	71.7	70.9	72.1	71.6
Ir-O	2.05	2.07	2.08	2.09	2.15	2.16
Ir-H2	1.58	1.59	1.58	1.58	1.57	1.56
Ir-H3	1.58	1.57	1.58	1.57	1.57	1.56
O-C	1.39	1.40	1.35	1.35	1.31	1.32
Ir-P1	2.42	2.41	2.41	2.43	2.42	2.41
Ir-P2	2.41	2.41	2.41	2.43	2.41	2.41
O-Ir-H2	144.3	145.6	144.2	145.5	144.0	145.2
O-Ir-P1	93.5	89.0	92.2	88.8	92.6	88.6
O-Ir-P2	86.1	89.0	86.9	88.8	86.3	88.6
C-O-Ir (ω)	132.9	139.8	134.4	138.9	134.5	139.3
E(SCF)	0.0	5.0	0.0	3.5	0.0	3.9

ditional verification of this point was done by calculating T_H^v with R = CH₂F, a good model for the experimental CH₂CF₃ group. This structure is found 10.0 kcal/mol above $Y_{OCH_2F}^v$, a value very close to that found in the case of R = H (9.6 kcal/mol). We can thus safely predict that the experimental complex **4b** has the $Y_{OCH_2CF_3}^v$ structure.

To examine further the π -donating effect of the OR group as a function of R, the rotation of the OR group in the Y_{OR} -type structure ($Y_{OR}^v \rightarrow Y_{OR}^h$) was studied (Table VIII). Y_{OR}^v is always favored over Y_{OR}^h due to the fact that the p lone pair of the alkoxy group is a better electron donor than the σ lone pair which lies in the Ir-O-R plane. Rotation of the OR group costs 5 kcal/mol (R = CH₃), 3.5 kcal/mol (R = CH₂F), or 3.9 kcal/mol (R = CF₃). The rotational barrier is always calculated to be smaller than in the NH₂ case, which reflects the lower electron-donating ability of the O lone pair compared to the N lone pair and the fact that the O center has two lone pairs of different donating ability. Since the electronic properties of the CH₂CF₃ group should lie between those of CH₂F and CF₃, we can predict that in the experimental structure the OR group prefers to eclipse a phosphine ligand, in contradiction with steric demands.

Examination of the geometrical details of the several calculated structures is illuminating (Table IX). The H-Ir-H angle is calculated to be around 70°, a very similar value to that calculated for the other complexes. The Ir-O bond length is found to be short in all the Y structures with values similar to the experimental bond length (2.032 Å). A lengthening of the OR bond is calculated as the electronegativity of R group increases (R = CH₃, CH₂F, CF₃) which correlates with the decreasing π -donating capability of the OR group. Despite this trend, it is remarkable that a fluoro-substituted alkoxy group still has the ability to π donate to the metal and thus stabilize an Ir(III) complex. The Ir-O-R angle is calculated to be large for all R with an average value of 135° when R is different from H, which compares very well to the experimental 138° value. The reason for the large value for the Ir-O-R angle (ω), when compared with organic ethers, is part electronic and part steric since when R = H, the ω angle is already significantly obtuse. It illustrates again the need for the OR group to be a strong electron-donating group. The phosphine ligand cis to R moves away from it in order to diminish the steric strain (interestingly, the calculations show that there is no tendency for the OR group to twist around the O-R bond). In the experimental complex this displacement is significant due to the size of the phosphine ligand. In the

calculated system the displacement is smaller although significant: the calculated average value for the O-Ir-P angle cis to the R group is 93° while that for the angle O-Ir-P trans to R is less than 90°. The other structural parameters are standard.

Saturated R groups do not significantly influence the ability of an OR group to donate electrons to the metal. However, results are different if R carries a π -electron-accepting system such as R = COR'. For R' = H with CO₂H group coplanar with a metal-phosphine bond (vertical orientation), a significant lengthening of the Ir-O bond length is calculated (2.14 Å, H-Ir-H = 70.8°) while the other structural parameters remain the same. This lengthening of the Ir-O bond length is due to the delocalization of the p orbital of the oxygen center into the CO₂H group which is thus less available for donation into the empty Ir xy orbital. The resulting complex may thus be less stable.

Conclusion

In this study, we have shown that the π -donating group X plays a determining role in stabilizing $d^6 ML_5$ species. If only one such group is ligated to the metal, the complex takes an unusual distorted trigonal-bipyramidal structure which maximized the electron-donating effect of X by creating a partial metal-X multiple bond. This electron-donating effect takes place even with weak electron donor groups like chlorine and fluoroalkoxy groups. This shows that the ability to donate electron density to an electron-poor metal is not limited to highly oxidized early transition metals²⁶ but can also take place with late transition metals in which a suitable acceptor orbital is present as mentioned by Caulton.¹³ This is the case of these distorted trigonal bipyramids but not that of the square pyramids since only in the first structures is there an empty metal orbital of proper symmetry to stabilize a ligand lone pair orbital. Our calculations also predict that, in the case of an OR ligand, π -electron-withdrawing R groups on the oxygen center may strongly diminish the ability of the alkoxy group to act as electron donor toward the metal. This should give the opportunity to build tailor-made complexes which could give a considerable amount of information on the stability and reactivity of electron-deficient intermediates.

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Supplementary Material Available: Cartesian and internal coordinates of the fully optimized structures (frequencies in cm^{-1}) (10 pages). Ordering information is given on any current masthead page.

(26) See for instance: *Metal-ligand Multiple bonds*; Nugent, W. A., Mayer, J. M., Eds.; Wiley: New York, 1988. Chisholm, M. H.; Clark, D. L. *Comments Inorg. Chem.* 1987, 6, 23. Chisholm, M. H. *Acc. Chem. Res.*, in press.