The calculated ligand dissociation energies of $\text{Ir}_x(\text{PH}_3)_y(\text{CO})_z$ ($x = 1, 2, 4$) provide insights into the bonding and structures of these complexes relevant to single site catalysis.

Structures, Relative Energies, and Ligand Dissociation Energies of Iridium Carbonyl Phosphine Clusters

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Abstract

There is significant interest in the catalytic properties of substituted iridium carbonyl clusters but little thermodynamic information available characterizing them. The low-energy isomers of $\text{Ir}_x(\text{PH}_3)_y(\text{CO})_z$ ($x = 1, 2, 4$) were investigated with density functional theory and correlated molecular orbital theory at the coupled cluster CCSD(T) level. The relative energies and ligand dissociation energies were calculated. Differences in relative energies are consequences of both electronic and steric effects of the phosphines and carbonyls. The calculations predict three fundamental structural types for $\text{Ir}_2(\text{PH}_3)_y(\text{CO})_z$: C_{2v} , C_2 , and D_{3d} . Ten exchange-correlation functionals were used for the ligand dissociation energy calculations in addition to CCSD(T) for the smaller clusters. The $\omega\text{B97X-D}$ functional gave the most consistent ligand dissociation energies as compared with the CCSD(T) benchmark calculations, and, so it was used to predict the dissociation energies for larger clusters when CCSD(T) calculations were infeasible. The dissociation energies characteristic of $\text{Ir}_4(\text{PH}_3)_y(\text{CO})_z$ were in the range of ~ 30 to ~ 60 kcal/mol. Dissociation of a bridging ligand often involved a hydrogen atom transfer from a phosphine to a coordinatively unsaturated iridium atom and a phosphine converting from a bridging site to an equatorial site. The products of such reactions are predicted to have lower relative energies than other isomers. Phosphines act as σ -electron donors, and there is a trend of an increase in carbonyl ligand dissociation energies as more phosphines are substituted in the small clusters.

Keywords: iridium carbonyl phosphine complexes; electronic structure calculations; ligand dissociation energies; coupled cluster (CCSD(T)) theory; density functional theory; catalysis

1. Introduction

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Iridium clusters catalyze a wide range of reactions, including oxidation, hydrogenation, C–H bond activation, cycloaddition, cycloisomerization,[1,2] and ring-opening.[3] Iridium complexes play important roles in oxidation (e.g., of alcohols,[4,5,6] phenols,[7,8,9] and amines[10,11]), hydrogenation,[12,13] C-H activation,[14,15,16] cycloaddition (e.g., [2 + 2 + 2],[17,18,19] [2 + 2 + 1],[20,21] and [4 + 2] [22,23]), cycloisomerization,[1,2] and ring-opening reactions.[24] The richness of this chemistry explains the broad interest in the properties of the family of iridium complexes and clusters.[25] Ozin and coworkers [26,27,28] reported the synthesis of $\text{Ir}(\text{CO})_n$ ($n = 1-4$) and $\text{Ir}_2(\text{CO})_8$ clusters in a matrix. $\text{Ir}_2(\text{CO})_8$ was reported to transform into the tetra-iridium carbonyl cluster $\text{Ir}_4(\text{CO})_{12}$ at ~ 200 K.[26,27] The tetra-iridium cluster framework is one of the simplest structures presenting neighbouring metal centers, and numerous tetra-iridium clusters are known. The chemistry of tetra-iridium carbonyl clusters is especially extensive, as the metal frame is relatively stable, so that many compounds in this class have been investigated, including those that are catalysts both in solution and on supports.[29,30,31,32] The parent tetra-iridium cluster $\text{Ir}_4(\text{CO})_{12}$ has two structures which are minima on the potential energy surface, one T_d structure with all 12 carbonyls being terminal, and one C_{3v} structure with nine terminal carbonyls and three bridging carbonyls on the basal plane (Figure 1). Different from $\text{Co}_4(\text{CO})_{12}$ and $\text{Rh}_4(\text{CO})_{12}$, which adopt C_{3v} symmetry[33,34] both in the gas phase and in solution, $\text{Ir}_4(\text{CO})_{12}$ adopts the T_d structure.[35,36,37] A single-crystal X-ray diffraction investigation yielded $r(\text{Ir}-\text{Ir}) = 2.693$ Å and $r(\text{Ir}-\text{C}) = 1.87$ Å.[36] An extended Hückel investigation of tetrahedral $\text{M}_4\text{CO}_{11}\text{L}$ clusters for $\text{M} = \text{Co}, \text{Rh},$ and Ir was combined with an analysis of reported crystal structure data to provide insights into the cluster properties, including the role of the ligand L on determining if bridging CO ligands are present.[38]

When a carbonyl is replaced by a phosphine ligand L , the cluster usually [39] shows a preference for the C_{3v} -type structure, and can adopt the structure of either isomer **b** or **c** (Figure 1) if the phosphine ligand L is small; isomer **b** becomes preferred as the bulk of L increases.[40] Electronic effects may also be significant in this chemistry, reflecting the electron withdrawing or donating tendencies of the groups bonded to the phosphorus.[38] When L is a phosphine or phosphite, its bulk also strongly influences the degree of ligand substitution in the parent cluster $\text{Ir}_4(\text{CO})_{12}$ —that is, determining whether $\text{Ir}_4(\text{CO})_8\text{L}_4$ or $\text{Ir}_4(\text{CO})_9\text{L}_3$ is the final product[41] —but synthesis of $\text{Ir}_4(\text{CO})_{10}\text{L}_2$ or $\text{Ir}_4(\text{CO})_{11}\text{L}$ directly from the parent through direct substitution is difficult.[41] Okrut et al. [42] demonstrated that as the number of strong σ -donor phosphine ligands increases, the thermomechanical stability against aggregation increases, whereas the thermochemical stability against decarbonylation varies inversely.

We were particularly motivated to investigate tetrairidium clusters with combinations of carbonyl and phosphine ligands, having recently demonstrated an on-off switch for the bonding and catalytic conversion of ethylene at single iridium sites on the tetrairidium frame, as triggered by a sheath of organic ligands bonded at neighboring iridium sites that control the electronic properties of the active site.[43] Ethylene binding and activation in a supported tetrairidium cluster catalyst were shown to be controlled by selective nanoenvironments at the metal surface, which are formed by three bulky calixarene-phosphine ligands surrounding and bonding to the cluster at sites neighbouring the site where reactivity is switched off and on. These

results point to the importance of understanding the bonding and energetics of CO/phosphine complexes of tetrairidium. However, the energetics of iridium carbonyl phosphine complexes are currently not available, either from experiment or theory.

We now report the structures and bond dissociation energies of $\text{Ir}_x(\text{PH}_3)_y(\text{CO})_z$ for values of x up to 4 determined by using density functional theory (DFT)[44,45,46] and coupled cluster theory (CCSD(T)) [47,48,49,50] to provide insights into the bonding of the simplest phosphine in such complexes. We compare the results determined with various DFT exchange-correlation functionals to provide a guide for their use with larger substituted phosphines. These results lead to a better understanding of carbonyl and phosphine chemisorption on iridium clusters and provide an improved basis for ultimately predicting their electronic structures and catalytic properties. In addition, the calculated structural and energetic information can be used as an aid in identifying various species that could be synthesized in matrix isolation experiments.

Figure 1: Isomers of $\text{Ir}_4(\text{CO})_{12}$ and $\text{Ir}_4(\text{CO})_{11}\text{L}$. In T_d structure **a**, all carbonyls are terminal. In C_{3v} structure **b**, Ir(1) is apical iridium, and Ir(2), Ir(3), and Ir(4) are basal iridiums that build up the basal plane. C(5), C(6), C(7), and C(8) are apical, bridging, equatorial, and axial carbon, respectively. L is the ligand that substitutes for axial carbonyl in **b** and for equatorial carbonyl in **c**.

2. Computational Methods

Previously, geometry parameters of $\text{Ir}_4(\text{CO})_{12}$ with T_d symmetry have been obtained from DFT with the SVWN5 exchange-correlation functional, which provides excellent geometry results that are very close to the experimental results, but gives poor relative energies that predict a lower-energy C_{3v} structure.[51] The CAM-B3LYP functional performs best in calculations of carbonyl dissociation energies for a number of $\text{Ir}_x(\text{CO})_y$ complexes, and the $\omega\text{B97X-D}$ functional gives the best predictions of total dissociation energies.[51] In most nucleation reactions, DFT calculations give higher energies than CCSD(T) results, whereas the reverse pertains to the prediction based on the MP2 method. Thus, the average of the MP2 and DFT values were considered to be suitable for predicting the carbonyl ligand dissociation energies.[51]

Following our previous work, the geometries of the $\text{Ir}_x(\text{PH}_3)_y(\text{CO})_z$ clusters were optimized by using DFT with the local density approximation functional SVWN5

(Slater exchange plus the VWN version 5 fit of the electron gas for the correlation potential).[52,53] Second-derivative frequency calculations were performed on every optimized geometry to confirm that the specific structure is a minimum.

Both the DFT and single-point CCSD(T) calculations were performed with the augmented correlation consistent double- ζ (aug-cc-pVDZ) basis set[54,55] for light elements and a relativistic pseudopotential with the aug-cc-pVDZ-pp basis set for iridium.[56] This combination is denoted as the ‘aD’ basis set. The PP on Ir includes the following 60 electrons in the PP: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14}$. The active electrons in the self-consistent field calculations for the Ir atom are the $5s^2 5p^6 5d^7$. In the valence CCSD(T) and MP2 calculations, the $5s^2 5p^6$ are in the core together with the 1s on C and O and the $1s^2 2s^2 2p^6$ on the P.

Single-point energies of the clusters were calculated by using CCSD(T) and DFT with the following exchange-correlation functionals: B3LYP,[57,58] B97-D,[59] B98,[60,61] BP86,[62] CAM-B3LYP,[63] M06,[64] PW91,[65,66,67] PBE,[68,69] ω B97X,[70] and ω B97X-D.[71] BP86, PBE, and PW91 are pure generalized gradient approximation (GGA) functionals; B3LYP, B98, and M06 are hybrid functionals; B97-D is a GGA functional with dispersion corrections; CAM-B3LYP and ω B97X are hybrid functionals with long-range corrections; and ω B97X-D is a hybrid functional with long-range corrections and dispersion corrections. The CCSD(T) energies of the open-shell molecules $\text{Ir}(\text{PH}_3)_y(\text{CO})_z$ were calculated by using the R/UCCSD(T) approach.[72,73,74] The open shell MP2 calculations were done at the ROMP2 level.[75]

Ligand dissociation energies (LDEs) were calculated from equation (1).

$$\text{LDE} = E(\text{product}) + E(\text{ligand}) - E(\text{parent cluster}) \quad (1)$$

All LDEs are electronic energies with zero point energy correction included at 0 K giving $\Delta H(0 \text{ K})$.

The DFT calculations were performed with the Gaussian09 suite of programs[76] and the MP2 and CCSD(T) calculations with the MOLPRO2010 suite of programs.[77]

3. Results and Discussion

3.1 $\text{Ir}(\text{PH}_3)_y(\text{CO})_z$ structures, relative energies, and ligand dissociation energies.

First consider the isomers of $\text{Ir}(\text{PH}_3)_y(\text{CO})_z$ shown in Figure 2. The optimized bond distances are given in the Supporting Information (SI), and the relative energies are listed in Table 1. Quartet states of $\text{Ir}(\text{PH}_3)_y(\text{CO})_z$ are of higher energy than doublet states for each structure, and so only the doublet states are compared in this work. The LDEs of the $\text{Ir}(\text{PH}_3)_y(\text{CO})_z$ complexes are listed in Table 2.

The $\text{Ir}(\text{CO})_2$, IrPH_3CO , and $\text{Ir}(\text{PH}_3)_2$ molecules have two minimum energy structures, one bent and one almost linear. The bent structures are lower in energy by 9.9, 6.8, and 5.9 kcal/mol, respectively. $\text{Ir}(\text{CO})_3$ has an almost planar geometry with one equatorial (*eq* = equatorial) CO and two axial (*ax* = axial) CO ligands. As one PH_3 is substituted for a CO, two $\text{IrPH}_3(\text{CO})_2$ isomers are formed, one with an axial PH_3 (*ax*, **1b**), which has a lower energy by 2.2 kcal/mol (CCSD(T)), and one with an equatorial PH_3 (*eq*, **1c**). In **1b**, the PIrCC plane is maintained, whereas the two carbonyls bend slightly out of the plane ($\angle \text{C-Ir-P-C} = 153^\circ$) in **1c** as a consequence of

Figure 2: Optimized geometries of low-lying $\text{Ir}(\text{PH}_3)_y(\text{CO})_z$ isomers and their symmetries. Only doublet states are shown. Relative energies are in kcal/mol.

Table 1. Relative Energies of $\text{Ir}(\text{PH}_3)_y(\text{CO})_z$ Isomers in kcal/mol, predicted by various electronic structure methods.^a

Molecule	Symmetry	BP86	PBE	PW91	B3LYP	CAM-B3LYP	B97-D	B98	ω B97X	ω B97X-D	M06	MP2	CCSD(T)
² IrCO	$C_{\infty v}$	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
⁴ IrCO	C_s	39.7	39.7	39.7	37.4	35.1	46.6	40.4	42.3	41.5	44.9	44.9	36.3
² Ir(CO) ₂	C_s bent	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
² Ir(CO) ₂	C_{2v} linear	-1.5	-0.1	-0.5	-8.7	-10.7	-2.3	-8.3	-11.3	-8.9	-6.3	15.8	9.9
² Ir(CO) ₃	C_s	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
⁴ Ir(CO) ₃	C_{2v}	49.9	49.6	49.8	47.8	45.3	54.5	49.0	49.0	49.9	55.8	58.1	49.2
² IrPH ₃ CO	C_s bent	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
² IrPH ₃ CO	C_1 linear	-7.0	-5.9	-6.2	-13.0	-15.0	-6.5	-12.9	-16.1	-14.0	-10.7	10.8	6.8
² IrPH ₃ (CO) ₂	C_s <i>ax</i>	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
² IrPH ₃ (CO) ₂	C_s <i>eq</i>	1.2	1.1	1.1	1.5	2.2	0.5	1.5	2.6	2.3	1.8	2.6	2.2
⁴ IrPH ₃ (CO) ₂	C_s <i>ax</i>	53.8	53.5	53.8	51.6	49.1	58.5	52.8	52.9	53.8	60.0	62.6	52.7
⁴ IrPH ₃ (CO) ₂	C_s <i>eq</i>	48.5	48.3	48.4	45.5	43.0	52.5	46.7	46.9	47.8	53.5	107.3	94.2
² IrPH ₃ (CO) ₃	C_s	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
⁴ IrPH ₃ (CO) ₃	C_s	60.9	60.6	60.5	61.8	64.4	61.4	63.6	69.9	68.7	67.4	76.6	66.3
² Ir(PH ₃) ₂	C_{2v} bent	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
² Ir(PH ₃) ₂	C_s linear	-11.7	-10.6	-10.9	-17.1	-19.1	-10.5	-17.0	-20.3	-18.4	-15.0	8.5	5.9
² Ir(PH ₃) ₂ CO	C_{2v} <i>ax, ax</i>	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
² Ir(PH ₃) ₂ CO	C_1 <i>ax, eq</i>	1.4	1.2	1.2	1.2	1.6	0.9	1.3	1.8	1.6	0.8	2.3	1.3
⁴ Ir(PH ₃) ₂ CO	C_s <i>ax, eq</i>	45.4	44.5	44.7	45.5	43.6	48.8	46.2	48.3	48.2	54.2	51.2	42.4
² Ir(PH ₃) ₂ (CO) ₂	C_{2v} <i>ax, ax</i>	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
² Ir(PH ₃) ₂ (CO) ₂	C_2 <i>ax, eq</i>	1.8	1.7	1.7	2.1	1.9	2.1	2.0	1.6	1.8	1.7	1.0	1.4
⁴ Ir(PH ₃) ₂ (CO) ₂	C_1 <i>ax, eq</i>	63.4	63.0	63.1	63.3	64.0	64.2	64.9	68.1	68.4	69.3	82.8	66.3
⁴ Ir(PH ₃) ₂ (CO) ₂	C_{2v} <i>ax, ax</i>	62.0	61.5	61.5	62.9	66.3	62.8	65.0	72.5	70.6	67.9	83.1	69.3
² Ir(PH ₃) ₃	C_s	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
⁴ Ir(PH ₃) ₃	C_s	53.4	53.2	53.4	50.4	47.7	58.8	51.6	51.6	52.8	58.8	77.0	64.7
² Ir(PH ₃) ₃ CO	C_s	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
⁴ Ir(PH ₃) ₃ CO	C_1	70.5	70.8	70.8	67.3	68.3	73.7	69.6	73.4	73.3	72.7	92.5	85.7

^a All energies are single-point energies at the SVWN5 optimized geometries.

Table 2. LDEs of $\text{Ir}(\text{PH}_3)_2(\text{CO})_2$ Isomers in kcal/mol, predicted by various electronic structure methods.^a

Reaction	BP86	PBE	PW91	B3LYP	CAM-B3LYP	B97-D	B98	ω B97X	ω B97X-D	M06	MP2	CCSD(T)
${}^2\text{Ir}(\text{CO})_3 \rightarrow {}^2\text{Ir}(\text{CO})_2(\text{bent}) + \text{CO}$	48.0	49.3	49.8	42.0	44.0	43.2	44.1	44.2	44.5	42.5	48.2	41.3
${}^2\text{Ir}(\text{CO})_2(\text{linear}) + \text{CO}$	46.5	49.2	49.2	33.4	33.3	40.8	35.9	33.0	35.6	36.2	64.0	51.2
${}^2\text{IrPH}_3(\text{CO})_2(ax) \rightarrow {}^2\text{Ir}(\text{CO})_2(\text{bent}) + \text{PH}_3$	35.7	37.0	37.6	32.7	36.6	33.8	35.5	39.4	38.6	34.6	45.3	38.1
${}^2\text{IrPH}_3(\text{CO})_2(ax) \rightarrow {}^2\text{IrPH}_3\text{CO}(\text{bent}) + \text{CO}$	53.8	55.3	55.7	47.1	49.0	48.0	49.4	49.6	50.1	47.5	55.6	46.5
${}^2\text{IrPH}_3(\text{CO})_2(ax) \rightarrow {}^2\text{IrPH}_3\text{CO}(\text{linear}) + \text{CO}$	46.8	49.4	49.5	34.0	33.9	41.5	36.6	33.5	36.1	36.8	66.4	53.3
${}^2\text{IrPH}_3(\text{CO})_2(eq) \rightarrow {}^2\text{Ir}(\text{CO})_2(\text{linear}) + \text{PH}_3$	33.1	35.8	36.0	22.5	23.8	30.9	25.7	25.5	27.4	26.5	58.6	45.8
${}^2\text{IrPH}_3(\text{CO})_2(eq) \rightarrow {}^2\text{IrPH}_3\text{CO}(\text{bent}) + \text{CO}$	52.5	54.1	54.6	45.5	46.8	47.5	48.0	46.9	47.9	45.7	53.0	44.3
${}^2\text{Ir}(\text{PH}_3)_2\text{CO}(ax, ax) \rightarrow {}^2\text{IrPH}_3\text{CO}(\text{bent}) + \text{PH}_3$	36.2	37.6	38.1	32.3	36.3	33.6	35.3	39.2	38.6	34.0	47.2	38.4
${}^2\text{Ir}(\text{PH}_3)_2\text{CO}(ax, ax) \rightarrow {}^2\text{Ir}(\text{PH}_3)_2(\text{linear}) + \text{CO}$	49.4	52.1	52.2	36.9	37.0	44.1	39.6	36.5	39.2	39.3	73.4	59.4
${}^2\text{Ir}(\text{PH}_3)_2\text{CO}(ax, eq) \rightarrow {}^2\text{IrPH}_3\text{CO}(\text{bent}) + \text{PH}_3$	34.8	36.4	36.9	31.1	34.6	32.6	34.1	37.4	37.0	33.2	44.9	37.1
${}^2\text{Ir}(\text{PH}_3)_2\text{CO}(ax, eq) \rightarrow {}^2\text{IrPH}_3\text{CO}(\text{linear}) + \text{PH}_3$	27.8	30.6	30.8	18.1	19.6	26.1	21.2	21.3	23.0	22.5	55.7	43.9
${}^2\text{Ir}(\text{PH}_3)_2\text{CO}(ax, eq) \rightarrow {}^2\text{Ir}(\text{PH}_3)_2(\text{bent}) + \text{CO}$	59.8	61.4	61.9	52.8	54.5	53.7	55.4	55.0	56.0	53.5	62.5	52.3
${}^2\text{Ir}(\text{PH}_3)_3 \rightarrow {}^2\text{Ir}(\text{PH}_3)_2(\text{bent}) + \text{PH}_3$	37.9	39.7	40.2	33.4	36.9	35.0	36.6	40.0	39.8	35.7	49.5	39.8
${}^2\text{Ir}(\text{PH}_3)_3 \rightarrow {}^2\text{Ir}(\text{PH}_3)_2(\text{linear}) + \text{PH}_3$	26.2	29.1	29.3	16.3	17.8	24.5	19.6	19.6	21.4	20.7	58.0	45.6

Table 2 (continued). LDEs of $\text{Ir}(\text{PH}_3)_y(\text{CO})_z$ Isomers in kcal/mol, predicted by various electronic structure methods.^a

Reaction	BP86	PBE	PW91	B3LYP	CAM-B3LYP	B97-D	B98	ω B97X	ω B97X-D	M06	MP2	CCSD(T)
${}^2\text{Ir}(\text{CO})_4 \rightarrow {}^2\text{Ir}(\text{CO})_3 + \text{CO}$	35.8	37.9	38.1	28.6	30.6	31.6	31.8	32.6	32.8	29.8	38.8	28.3
${}^2\text{IrPH}_3(\text{CO})_3 \rightarrow {}^2\text{Ir}(\text{CO})_3 + \text{PH}_3$	24.4	26.5	26.8	19.7	23.4	23.1	23.7	27.7	27.2	22.2	36.5	25.3
${}^2\text{IrPH}_3(\text{CO})_3 \rightarrow {}^2\text{IrPH}_3(\text{CO})_2(ax) + \text{CO}$	36.6	38.8	39.0	29.0	30.8	32.5	32.4	32.5	33.1	30	39.5	28.5
${}^2\text{IrPH}_3(\text{CO})_3 \rightarrow {}^2\text{IrPH}_3(\text{CO})_2(eq) + \text{CO}$	37.8	39.9	40.1	30.6	32.9	33.0	33.8	35.1	35.3	31.8	42.0	30.6
${}^2\text{Ir}(\text{PH}_3)_2(\text{CO})_2(ax, ax) \rightarrow {}^2\text{IrPH}_3(\text{CO})_2(eq) + \text{PH}_3$	22.4	24.7	25.0	17.8	21.3	21.6	21.9	25.4	25.2	20.3	34.4	23.7
${}^2\text{Ir}(\text{PH}_3)_2(\text{CO})_2(ax, ax) \rightarrow {}^2\text{Ir}(\text{PH}_3)_2\text{CO}(ax, ax) + \text{CO}$	40.0	42.3	42.6	32.5	34.0	36.0	36.0	35.8	36.7	33.8	42.8	31.8
${}^2\text{Ir}(\text{PH}_3)_2(\text{CO})_2(ax, eq) \rightarrow {}^2\text{IrPH}_3(\text{CO})_2(ax) + \text{PH}_3$	20.6	23.0	23.3	15.7	19.4	19.5	19.9	23.8	23.4	18.6	33.4	22.2
${}^2\text{Ir}(\text{PH}_3)_2(\text{CO})_2(ax, eq) \rightarrow {}^2\text{Ir}(\text{PH}_3)_2\text{CO}(ax, eq) + \text{CO}$	39.5	41.9	42.0	31.7	33.7	34.8	35.3	36.0	36.5	32.9	44.1	31.6
${}^2\text{Ir}(\text{PH}_3)_3\text{CO} \rightarrow {}^2\text{Ir}(\text{PH}_3)_3 + \text{CO}$	43.4	45.7	46.0	35.7	37.6	38.8	39.4	39.9	40.6	37.1	48.5	35.6
${}^2\text{Ir}(\text{PH}_3)_3\text{CO} \rightarrow {}^2\text{Ir}(\text{PH}_3)_2\text{CO}(ax, eq) + \text{PH}_3$	21.5	24.0	24.3	16.3	20.0	20.1	20.7	24.8	24.4	19.3	35.5	23.1
${}^2\text{Ir}(\text{PH}_3)_2\text{CO}(ax, ax) + \text{PH}_3$	20.2	22.8	23.1	15.1	18.3	19.2	19.4	23	22.8	18.5	33.2	21.8
${}^2\text{Ir}(\text{PH}_3)_4 \rightarrow {}^2\text{Ir}(\text{PH}_3)_3 + \text{PH}_3$	21.8	24.5	24.7	16.6	20.1	20.7	21.2	25.1	24.9	19.9	36.8	24.0

^a All energies are single-point energies at the SVWN5 optimized geometries.

the bulk of the phosphine ligand. Substitution of a second PH_3 leads to $\text{Ir}(\text{PH}_3)_2\text{CO}$, which has two isomers, one with the PH_3 ligands cis to each other in an axial and an equatorial position (**1e**) and one with the PH_3 groups trans to each other, both in axial positions (**1d**). Structure **1d** has a lower energy by 1.3 kcal/mol than **1e**, showing that axial substitution isomers are again favored. $\text{Ir}(\text{CO})_4$ has D_{2d} symmetry, falling between planar D_{4h} and tetrahedral T_d structures. Substitution of a CO by PH_3 leads to $\text{IrPH}_3(\text{CO})_3$ (**1h**) and lowers the symmetry to C_∞ . Substitution of a second PH_3 can occur either trans (two *ax*, **1i**) or cis (one *ax* and one *eq*, **1j**). Structure **1i** leads to the lower-energy structure by 1.4 kcal/mol, essentially the same energy difference as found in $\text{Ir}(\text{PH}_3)_2\text{CO}$.

The results for the LDEs of the $\text{Ir}(\text{PH}_3)_y(\text{CO})_z$ complexes can be explained in terms of the basic Dewar-Chatt-Duncanson model of σ -electron donation from the ligand to the metal coupled with π -back-bonding to the ligand unoccupied orbitals to explain the LDEs.[78,79] This model has been expanded by considering other orbitals beyond the frontier molecular orbitals.[80] When a PH_3 , a stronger σ -electron donor than carbonyl, is substituted for CO on an iridium carbonyl cluster, more electrons occupy the Ir d orbitals. The increase in electron density on the Ir core can lead to more π -back-bonding to the CO π^* orbitals and to the P-H σ^* orbitals. The Ir-C bond lengths decrease and the C-O bond length increases with a concomitant decrease in the CO stretching frequency as PH_3 groups are added to a single Ir, as the occupation of the π^* orbitals weakens the C-O bonds. The P-H σ^* orbitals are significantly less energetically available than the CO π^* orbitals, and so PH_3 is a weaker electron acceptor than CO. Back-bonding of the metal d orbitals to these P-H σ^* orbitals can increase on binding a second PH_3 as a consequence of the increased electron density on the metal because of binding the first PH_3 . However, the increase in electron density on the metal can repel the lone-pair electrons on PH_3 , which form the donor σ -bonds, thus counteracting the back-bonding. The back-bonding results in competition between the two ligands trans to each other for these electrons because of the shape of the d orbitals. In $\text{Ir}(\text{PH}_3)_y(\text{CO})_z$ molecules, carbonyls are stronger π -electron acceptors than PH_3 ligands. Thus, a ligand-metal bond is weakened when there is a carbonyl instead of PH_3 trans to it, and carbonyls are considered to have a stronger trans effect.

The calculated NBO charge,[81,82,83,84,85,] natural Ir 5d orbital population, C–O stretching frequency, bond length, and LDEs of CO and PH_3 ligands of $\text{Ir}(\text{PH}_3)_y(\text{CO})_z$ are listed in Table 3. For IrL_3 , the expected trend as stated above is evident. As more carbonyls are replaced by phosphines, the 5d orbital population and charge on the iridium atom increase, concomitant with stronger Ir–C bonds and weaker C–O bonds. Because the product linear IrL_2 is of higher energy, the *eq* CO ligands have the highest LDEs, 51 to 59 kcal/mol. Because *eq* CO ligands in IrL_3 do not have a ligand trans to them, the 8 kcal/mol energy difference suggests that electron density is transferred from ligands cis to the *eq* CO through σ -donation. The difference in the LDEs between *ax* COs in **1a** and **1e** is 11 kcal/mol and suggests that transfer of electrons to the trans position is more efficient than to the cis. More efficient electron transfer, a smaller trans effect, and a smaller steric effect make **1b** the lower energy isomer.

The trend of the PH_3 LDEs is more complicated. From **1b** to **1f**, the energy differences in both *eq* PH_3 and *ax* PH_3 LDEs are less than 3 kcal/mol. In most cases, the strength of the bonds is reflected by bond lengths and LDEs, but this may not

Table 3. Calculated NBO Charges on Ir,^a Average C–O Stretching Frequencies (ν_{C-O}),^a Bond Distances (r),^a and LDEs for Ir(PH₃)_y(CO)_z.^b

Property	Ir(CO) ₃	IrPH ₃ (CO) ₂			Ir(PH ₃) ₂ CO		Ir(PH ₃) ₃
	1a	<i>ax</i> 1b	<i>eq</i> 1c	<i>ax, ax</i> 1d	<i>ax, eq</i> 1e	1f	
Ir NBO charge	0.02	-0.13	-0.13	-0.31	-0.38	-0.59	
Ir NBO 5d	8.17	8.30	8.35	8.51	8.57	8.80	
Average ν_{C-O} (cm ⁻¹)	2054	2022	2011	1992	2002		
$r(C-O)$ (<i>ax</i> , Å)	1.156	1.162	1.164		1.167		
$r(C-O)$ (<i>eq</i> , Å)	1.159	1.165		1.171			
$r(Ir-C)$ (<i>ax</i> , Å)	1.901	1.865	1.877		1.849		
$r(Ir-C)$ (<i>eq</i> , Å)	1.827	1.820		1.813			
LDE(CO) (<i>ax</i> , kcal/mol)	41.3	46.5	44.3		52.3		
LDE(CO) (<i>eq</i> , kcal/mol)	51.2	53.3		59.4			
$r(Ir-P)$ (<i>ax</i> , Å)		2.315		2.264	2.294	2.243	
$r(Ir-P)$ (<i>eq</i> , Å)			2.230		2.211	2.198	
LDE (PH ₃) (<i>ax</i> , kcal/mol)		38.1		38.4	37.1	39.8	
LDE (PH ₃) (<i>eq</i> , kcal/mol)			45.8		43.9	45.6	

Table 3 (continued). Calculated NBO Charges on Ir,^a Average C–O Stretching Frequencies (ν_{C-O}),^a Bond Distances (r),^a and LDEs for Ir(PH₃)_y(CO)_z.^b

Property	Ir(CO) ₄	IrPH ₃ (CO) ₃	Ir(PH ₃) ₂ (CO) ₂	Ir(PH ₃) ₂ (CO) ₂	Ir(PH ₃) ₃ CO	Ir(PH ₃) ₄
	1g	1h	<i>ax, ax</i> 1i	<i>ax, eq</i> 1j	1k	1l
Ir NBO charge	0.16	0.07	-0.15	-0.09	-0.29	-0.51
Ir NBO 5d	8.21	8.27	8.44	8.43	8.63	8.87
Average ν_{C-O} (cm ⁻¹)	2054	2023	1988	2000	1975	
r (C–O) (<i>ax</i> , Å)	1.156	1.160		1.166		
r (C–O) (<i>eq</i> , Å)		1.162	1.168		1.170	
r (Ir–C) (<i>ax</i> , Å)	1.901	1.874		1.867		
r (Ir–C) (<i>eq</i> , Å)		1.892	1.879		1.858	
LDE(CO) (<i>ax</i> , kcal/mol)	28.3	30.6		31.6		
LDE(CO) (<i>eq</i> , kcal/mol)		28.5	31.8		35.6	
r (Ir–P) (<i>ax</i> , Å)		2.316	2.285	2.300	2.270	2.254
r (Ir–P) (<i>eq</i> , Å)					2.281	
LDE (PH ₃) (<i>ax</i> , kcal/mol)		25.3	23.7	22.2	23.1	24.0
LDE (PH ₃) (<i>eq</i> , kcal/mol)					21.8	

^a All bond distances, frequencies, and NBO charges are calculated at the SVWN5 level.

^b All LDEs are calculated by CCSD(T) at the SVWN5 optimized geometries

always be true.[86] The carbonyl cis to the *ax* (*eq*) PH_3 is replaced by PH_3 to form **1e** from **1b** and **1c**. The new PH_3 increases the electron density on the Ir atom, which strengthens the π -back-bonding and increases repulsion between the two σ -electrons from each PH_3 . The decrease in the Ir–P bond lengths suggests that the iridium and PH_3 orbitals have better overlap, but the decrease in the LDE of the *ax* (*eq*) PH_3 shows that it is easier to dissociate. It is likely that the decrease in LDE is a consequence of the product IrL_2 becoming of lower energy, i.e., more stable. Substitution from **1e** to generate **1f** (and from **1b** to **1d**) leads to the replacement of the carbonyl trans to an *ax* PH_3 . In this case, the Ir–P bond length decreases, and there is an increase in the LDE. In this case, the product IrL_2 is higher in energy, giving a higher LDE.

For IrL_4 clusters, we predict that the LDEs are ~ 10 to 20 kcal/mol less than that of IrL_3 , whether a PH_3 or a CO is added, and there are no remarkable changes in the *ax* bond lengths and frequencies. Different from the almost planar structure of IrL_3 , IrL_4 isomers are distorted with dihedral angles $\angle \text{L}(\text{ax})\text{--L}(\text{eq})\text{--Ir--L}(\text{ax})$ of 140° to 147° . This result suggests there are more steric interactions in IrL_4 isomers leading to the distortion and decreasing the LDEs. Analogous to the trend in the IrL_3 LDEs, the LDEs of the carbonyls increase as more CO ligands are replaced by PH_3 . The difference is less than in IrL_3 , which is likely best attributed to the smaller LDEs. The LDEs of PH_3 show a small decrease of 3 kcal/mol from **1h** to **1i/1j** to **1k** for PH_3 trans to CO and a smaller decrease of < 1 kcal/mol for PH_3 trans to PH_3 . Replacement of CO by PH_3 to generate **1k** from **1i** (and **1k** from **1j**), leads to trends similar to those found for IrL_3 . When the carbonyl cis to the PH_3 is replaced, both the Ir–P bond length and the LDE of the PH_3 decrease. If the carbonyl trans to the PH_3 is replaced (converting **1j** to **1k**), the Ir–P bond length decreases and the PH_3 LDE increases.

3.2 $\text{Ir}_2(\text{PH}_3)_y(\text{CO})_z$ structures, relative energies, and ligand dissociation energies.

$\text{Ir}_2(\text{CO})_8$ has three low-energy isomers,[51] which we previously optimized, and three fundamental structures of $\text{Ir}_2(\text{PH}_3)_y(\text{CO})_z$ are predicted: C_{2v} (C_s), C_2 , and D_{3d} (Figure 3). The lowest energy of $\text{Ir}_2(\text{CO})_8$ has a Ir–Ir bond consistent with the matrix observations of Ozin.[27] The bond distances are given in the Supporting Information, and relative energies of the isomers and derivatives are listed in Table 4. The C_{2v} (C_s) structure has two bridging CO ligands above two Ir atoms (**2a**, **2d**, **2g**, **2h**, **2j**, **2l**, **2n**, **2p**, **2q**, and **2s**) and results in shorter Ir–Ir bonds than in the C_2 and D_{3d} structures. The Ir–C (bridging = *bri*) bond lengths are usually greater than other Ir–C (*ter* = terminal) bond distances by 0.1–0.2 Å. As one bridging CO is dissociated (**4** and **12**), the two *ax* ligands on that side and the other bridging CO move towards the same plane (**2g** and **2p**). As one terminal CO is dissociated, the C_{2v} isomer transitions to a structure with the two remaining ligands more nearly equatorial (**2a**, **2h** and **2q**); the C_s isomer prefers two more *ax* ligands (**2j** and **2s**).

In the C_2 structure, the C_2 axis is perpendicular to the Ir–Ir bond. Each Ir atom binds four ligands, with two closer to the other Ir atom and two farther from the other Ir atom. The Ir–C bond length depends on the carbonyl’s direction; the CO ligands that are closer to the other Ir atom have a longer Ir–C bond than the ones that face away from the other Ir atom. The Ir–C bonds along the Ir–Ir bond axis (**2b** and **2i**) are always the shortest. For example, the average “farther” and “closer” Ir–C bond lengths are 1.887 and 1.900 Å in **2i**, and 1.874 and 1.899 Å in **2m**. Usually a C_s structure is

formed as one ligand is dissociated (**2b** and **2i**), except for **14**, which has the same product as **13**.

There are two staggered trigonal planar $\text{Ir}(\text{CO})_3$ moieties in the D_{3d} structure of $\text{Ir}_2(\text{CO})_8$, and the other two ligands bind to each Ir atom along the C_3 axis. Analogous to the C_2 isomers, the *ax* Ir–C bonds (1.882 Å) are shorter than the Ir–C bonds (1.906 Å) in the two $\text{Ir}(\text{CO})_3$ moieties.[51] The D_{3d} structure does not change much as one ligand is dissociated or replaced.

Figure 3: Optimized geometries of low-lying $\text{Ir}_2(\text{PH}_3)_y(\text{CO})_z$ isomers.

Table 4. Relative Energies of $\text{Ir}_2(\text{PH}_3)_7(\text{CO})_8$ Isomers in kcal/mol, predicted by various electronic structure methods.^a

Molecule	BP86	PBE	PW91	B3LYP	CAM-B3LYP	B97-D	B98	ω B97X	ω B97X-D	M06	MP2	CCSD(T)
$\text{Ir}_2(\text{CO})_7$ 2b	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$\text{Ir}_2(\text{CO})_7$ 2a	7.2	6.6	6.7	10.7	11.5	12.1	10.0	12.2	11.7	8.3	5.7	11.2
$\text{Ir}_2(\text{CO})_7$ 2c	29.9	29.8	29.7	29.5	29.7	24.0	29.5	29.7	29.5	30.4	29.0	28.0
$\text{Ir}_2\text{PH}_3(\text{CO})_7$ 2f	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$\text{Ir}_2\text{PH}_3(\text{CO})_7$ 2d	-2.2	-2.7	-2.5	1.3	1.8	5.7	0.6	2.5	1.6	0.0	1.9	2.7
$\text{Ir}_2\text{PH}_3(\text{CO})_7$ 2e	-0.9	-1.1	-1.1	1.3	2.2	4.2	1.3	2.6	1.9	0.0	3.9	3.0
$\text{Ir}_2\text{PH}_3(\text{CO})_6$ 2i	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$\text{Ir}_2\text{PH}_3(\text{CO})_6$ 2j	1.7	0.9	1.2	7.2	8.5	6.7	6.3	9.2	8.2	7.5	3.0	8.3
$\text{Ir}_2\text{PH}_3(\text{CO})_6$ 2h	4.7	3.9	4.1	8.9	9.8	9.6	8.2	10.7	9.9	6.6	4.3	10.0
$\text{Ir}_2\text{PH}_3(\text{CO})_6$ 2g	9.4	8.9	9.2	15.1	16.3	13.4	14.4	16.8	16.1	19.4	1.6	14.9
$\text{Ir}_2\text{PH}_3(\text{CO})_6$ 2k	29.6	29.7	29.6	30.1	31.0	23.6	30.4	31.9	31.2	32.7	29.8	30.0
$\text{Ir}_2(\text{PH}_3)_2(\text{CO})_6$ 2l	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$\text{Ir}_2(\text{PH}_3)_2(\text{CO})_6$ 2o	3.1	4.0	3.8	0.1	0.6	-4.5	0.9	0.9	1.4	3.6	-0.6	0.0
$\text{Ir}_2(\text{PH}_3)_2(\text{CO})_6$ 2m	2.2	2.7	2.6	0.8	1.7	-1.2	1.6	1.5	1.7	1.6	2.4	1.2
$\text{Ir}_2(\text{PH}_3)_2(\text{CO})_6$ 2n	12.6	12.3	12.3	15.5	17.1	13.0	15.1	17.6	16.5	13.5	9.1	14.9
$\text{Ir}_2(\text{PH}_3)_2(\text{CO})_5$ 2r	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$\text{Ir}_2(\text{PH}_3)_2(\text{CO})_5$ 2t	12.0	13.4	12.9	6.6	10.6	4.1	9.5	12.9	12.5	5.3	14.4	12.8
$\text{Ir}_2(\text{PH}_3)_2(\text{CO})_5$ 2s	11.5	11.8	11.6	12.0	17.0	10.8	13.8	19.3	17.7	6.9	15.4	18.7
$\text{Ir}_2(\text{PH}_3)_2(\text{CO})_5$ 2q	12.4	12.7	12.5	12.2	16.7	11.2	14.1	18.9	17.6	7.4	17.2	18.8
$\text{Ir}_2(\text{PH}_3)_2(\text{CO})_5$ 2p	18.4	19.0	18.8	18.7	23.1	15.7	20.6	25.2	24.1	18.7	13.8	23.7

^a All energies are single-point energies from SVWN5 optimized geometries.

Relative energies of the $\text{Ir}_2(\text{PH}_3)_y(\text{CO})_z$ isomers are quite different between the coordinatively saturated clusters ($\text{Ir}_2\text{PH}_3(\text{CO})_7$ and $\text{Ir}_2(\text{PH}_3)_2(\text{CO})_6$) and the unsaturated clusters ($\text{Ir}_2(\text{CO})_7$, $\text{Ir}_2\text{PH}_3(\text{CO})_6$, and $\text{Ir}_2(\text{PH}_3)_2(\text{CO})_5$). Among the saturated clusters, the C_{2v} and C_2 isomers have similar relative energies (**2d**, **2e**, and **2l**, **2m**, $\Delta E_{\text{rel}} < 1.2$ kcal/mol). The higher energy isomer **2n** has an imaginary frequency of $65i\text{ cm}^{-1}$ which is a rotation of the two IrL_3 moieties about the Ir–Ir axis. This structure is included because the compounds **2j**, **2r**, and **2s** generated from it by a gain of PH_3 or a loss of CO are minima. Among unsaturated clusters, the C_2 structure derivatives (**2b** and **2i**) are lower in energy by ~ 10 kcal/mol than the C_{2v} structures. Among the C_{2v} derivatives formed when one terminal ligand is dissociated, the isomers with two more equatorial ligands, **2h** and **2q**, have slightly higher energies than those with two more *ax* ligands, **2j** and **2s**. The bridging-CO-dissociated C_{2v} derivatives (**2g** and **2p**) are even higher in energy, by ~ 5 kcal/mol, than those with the terminal CO ligands dissociated. The relative energies of isomers with D_{3d} symmetry depends on the nature of the two ligands on the Ir–Ir axis. If one of these two ligands is dissociated, the product becomes the one with highest energy among the isomers with higher relative energies (**2c** and **2k**). However, the isomers with two such ligands are the lowest energy ones. Isomer **2t** is an exception as **2r** is lower in energy, but **2t** does have a lower energy than any among **2q**, **2p**, and **2s**.

Dissociation of a bridging carbonyl from **2n** to generate **2r** (reaction 15) leads to a hydrogen atom transfer from a terminal PH_3 to the Ir atom binding this PH_3 , and the PH_2 now bridges the two Ir atoms. The product, **2r**, has a *bri* phosphido group occupying a similar position to the dissociated carbonyl. As discussed below, we find for the tetrairidium clusters that such hydrogen transfers often occur when a bridging carbonyl is dissociated, especially if there is a *bri* PH_3 connecting to the same Ir atom, and that the products of such reactions always have much lower relative energies than other isomers.

The $\text{Ir}_2(\text{PH}_3)_y(\text{CO})_z$ CO and PH_3 LDEs are listed in Table 5, and we readily conclude that (1) the ligands on the Ir–Ir axis in the isomers with a D_{3d} structure have the highest LDEs, nearly 50 kcal/mol; (2) bridging carbonyls have the second highest LDEs, ~ 30 kcal/mol; (3) the LDEs of terminal ligands in the C_{2v} structure are ~ 25 to 29 kcal/mol; and (4) ligands in the C_2 structure have the lowest LDEs, ~ 15 to 17 kcal/mol. This set of results excludes reaction 15, which involves hydrogen transfer from PH_3 to Ir. The difference in the LDEs for all terminal ligands is less than 3 kcal/mol, and a similar range is found for the bridging ligands.

The influence of replacing CO by PH_3 on the Ir–Ir bond lengths and bond energies is given in Table 6. The results suggest that the increase in electron density on the Ir associated with the CO replacement leads to an increase in the Ir–Ir bond energy. The NBO charges on Ir do not change significantly on substitution of CO by PH_3 . The NBO charge on Ir that binds a PH_3 in $\text{Ir}_2\text{PH}_3(\text{CO})_7$ is the same as that of Ir in $\text{Ir}_2(\text{PH}_3)_2(\text{CO})_6$, whereas that of the other Ir is the same as that of Ir in $\text{Ir}_2(\text{CO})_8$. The Ir–Ir bond energy increases as PH_3 is substituted for CO. The two bridging Ir–C bond lengths in $\text{Ir}_2\text{PH}_3(\text{CO})_7$ differ, with one being shorter, as expected, and the other longer than that in C_{2v} $\text{Ir}_2(\text{CO})_8$. The higher occupancy on the C–O antibonding orbital resulting from increasing the electron density of the Ir atom that binds a phosphine

Table 5. $\text{Ir}_2(\text{PH}_3)_y(\text{CO})_z$ LDEs in kcal/mol, predicted by various electronic structure methods.^a

Reaction	Leaving Ligand	BP86	PBE	PW91	B3LYP	CAM- B3LYP	B97-D	B98	ω B97X	ω B97X -D	M06	MP2	CCSD(T)
1	PH_3	21.2	23.8	24.1	18.2	23.8	23.5	22.5	27.7	28.4	18.7	36.3	28.6
2	PH_3	12.7	15.6	16.0	7.5	11.9	12.9	11.7	15.4	16.3	10.4	28.6	17.1
3	PH_3	41.7	44.2	44.6	38.3	43.8	41.1	42.6	47.7	47.7	40.9	61.5	48.1
4	$\text{CO } bri$	32.4	34.9	35.3	27.8	31.6	30.2	31.2	32.7	34.0	32.5	31.3	30.8
5	$\text{CO } ter$	27.7	29.9	30.1	21.6	25.1	26.4	25.1	26.6	27.7	19.8	34.0	25.8
6	CO	21.7	24.5	24.6	12.7	15.0	18.3	16.1	15.8	17.5	13.1	27.8	15.6
7	CO	50.4	53.0	53.1	44.1	48.2	46.1	47.8	50.3	50.6	45.8	61.5	48.6
8	PH_3	18.9	21.5	21.9	16.2	22.2	21.3	20.4	26.4	26.8	17.3	34.5	27.4
9	PH_3	12.0	14.9	15.3	6.5	10.7	13.0	10.6	14.3	15.2	9.1	27.9	16.2
10	PH_3	3.3	6.3	6.8	-1.0	3.8	5.4	3.4	7.5	8.6	4.7	24.2	10.9
11	PH_3	40.7	43.3	43.6	37.3	42.8	39.8	41.7	46.7	46.7	39.8	60.6	47.5
12	$\text{CO } bri$	34.2	36.9	37.3	30.0	34.0	31.9	33.4	35.5	36.8	35.3	32.4	33.2
13	$\text{CO } ter$	28.2	30.7	31.0	23.5	27.6	27.5	26.9	29.3	30.3	24.0	35.9	28.3
14	CO	26.0	28.0	28.4	22.7	25.9	28.7	25.3	27.8	28.6	22.4	33.5	27.1
15	$\text{CO } bri$	3.2	5.6	6.1	-4.2	-6.2	3.3	-2.3	-7.2	-3.8	3.1	9.0	-5.3
16	$\text{CO } ter$	14.7	17.4	17.8	7.8	10.8	14.1	11.5	12.0	13.9	10.0	25.0	13.4
17	CO	24.7	27.3	27.6	17.8	20.9	24.9	21.3	22.3	23.7	18.4	33.7	22.4

^a All energies are single point energies from SVWN5 optimized geometries. Reaction numbering from Figure 3.

reduces its ability to accept electrons from the other Ir atom. Such asymmetry in Ir–C (*bri*) bond lengths was observed in tetrairidium clusters and can be considered as a transformation from a bridging carbonyl to terminal one binding to the Ir atom with high electron density.[87,88] The changes in the LDEs are similar to the trends predicted for $\text{Ir}(\text{PH}_3)_y(\text{CO})_z$. As more PH_3 's are substituted, the LDEs of the carbonyl increase moderately, whereas those of the PH_3 's decrease slightly, and both the Ir–C and Ir–P bond lengths decrease. For coordinatively saturated $\text{Ir}_2(\text{PH}_3)_y(\text{CO})_z$ clusters, most LDEs range from ~ 15 to ~ 35 kcal/mol, closer to those of IrL_4 and less than for IrL_3 .

Table 6. Calculated NBO Charges on Ir,^a Average C-O Stretching Frequencies ($\nu_{\text{C-O}}$),^a Ir-Ir Bond Energies (BDE),^b Bond Distances (r)^a, and LDEs for $\text{Ir}_2(\text{PH}_3)_y(\text{CO})_z$.^b

Property	$\text{Ir}_2(\text{CO})_8 \text{C}_{2v}$	$\text{Ir}_2\text{PH}_3(\text{CO})_7$ (2d)	$\text{Ir}_2(\text{PH}_3)_2(\text{CO})_6$ (2l)
Ir NBO charge	0.22	0.23 ^c , 0.06 ^d	0.07
Ir NBO 5d	8.21	8.20 ^c , 8.33 ^d	8.32
$r(\text{Ir-Ir})$ (Å)	2.774	2.760	2.744
BDE(Ir-Ir) (kcal/mol)	45.7	52.7	57.2
Average $\nu_{\text{C-O}}$ (cm^{-1})	2026	2002	1972
$r(\text{C-O})$ (<i>ter</i> , Å)	1.152	1.154	1.156
$r(\text{C-O})$ (<i>bri</i> , Å)	1.180	1.186	1.193
$r(\text{Ir-C})^c$ (<i>ter</i> , Å)	1.927	1.925 ^c , 1.916 ^d	1.914
$r(\text{Ir-C})^c$ (<i>bri</i> , Å)	2.090	2.106 ^c , 2.061 ^d	2.075
LDE(<i>ter</i> CO) (kcal/mol)		25.8	28.3
LDE(<i>bri</i> CO) (kcal/mol)		30.8	33.2
$r(\text{Ir-P})$ (Å)		2.309	2.300
LDE(PH_3) (kcal/mol)		28.6	27.4

^a All bond distances, frequencies, and NBO charges are calculated at the SVWN5 level.

^b All BDEs and LDEs are calculated by CCSD(T) at the SVWN5 optimized geometries.

^c Ir not bonded to PH_3 .

^d Ir bonded to PH_3 .

3.3 DFT Benchmarks for the LDEs for Ir and Ir_2 Clusters.

The catalytic character of tetrairidium clusters is generally associated with the exposed metal core that is generated by the dissociation of ligands.[89] We have discussed the LDEs of $\text{Ir}(\text{PH}_3)_y(\text{CO})_z$ and $\text{Ir}_2(\text{PH}_3)_y(\text{CO})_z$ clusters at the CCSD(T) level. It is difficult to perform CCSD(T) calculations for the ligated tetrairidium clusters because of their size, and so we need to find a DFT functional that can be used to predict the LDEs of the larger clusters. The functionals used for the benchmarking and their LDEs are given in Tables 2 and 5. Generalized gradient approximation (GGA) hybrid functionals with long-range corrections (LR-HGGA), CAM-B3LYP, ωB97X , and $\omega\text{B97X-D}$ perform the best, followed by hybrid GGA functionals (M06, B3LYP, B98) and pure GGA functionals (BP86, PBE, and PW91). Although SVWN5,

a local density approximation (LDA) functional, gives good predictions of the geometry, the LDEs are predicted to be too large, as expected for the overbinding of local functionals. The energies of $\text{Ir}_4(\text{PH}_3)_y(\text{CO})_z$ clusters were thus calculated at the $\omega\text{B97X-D}$ level, which has deviations of less than 5 kcal/mol from CCSD(T) results for $\text{Ir}(\text{PH}_3)_y(\text{CO})_z$ and $\text{Ir}_2(\text{PH}_3)_y(\text{CO})_z$ clusters.

3.4 $\text{Ir}_4(\text{PH}_3)_y(\text{CO})_z$ structures, relative energies, and dissociation energies.

Because it has been shown experimentally [40] that no more than four carbonyls can be substituted by phosphines, only the $\text{Ir}_4\text{PH}_3(\text{CO})_{11}$, $\text{Ir}_4(\text{PH}_3)_2(\text{CO})_{10}$, $\text{Ir}_4(\text{PH}_3)_3(\text{CO})_9$, and $\text{Ir}_4(\text{PH}_3)_4(\text{CO})_8$ clusters are considered here. Besides the lowest energy isomers characterized by experiment, other isomers with substitution at various positions were also investigated, including both C_{3v} and T_d structures and terminal and bridging position substitution and dissociation. In total, 87 $\text{Ir}_4(\text{PH}_3)_y(\text{CO})_z$ isomers have been optimized, as shown in Figure 4; their bond distances are given in the SI, and relative energies are listed in Tables 7 and 8.

Different DFT functionals give different relative energies for the $\text{Ir}_4(\text{CO})_{12}$ cluster. $\omega\text{B97X-D}$, which we use to predict the energetics of the $\text{Ir}_4(\text{PH}_3)_y(\text{CO})_z$ isomers, correctly predicts that the lowest energy isomer of $\text{Ir}_4(\text{CO})_{12}$ is the T_d isomer.[51] The axial sites in the C_{3v} structures are less crowded, and axial site substitution by PH_3 is favoured and controlled by steric effects. Whether a C_{3v} or T_d structure is adopted is determined by the π -acidity of the substituting ligands (i.e., the exact structure is controlled by electronic effects).[38,39,40] As the electronegativity of the groups bonded to phosphorus increases, the contribution of the phosphorus to the LUMO that accepts π -electrons from Ir atom increases. Thus, the order of the π -acidity for common phosphine ligands is $\text{PR}_3 < \text{PAr}_3 < \text{P(OR)}_3 < \text{P(OAr)}_3 < \text{PF}_3$ ($\text{R} = \text{alkyl}$).[90] It has been reported that a good π -acceptor phosphite ligand, $\text{P(OCH}_2)_3\text{CEt}$, can maintain the T_d structure in monosubstitution of $\text{Ir}_4(\text{CO})_{12}$,[39] whereas for some poor π -acceptors, such as PPh_2Me , substitution leads to a C_{3v} structure.[39,91] The PH_3 ligand used in the current investigation is a stronger π -acceptor than most phosphines but is not as strong as phosphites. Most of these phosphines and phosphites are poor π -acceptors as compared with carbonyl. Our calculations show that the T_d structure of $\text{Ir}_4\text{PH}_3(\text{CO})_{11}$ is lower in energy by only 0.3 kcal/mol than the C_{3v} structure. As more CO ligands are replaced by PH_3 ligands, the C_{3v} structure becomes more favoured.

The NBO charges on Ir atoms were calculated to provide more insight into the chemistry. We discuss changes in the Ir NBO charge relative to that in $\text{T}_d \text{Ir}_4(\text{CO})_{12}$ as given in Equation (2):

$$\Delta\text{NBO} = [\text{NBO}_{\text{Ir}_4(\text{CO})_{12}(\text{T}_d)} \text{ charge}] - [\text{average NBO}_{\text{Ir}_4(\text{PH}_3)_y(\text{CO})_z} \text{ charge}] \quad (2)$$

These ΔNBO values with their relative energies are given in Table 8. For $\text{Ir}_4\text{PH}_3(\text{CO})_{11}$ isomers (**4a**, **4b**, **4d**, and **4e**), although one PH_3 ligand has been introduced, the Ir NBO charge does not change much (-0.01 to 0.02), and so the T_d structure is maintained. From $\text{Ir}_4(\text{PH}_3)_2(\text{CO})_{10}$ to $\text{Ir}_4(\text{PH}_3)_4(\text{CO})_8$ isomers (**6a**, **6c**, **6d**, **6e**, **8a**, **8b**, **8d**, **8e**, **10a**, **10b**, and **10d**), the negative charge on the Ir atom and ΔNBO increases, and our calculations predict that the C_{3v} isomers are more stable than the T_d isomers. These trends suggest that the average charge on the Ir atom in tetra-iridium clusters plays a role in the energetics of the clusters. When a carbonyl is replaced by a ligand that has a similar π -acidity, the T_d structure is maintained, because the Ir charge does not change

much. If it is a weak π -acceptor that increases the electron density on the Ir atom, the C_{3v} structure is adopted, because in this structure, an Ir atom can bind to more carbonyls and transfer more electron density to get closer to the charge in T_d $Ir_4(CO)_{12}$.

There is an apparent equilibrium between increased π -back-bonding and lower electron repulsion in the σ orbitals. Steric effects are lower in the C_{3v} structure, leading to an additional decrease in energy. The energy differences between the T_d and C_{3v} structures are often not large, and thus, an interconversion between isomers with *ax* ligands and *eq* ligands is often observed experimentally. This was explained by Cotton in terms of a merry-go-round mechanism.[92,93] Different from the isomers discussed above that have terminal PH_3 ligands, those with bridging PH_3 ligands (**4c**, **6b**, **8c**, and **10c**) have higher energies than other isomers by 7 to 10 kcal/mol. This difference results because the phosphine lone pair electrons have high s character and cannot bind efficiently to two Ir atoms at the same time.

Carbonyl dissociation from a coordinatively saturated tetrairidium cluster can lead to a hydrogen atom transfer from the PH_3 to a nearby Ir atom, analogous to reaction (15) for $Ir_2(PH_3)_y(CO)_z$. If one bridging carbonyl is dissociated from a tetrairidium cluster that has a bridging PH_3 , a H atom transfer always takes place, as shown in Figure 5 (a) (this corresponds to reactions (14), (34), (60), and (79) in Figure 4). As a bridging carbonyl is removed, an *eq* CO moves to the *bri* position of the removed CO, and an H atom transfers to the original position of the *eq* CO and binds to the Ir atom to maintain Ir coordination. In the final product, there is a bridging phosphido group. Comparing **4c** with **5k**, we see that the total reaction can be regarded as a dissociation of *eq* CO, compensated by a hydrogen atom from a PH_3 and keeping the cluster coordinatively saturated. A second type of hydrogen atom transfer is illustrated in Figure 5 (b) (which corresponds to reaction 70 in Figure 4). Dissociation of a bridging carbonyl leads to rotation of an adjacent PH_3 to form a bridge PH_2 group and a hydrogen bonded to Ir to maintain as high a coordination at Ir as possible. A similar reaction has been reported in which a basal phosphine monosubstituted tetrairidium cluster yields a product with both a bridging phosphido and a bridging H atom by deprotonation of the phosphine.[94] However, in our investigation, no H atom transfers involving basal PH_3 have been found for C_{3v} isomers. The two kinds of H atom transfers described above correspond (a) to transfer from a bridging PH_3 that does not bind efficiently because of its lone pair orientation and (b) to transfer from an apical (*api* = apical) PH_3 that has the lowest dissociation energy (see below). These results suggest that each PH_3 with a low LDE is more likely to lose an H atom forming a lower energy structure with a bridging phosphido group.

For all CO and PH_3 dissociation processes, there are no transformations from C_{3v} structures to T_d structures, but the reverse is possible. The third type of H atom transfer (Figure 5 (c)) is an example of such a transformation (reactions (65) and (82) in Figure 4). In a T_d isomer, a terminal PH_3 moves close to an unsaturated Ir atom as a result of a carbonyl dissociation, and one of its H atoms moves farther to bind to the Ir atom to maintain coordination, leaving a bridging phosphido group. During this process, two carbonyls are converted into bridging carbonyls, and the isomer switches to a C_{3v} structure.

Figure 4: Optimized geometries of low-lying $\text{Ir}_4(\text{PH}_3)_y(\text{CO})_z$ isomers

Figure 4 (continued): Optimized geometries of low-lying $\text{Ir}_4(\text{PH}_3)_y(\text{CO})_z$ isomers.

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Figure 4 (continued): Optimized geometries of low-lying $\text{Ir}_4(\text{PH}_3)_y(\text{CO})_z$ isomers.

Table 8. Average Ir NBO Charges,^a Δ NBO, and Relative Energies (ΔE , kcal/mol)b for $\text{Ir}_4(\text{PH}_3)_y(\text{CO})_z$ Isomers, $y + z = 12$.

Property/Molecule	C_{3v}			T_d	
$\text{Ir}_4(\text{CO})_{12}$					
Ave NBO charge	0.10			0.08	
Δ NBO	-0.02			0.00	
ΔE	2.8			0.0	
$\text{Ir}_4\text{PH}_3(\text{CO})_{11}$	4a	4b	4c	4d	4e
Ave NBO charge	0.07	0.07	0.06	0.09	0.06
Δ NBO	0.01	0.01	0.02	-0.01	0.02
ΔE	0.3	1.1	10.0	1.5	0.0
$\text{Ir}_4(\text{PH}_3)_2(\text{CO})_{10}$	6a	6b	6c	6d	6e
Ave NBO charge	0.05	0.04	0.05	0.03	0.03
Δ NBO	0.03	0.04	0.03	0.05	0.05
ΔE	0.0	8.2	1.1	0.8	0.6
$\text{Ir}_4(\text{PH}_3)_3(\text{CO})_9$	8a	8b	8c	8d	8e
Ave NBO charge	0.02	0.00	0.00	-0.01	-0.04
Δ NBO	0.06	0.08	0.08	0.09	0.12
ΔE	0.1	0.0	6.8	3.4	2.4
$\text{Ir}_4(\text{PH}_3)_4(\text{CO})_8$	10a	10b	10c	10d	
Ave NBO charge	-0.02	-0.02	-0.03	-0.04	
Δ NBO	0.10	0.10	0.11	0.12	
ΔE	0.0	0.1	7.4	2.6	

^a All NBO charges are calculated at the SVWN5 level.

^b All relative energies are calculated at the ω B97x-D level at the SVWN5 optimized geometries.

All of the predicted H-atom transfer reactions occur on removal of a CO ligand from the cluster. The H atom that binds to the unsaturated Ir atom generated by CO removal comes from a PH_3 bonded to an adjacent saturated Ir atom. If a terminal PH_3 is directly bonded to the unsaturated Ir, it does not transfer an H atom. The H atom transfer reaction results in a cluster with a bridging phosphide group. Bridging H atoms are not found, although clusters with a bridging H atom are commonly observed experimentally.[17,94,95] One possible reason for the lack of bridging H atoms is that the H atom needs to be a formal hydride in order to form an Ir–H–Ir bridge, as can be achieved experimentally by making the cluster an anion. For our neutral cluster, the H atom is unlikely to have very much hydridic character.

Figure 5: Three types of H atom transfer reactions that occur on CO dissociation. The H and P atoms involved in the transfer reactions are marked in red and blue, respectively. The isomers in mid two columns are for description, not transition states or intermediates.

Figure 6: (a) A Bridging PH₃ Maintained Process. (b) A Transformation from Bridging PH₃ to Equatorial One. The P atoms involved in the transformation are marked in blue.

Another transformation involved in carbonyl dissociation involves changing the PH₃ from a bridging site to an equatorial site. Figure 6a illustrates a case in which dissociation of an *eq* CO does not convert a bridging PH₃ into a terminal one. When an *eq* CO that shares the Ir atom with the PH₃ is removed, the PH₃ leaves the bridging site and takes the place of the dissociated *eq* CO (Figure 6b).

The LDEs of PH₃ and CO ligands of the Ir₄ clusters are given in Table 9. (See also the Supporting Information, where they are arranged according to the reaction numbers in Figure 4.) The LDEs of carbonyls at various sites in the C_{3v} isomers follow the general order: *eq* > *ax* > *bri* > *api* for the lowest LDE in a group when PH₃ does not change from a *bri* to an *eq*. The *bri* vs. *api* ordering is isomer-dependent, and so this order can switch, but clearly the *eq* have the highest LDEs followed by the *ax* LDEs. If the PH₃ can rearrange to an *eq* from a *bri* position, then the *eq* CO ligands have the lowest LDE. The hydrogen atom transfer processes that can occur when CO is removed lead to a lower energy product cluster, and so the CO LDEs decrease by ~ 8 to ~ 33 kcal/mol.

As PH₃ ligands are substituted for CO, there is not a clear trend in the CO LDEs for the lowest energy species up to x = 3. The specific details regarding which CO will be lost are complicated by the similar energies of the various C_{3v} (and even T_d) isomers. For x = 4, the lowest-energy CO LDE is clearly greater than those characterizing the other low-energy isomers. We emphasize that these values are adiabatic thermodynamic values going to the lowest-energy product cluster.[86] Experimentally, as observed for much bulkier phosphines, the decarbonylation rates increase with increasing numbers of phosphines.[96] Our results are indeed consistent with these

observations, because of the small steric bulk of PH_3 and the fact that kinetic control may also pertain if there is an additional barrier to decarbonylation above that for the LDE. If carbonyl dissociation does occur with an additional energy barrier by an $\text{S}_{\text{N}}1$ process,[97] the transition state will be of lower energy if there is a strong σ -donor in the cluster that increases the electron density on the Ir core. Such a transition state influence has been assumed for mononuclear complexes[98] and was used as a basis for inferring ligand dissociation rates for bi- and higher-nuclearity iridium clusters.[96] For $\text{Ir}_x(\text{PH}_3)_y(\text{CO})_z$ clusters, this reasoning would suggest that decarbonylation will take place at an increasing rate as more phosphines are substituted, in agreement with what has been reported.[42]

Given that the *api* and *bri* sites in the C_{3v} structures are comparable, the following question arises: at which site would ligand dissociation likely have the highest reaction rate? Our calculations predict NBO charges of the *eq*, *ax*, *api*, and *bri* carbonyls (charge on C plus the charge on O) in C_{3v} $\text{Ir}_4(\text{CO})_{12}$ to be 0.07 e, 0.06 e, -0.02 e, and -0.25 e, respectively, with a total charge on the Ir_4 cluster of 0.41 e. The corresponding charges on the Ir_4 core in $\text{Ir}_4(\text{CO})_{11}$ generated after removal of an *eq*, *ax*, *api*, or *bri* CO are 0.52 e, 0.40 e, 0.40 e, and 0.33 e, respectively. This comparison suggests that removal of a *bri* CO leads to the largest increase in the electron density of the Ir core. Thus, we suggest, if a transition state for CO loss is present, that such a transition state would have the lowest energy for a *bri* CO. This inference is consistent with the experimental result that bridging carbonyls dissociate more readily in thermal decarbonylation.[42] Because *bri* CO ligands and *eq*, *ax* CO ligands can be readily interconverted,[40] substitution with a new ligand can take place at any basal position determined by its bulk and orbital direction; *api* substitutions are rare except through some selectively reactive decarbonylations that lower the activation energy, as they are not readily interconverted.[43]

The *eq* CO position has very high LDEs, ranging from ~ 51 to 60 kcal/mol, except for dissociation involving the transformation of PH_3 from *bri* to *eq*, which lowers the LDE to ~ 37 kcal/mol, because the product is of lower energy. Different from the PH_3 LDEs discussed below, the other *bri* CO LDEs, from ~ 39 to ~ 46 kcal/mol, are close to or even slightly greater than those of *api* CO, ranging from ~ 37 to ~ 47 kcal/mol. This result suggests that carbonyls can bind to two Ir atoms more efficiently than PH_3 . The LDEs of CO in the T_d isomers, from ~ 38 to 44 kcal/mol, are close to those for *api* CO (the same trend was found for PH_3 LDEs) and *bri* CO in the C_{3v} isomers.

For PH_3 in the C_{3v} isomers, the LDEs range from ~ 29 to ~ 51 kcal/mol. The *eq* PH_3 ligands have the highest LDEs, from ~ 45 to ~ 51 kcal/mol, much higher than others by at least ~ 10 kcal/mol. In the remainder, the *ax* PH_3 's have LDEs from ~ 35 to ~ 41 kcal/mol, followed by *api* LDEs from ~ 32 to ~ 37 kcal/mol. As a consequence of the higher energies of the *bri* PH_3 isomers, their LDEs are the lowest, ~ 30 kcal/mol. The range of PH_3 LDEs in the T_d structure, from ~ 33 to ~ 38 kcal/mol, is relatively narrow with respect to those in the C_{3v} isomer. Even if the product changes to the C_{3v} structure, the LDEs of the T_d PH_3 ligands are very close to the *api* values. This result can be explained by the similar environment of the *api* Ir atom and the Ir atoms in the T_d isomers, both of which are three-fold ligand

Table 9. PH₃ and CO LDEs for Ir_x(PH₃)_y(CO)_z clusters in kcal/mol at the ωB97x-D level.^a

Molecule	C _{3v} <i>eq</i>	C _{3v} <i>ax</i>	C _{3v} <i>api</i>	C _{3v} <i>bri</i>	C _{3v} H-trans	T _d	T _d H-trans
PH ₃							
Ir ₄ PH ₃ (CO) ₁₁	50.8(4a)	40.2(4b)	37.1(4d)	29.1(4c)		38.0(4e)	
Ir ₄ (PH ₃) ₂ (CO) ₁₀	49.4(6a)	40.7(6a)	33.8(6b)	30.0(6b)		37.8(6d)	
		39.8(6c)				34.1(6e)	
Ir ₄ (PH ₃) ₃ (CO) ₉	49.7(8a)	41.5(8a)	32.7(8c)	29.2(8c)		34.9 ^b (8d)	
	51.1(8b)					33.6 ^b (8e)	
Ir ₄ (PH ₃) ₄ (CO) ₈	48.5(10a)	35.4(10b)	32.0(10a)	28.3(10c)		32.7(10d)	
	45.2(10c)						
CO							
Ir ₄ (CO) ₁₂	52.6	42.7	40.1	40.5		39.4	
Ir ₄ PH ₃ (CO) ₁₁	53.5(4a)	47.1(4a) 43.9(4a)	42.5(4a)	43.5(4a)		42.1(4e)	
	51.9(4b)		38.3(4b)	39.1(4b)		38.2(4e)	
Ir ₄ PH ₃ (CO) ₁₁	50.9(4c)		41.1(4c) 35.6(4c)		8.0 (4c)		
	53.3(4d)	43.0(4d)	46.0(4d)	42.5(4d) 40.3(4d)			
Ir ₄ (PH ₃) ₂ (CO) ₁₀	53.5(6a)	48.9(6a)	39.2(6a)	45.9(6a)	11.2(6b)	41.2 ^c (6d)	
	36.8 ^b (6b)		44.6(6b)			38.9(6d)	
	54.9(6c)		42.9(6c)	41.0(6c)		39.2 ^c (6e) 42.4 ^c (6e)	
Ir ₄ (PH ₃) ₃ (CO) ₉	59.4(8a)	50.5(8a)	37.7(8a)	45.2(8a)	15.2(8c)	43.6(8d)	
		50.9(8b)	40.7(8b)	43.7(8b)		38.7(8e)	17.4(8e)
	36.5 ^b (8c)		45.9(8c)				
Ir ₄ (PH ₃) ₄ (CO) ₈	60.3(10a)		47.0(10a)		33.6(10a)		
Ir ₄ (PH ₃) ₄ (CO) ₈	58.6(10b)		46.4(10b)	43.3(10b)			27.4(10d)
	36.9 ^b (10c)		41.0(10c)		16.4(10c)		

^a Letters in parentheses correspond to structures in Figure 4. ^b A bridging PH₃ changes into a equatorial one after the ligand dissociation.

^c Isomers turn into C_{3v} structure after ligand dissociation.

coordinated. As more carbonyls are replaced, the LDEs gradually decrease, similar to the trend found in $\text{Ir}(\text{PH}_3)_y(\text{CO})_z$ and $\text{Ir}_2(\text{PH}_3)_y(\text{CO})_z$ clusters.

4. Conclusions

Calculations of the structures and energetics of a range of $\text{Ir}_x(\text{PH}_3)_y(\text{CO})_z$ ($x = 1, 2, 4$) have been performed. Benchmark calculations for the LDEs for the $x = 1$ and 2 clusters were performed at the DFT level with 10 exchange-correlation functionals as well as at the correlated molecular orbital MP2 and CCSD(T) levels. The best agreement with CCSD(T) was found by using the $\omega\text{B97X-D}$ functional so it was used for the $x = 4$ LDE calculations. The doublet states of the $\text{Ir}(\text{PH}_3)_y(\text{CO})_z$ clusters are significantly lower in energy than the quartet states. The carbonyls are stronger π -electron acceptor ligands than PH_3 , and the PH_3 ligands act as stronger σ -electron donors and weaker π -electron acceptors than CO. Such electronic effects strengthen the Ir-C bond and increase the LDEs of the CO ligand for the complexes with a single Ir atom. The σ -electron donation ability of PH_3 provides more electron density on the Ir atom that can be used for π -back-bonding to the carbonyl. Yet this increased σ -electron donation leads to an increased repulsion with the d valence electrons from the Ir (often called Pauli repulsion). The balance of these two effects will govern the properties at the minimum for the mononuclear iridium complexes, and it is also relevant to the LDE if the properties of the Ir-containing product are similar. The trans influence of carbonyls is important in determining the structure, relative energies, and dissociation energies of these mononuclear iridium complexes. The isomers of these complexes with *ax* phosphines are of lower energy. The Ir-CO LDE increases with increasing substitution of CO by PH_3 ligands, whereas the LDEs of PH_3 ligands decrease slightly as more PH_3 ligands are added. IrL_4 complexes are more distorted, with lower LDEs, than IrL_3 , and steric effects also play roles even in these small complexes.

The three basic structures of $\text{Ir}_2(\text{PH}_3)_y(\text{CO})_z$ isomers have C_{2v} , C_2 , and D_{3d} symmetry. The two trans ligands along the Ir-Ir axis in the D_{3d} isomers are strongly bonded, leading to lower energy structures. The dissociation of such ligands results in higher energy isomers. C_2 and C_{2v} are coordinatively saturated isomers with energies that are close to each other, whereas the C_2 isomers of coordinatively unsaturated species are of lower energy. The changes are similar to those found for $\text{Ir}(\text{PH}_3)_y(\text{CO})_z$ complexes as more PH_3 ligands are introduced. PH_3 substitution increases the negative charge on the Ir atom and strengthens the binding between the carbonyls and the Ir atom and slightly decreases the LDEs of the PH_3 ligands. This trend is the same as that predicted for $\text{Ir}(\text{PH}_3)_y(\text{CO})_z$ complexes.

The C_{3v} structures of $\text{Ir}_4(\text{PH}_3)_y(\text{CO})_z$ clusters have similar energies with respect to the T_d isomers for $\text{Ir}_4\text{PH}_3(\text{CO})_{11}$ and $\text{Ir}_4(\text{PH}_3)_2(\text{CO})_{10}$, and the C_{3v} structures are of even lower energy for $\text{Ir}_4(\text{PH}_3)_3(\text{CO})_9$ and $\text{Ir}_4(\text{PH}_3)_4(\text{CO})_8$. This conclusion is consistent with observations of C_{3v} structures for mono-phosphine Ir_4 clusters with larger and more electron-withdrawing R groups on the phosphorus.[40] Our explanation for these energy differences is that the charge differences on the Ir atoms do not vary much from those in the $\text{Ir}_4(\text{CO})_{12}$ T_d structure and that steric interactions are minimized. Structural transformations in the process of carbonyl dissociation can occur with T_d isomers converting into C_{3v} isomers; the reverse does not occur. Hydrogen atom transfer from a PH_3 usually occurs with a bridging carbonyl

dissociation coupled with a weakly bonded PH_3 and results in a bridging phosphido group and an Ir–H bond that makes the cluster coordinatively saturated. A bridging PH_3 can move to an equatorial position as that *eq* carbonyl is dissociated. Such a transformation stabilizes the product cluster and reduces the LDEs. When hydrogen atom transfer and the rearrangement of the PH_3 from a *bri* to an *eq* position does not occur, the lowest CO LDE for a given site follows the order $eq > ax > bri > api$. Up to $x = 3$, the lowest energy CO LDEs are approximately the same as PH_3 ligands are substituted for CO. Experimentally, an increase in the numbers of phosphines leads to an increase in the decarbonylation rates,[42] most likely a consequence of the use of much bulkier phosphines and potentially kinetic control of the decarbonylation. The addition of the phosphines makes the Ir atoms more electron rich, leading, it has been hypothesized, to a lower-energy transition state for thermal decarbonylation.[96] The NBO calculations for the C_{3v} isomers show that the bridging carbonyls donate less electron density to the tetrairidium core (are less positive) than do the terminal carbonyls. The transition state for dissociation of a bridging carbonyl has more electron density on the tetrairidium core than those involving carbonyls in other sites, as shown by the charge distributions in the respective $\text{Ir}_4(\text{CO})_{11}$ clusters. Thus, one should expect lower-energy transition states for the dissociation of bridging carbonyls. Because CO ligands can switch between the basal and bridging sites,[40] basal substitution can occur more readily than apical substitution.[42] Similar to the trend found for $\text{Ir}(\text{PH}_3)_y(\text{CO})_z$ and $\text{Ir}_2(\text{PH}_3)_y(\text{CO})_z$, the LDEs of the PH_3 's in the tetra-iridium cluster gradually decrease with an increasing number of PH_3 's.

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Figure 1

Figure 1: Isomers of $\text{Ir}_4(\text{CO})_{12}$ and $\text{Ir}_4(\text{CO})_{11}\text{L}$. In T_d structure **a**, all carbonyls are terminal. In C_{3v} structure **b**, Ir(1) is apical iridium, and Ir(2), Ir(3), and Ir(4) are basal iridiums that build up the basal plane. C(5), C(6), C(7), and C(8) are apical, bridging, equatorial, and axial carbon, respectively. L is the ligand that substitutes for axial carbonyl in **b** and for equatorial carbonyl in **c**.

Figure 2

Figure 1: Optimized geometries of low-lying $\text{Ir}(\text{PH}_3)_y(\text{CO})_z$ isomers and their symmetries. Only doublet states are shown. Relative energies are in kcal/mol.

Figure 3

Figure 1: Optimized geometries of low-lying $\text{Ir}_2(\text{PH}_3)_y(\text{CO})_z$ isomers.

Figure 4

Figure 1: Optimized geometries of low-lying $\text{Ir}_4(\text{PH}_3)_y(\text{CO})_z$ isomers

Figure 4 (continued): Optimized geometries of low-lying $\text{Ir}_4(\text{PH}_3)_y(\text{CO})_z$ isomers.

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Figure 2: Optimized geometries of low-lying $\text{Ir}_4(\text{PH}_3)_y(\text{CO})_z$ isomers

Figure 5

Figure 1: Three types of H atom transfer reactions that occur on CO dissociation. The H and P atoms involved in the transfer reactions are marked in red and blue, respectively. The isomers in mid two columns are for description, not transition states or intermediates.

Figure 6

Figure 1: (a) A Bridging PH₃ Maintained Process. (b) A Transformation from Bridging PH₃ to Equatorial One. The P atoms involved in the transformation are marked in blue.

Table 1

Table 1. Relative Energies of Ir(PH₃)_y(CO)_z Isomers in kcal/mol, predicted by various electronic structure methods.^a

Molecule	Symmetry	BP86	PBE	PW91	B3LYP	CAM-B3LYP	B97-D	B98	ωB97X	ωB97X-D	M06	MP2	CCSD(T)
² IrCO	C _{∞v}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
⁴ IrCO	C _s	39.7	39.7	39.7	37.4	35.1	46.6	40.4	42.3	41.5	44.9	44.9	36.3
² Ir(CO) ₂	C _s bent	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
² Ir(CO) ₂	C _{2v} linear	-1.5	-0.1	-0.5	-8.7	-10.7	-2.3	-8.3	-11.3	-8.9	-6.3	15.8	9.9
² Ir(CO) ₃	C _s	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
⁴ Ir(CO) ₃	C _{2v}	49.9	49.6	49.8	47.8	45.3	54.5	49.0	49.0	49.9	55.8	58.1	49.2
² IrPH ₃ CO	C _s bent	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
² IrPH ₃ CO	C ₁ linear	-7.0	-5.9	-6.2	-13.0	-15.0	-6.5	-12.9	-16.1	-14.0	-10.7	10.8	6.8
² IrPH ₃ (CO) ₂	C _s <i>ax</i>	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
² IrPH ₃ (CO) ₂	C _s <i>eq</i>	1.2	1.1	1.1	1.5	2.2	0.5	1.5	2.6	2.3	1.8	2.6	2.2
⁴ IrPH ₃ (CO) ₂	C _s <i>ax</i>	53.8	53.5	53.8	51.6	49.1	58.5	52.8	52.9	53.8	60.0	62.6	52.7
⁴ IrPH ₃ (CO) ₂	C _s <i>eq</i>	48.5	48.3	48.4	45.5	43.0	52.5	46.7	46.9	47.8	53.5	107.3	94.2
² IrPH ₃ (CO) ₃	C _s	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
⁴ IrPH ₃ (CO) ₃	C _s	60.9	60.6	60.5	61.8	64.4	61.4	63.6	69.9	68.7	67.4	76.6	66.3
² Ir(PH ₃) ₂	C _{2v} bent	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
² Ir(PH ₃) ₂	C _s linear	-11.7	-10.6	-10.9	-17.1	-19.1	-10.5	-17.0	-20.3	-18.4	-15.0	8.5	5.9
² Ir(PH ₃) ₂ CO	C _{2v} <i>ax, ax</i>	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
² Ir(PH ₃) ₂ CO	C ₁ <i>ax, eq</i>	1.4	1.2	1.2	1.2	1.6	0.9	1.3	1.8	1.6	0.8	2.3	1.3
⁴ Ir(PH ₃) ₂ CO	C _s <i>ax, eq</i>	45.4	44.5	44.7	45.5	43.6	48.8	46.2	48.3	48.2	54.2	51.2	42.4
² Ir(PH ₃) ₂ (CO) ₂	C _{2v} <i>ax, ax</i>	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
² Ir(PH ₃) ₂ (CO) ₂	C ₂ <i>ax, eq</i>	1.8	1.7	1.7	2.1	1.9	2.1	2.0	1.6	1.8	1.7	1.0	1.4
⁴ Ir(PH ₃) ₂ (CO) ₂	C ₁ <i>ax, eq</i>	63.4	63.0	63.1	63.3	64.0	64.2	64.9	68.1	68.4	69.3	82.8	66.3
⁴ Ir(PH ₃) ₂ (CO) ₂	C _{2v} <i>ax, ax</i>	62.0	61.5	61.5	62.9	66.3	62.8	65.0	72.5	70.6	67.9	83.1	69.3
² Ir(PH ₃) ₃	C _s	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
⁴ Ir(PH ₃) ₃	C _s	53.4	53.2	53.4	50.4	47.7	58.8	51.6	51.6	52.8	58.8	77.0	64.7
² Ir(PH ₃) ₃ CO	C _s	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
⁴ Ir(PH ₃) ₃ CO	C ₁	70.5	70.8	70.8	67.3	68.3	73.7	69.6	73.4	73.3	72.7	92.5	85.7

^a All energies are single-point energies at the SVWN5 optimized geometries.

Table 2

Table 2. LDEs of Ir(PH₃)_y(CO)_z Isomers in kcal/mol, predicted by various electronic structure methods.^a

Reaction	BP86	PBE	PW91	B3LYP	CAM-B3LYP	B97-D	B98	ωB97X	ωB97X-D	M06	MP2	CCSD(T)
² Ir(CO) ₃ → ² Ir(CO) ₂ (bent) + CO	48.0	49.3	49.8	42.0	44.0	43.2	44.1	44.2	44.5	42.5	48.2	41.3
² Ir(CO) ₃ → ² Ir(CO) ₂ (linear) + CO	46.5	49.2	49.2	33.4	33.3	40.8	35.9	33.0	35.6	36.2	64.0	51.2
² IrPH ₃ (CO) ₂ (ax) → ² Ir(CO) ₂ (bent) + PH ₃	35.7	37.0	37.6	32.7	36.6	33.8	35.5	39.4	38.6	34.6	45.3	38.1
² IrPH ₃ (CO) ₂ (ax) → ² IrPH ₃ CO (bent) + CO	53.8	55.3	55.7	47.1	49.0	48.0	49.4	49.6	50.1	47.5	55.6	46.5
² IrPH ₃ (CO) ₂ (ax) → ² IrPH ₃ CO (linear) + CO	46.8	49.4	49.5	34.0	33.9	41.5	36.6	33.5	36.1	36.8	66.4	53.3
² IrPH ₃ (CO) ₂ (eq) → ² Ir(CO) ₂ (linear) + PH ₃	33.1	35.8	36.0	22.5	23.8	30.9	25.7	25.5	27.4	26.5	58.6	45.8
² IrPH ₃ (CO) ₂ (eq) → ² IrPH ₃ CO (bent) + CO	52.5	54.1	54.6	45.5	46.8	47.5	48.0	46.9	47.9	45.7	53.0	44.3
² Ir(PH ₃) ₂ CO (ax, ax) → ² IrPH ₃ CO (bent) + PH ₃	36.2	37.6	38.1	32.3	36.3	33.6	35.3	39.2	38.6	34.0	47.2	38.4
² Ir(PH ₃) ₂ CO (ax, ax) → ² Ir(PH ₃) ₂ (linear) + CO	49.4	52.1	52.2	36.9	37.0	44.1	39.6	36.5	39.2	39.3	73.4	59.4
² Ir(PH ₃) ₂ CO (ax, eq) → ² IrPH ₃ CO (bent) + PH ₃	34.8	36.4	36.9	31.1	34.6	32.6	34.1	37.4	37.0	33.2	44.9	37.1
² Ir(PH ₃) ₂ CO (ax, eq) → ² IrPH ₃ CO (linear) + PH ₃	27.8	30.6	30.8	18.1	19.6	26.1	21.2	21.3	23.0	22.5	55.7	43.9
² Ir(PH ₃) ₂ CO (ax, eq) → ² Ir(PH ₃) ₂ (bent) + CO	59.8	61.4	61.9	52.8	54.5	53.7	55.4	55.0	56.0	53.5	62.5	52.3
² Ir(PH ₃) ₃ → ² Ir(PH ₃) ₂ (bent) + PH ₃	37.9	39.7	40.2	33.4	36.9	35.0	36.6	40.0	39.8	35.7	49.5	39.8
² Ir(PH ₃) ₃ → ² Ir(PH ₃) ₂ (linear) + PH ₃	26.2	29.1	29.3	16.3	17.8	24.5	19.6	19.6	21.4	20.7	58.0	45.6

Table 2 (continued). LDEs of Ir(PH₃)_y(CO)_z Isomers in kcal/mol, predicted by various electronic structure methods.^a

Reaction	BP86	PBE	PW91	B3LYP	CAM-B3LYP	B97-D	B98	ωB97X	ωB97X-D	M06	MP2	CCSD(T)
${}^2\text{Ir}(\text{CO})_4 \rightarrow {}^2\text{Ir}(\text{CO})_3 + \text{CO}$	35.8	37.9	38.1	28.6	30.6	31.6	31.8	32.6	32.8	29.8	38.8	28.3
${}^2\text{IrPH}_3(\text{CO})_3 \rightarrow {}^2\text{Ir}(\text{CO})_3 + \text{PH}_3$	24.4	26.5	26.8	19.7	23.4	23.1	23.7	27.7	27.2	22.2	36.5	25.3
${}^2\text{IrPH}_3(\text{CO})_3 \rightarrow {}^2\text{IrPH}_3(\text{CO})_2(ax) + \text{CO}$	36.6	38.8	39.0	29.0	30.8	32.5	32.4	32.5	33.1	30	39.5	28.5
${}^2\text{IrPH}_3(\text{CO})_3 \rightarrow {}^2\text{IrPH}_3(\text{CO})_2(eq) + \text{CO}$	37.8	39.9	40.1	30.6	32.9	33.0	33.8	35.1	35.3	31.8	42.0	30.6
${}^2\text{Ir}(\text{PH}_3)_2(\text{CO})_2(ax, ax) \rightarrow {}^2\text{IrPH}_3(\text{CO})_2(eq) + \text{PH}_3$	22.4	24.7	25.0	17.8	21.3	21.6	21.9	25.4	25.2	20.3	34.4	23.7
${}^2\text{Ir}(\text{PH}_3)_2(\text{CO})_2(ax, ax) \rightarrow {}^2\text{Ir}(\text{PH}_3)_2\text{CO}(ax, ax) + \text{CO}$	40.0	42.3	42.6	32.5	34.0	36.0	36.0	35.8	36.7	33.8	42.8	31.8
${}^2\text{Ir}(\text{PH}_3)_2(\text{CO})_2(ax, eq) \rightarrow {}^2\text{IrPH}_3(\text{CO})_2(ax) + \text{PH}_3$	20.6	23.0	23.3	15.7	19.4	19.5	19.9	23.8	23.4	18.6	33.4	22.2
${}^2\text{Ir}(\text{PH}_3)_2(\text{CO})_2(ax, eq) \rightarrow {}^2\text{Ir}(\text{PH}_3)_2\text{CO}(ax, eq) + \text{CO}$	39.5	41.9	42.0	31.7	33.7	34.8	35.3	36.0	36.5	32.9	44.1	31.6
${}^2\text{Ir}(\text{PH}_3)_3\text{CO} \rightarrow {}^2\text{Ir}(\text{PH}_3)_3 + \text{CO}$	43.4	45.7	46.0	35.7	37.6	38.8	39.4	39.9	40.6	37.1	48.5	35.6
${}^2\text{Ir}(\text{PH}_3)_3\text{CO} \rightarrow {}^2\text{Ir}(\text{PH}_3)_2\text{CO}(ax, eq) + \text{PH}_3$	21.5	24.0	24.3	16.3	20.0	20.1	20.7	24.8	24.4	19.3	35.5	23.1
${}^2\text{Ir}(\text{PH}_3)_3\text{CO} \rightarrow {}^2\text{Ir}(\text{PH}_3)_2\text{CO}(ax, ax) + \text{PH}_3$	20.2	22.8	23.1	15.1	18.3	19.2	19.4	23	22.8	18.5	33.2	21.8
${}^2\text{Ir}(\text{PH}_3)_4 \rightarrow {}^2\text{Ir}(\text{PH}_3)_3 + \text{PH}_3$	21.8	24.5	24.7	16.6	20.1	20.7	21.2	25.1	24.9	19.9	36.8	24.0

^a All energies are single-point energies at the SVWN5 optimized geometries.

Table 3

Table 3. Calculated NBO Charges on Ir,^a Average C–O Stretching Frequencies ($\nu_{\text{C-O}}$),^a Bond Distances (r),^a and LDEs for Ir(PH₃)_y(CO)_z.^b

Property	Ir(CO) ₃	IrPH ₃ (CO) ₂		Ir(PH ₃) ₂ CO		Ir(PH ₃) ₃
	1a	<i>ax</i> 1b	<i>eq</i> 1c	<i>ax, ax</i> 1d	<i>ax, eq</i> 1e	1f
Ir NBO charge	0.02	-0.13	-0.13	-0.31	-0.38	-0.59
Ir NBO 5d	8.17	8.30	8.35	8.51	8.57	8.80
Average $\nu_{\text{C-O}}$ (cm ⁻¹)	2054	2022	2011	1992	2002	
$r(\text{C-O})$ (<i>ax</i> , Å)	1.156	1.162	1.164		1.167	
$r(\text{C-O})$ (<i>eq</i> , Å)	1.159	1.165		1.171		
$r(\text{Ir-C})$ (<i>ax</i> , Å)	1.901	1.865	1.877		1.849	
$r(\text{Ir-C})$ (<i>eq</i> , Å)	1.827	1.820		1.813		
LDE(CO) (<i>ax</i> , kcal/mol)	41.3	46.5	44.3		52.3	
LDE(CO) (<i>eq</i> , kcal/mol)	51.2	53.3		59.4		
$r(\text{Ir-P})$ (<i>ax</i> , Å)		2.315		2.264	2.294	2.243
$r(\text{Ir-P})$ (<i>eq</i> , Å)			2.230		2.211	2.198
LDE (PH ₃) (<i>ax</i> , kcal/mol)		38.1		38.4	37.1	39.8
LDE (PH ₃) (<i>eq</i> , kcal/mol)			45.8		43.9	45.6

Table 3 (continued). Calculated NBO Charges on Ir,^a Average C–O Stretching Frequencies ($\nu_{\text{C-O}}$),^a Bond Distances (r),^a and LDEs for $\text{Ir}(\text{PH}_3)_y(\text{CO})_z$.^b

Property	$\text{Ir}(\text{CO})_4$	$\text{IrPH}_3(\text{CO})_3$	$\text{Ir}(\text{PH}_3)_2(\text{CO})_2$	$\text{Ir}(\text{PH}_3)_2(\text{CO})_2$	$\text{Ir}(\text{PH}_3)_3\text{CO}$	$\text{Ir}(\text{PH}_3)_4$
	1g	1h	<i>ax, ax</i> 1i	<i>ax, eq</i> 1j	1k	1l
Ir NBO charge	0.16	0.07	-0.15	-0.09	-0.29	-0.51
Ir NBO 5d	8.21	8.27	8.44	8.43	8.63	8.87
Average $\nu_{\text{C-O}}$ (cm^{-1})	2054	2023	1988	2000	1975	
$r(\text{C-O})$ (<i>ax</i> , Å)	1.156	1.160		1.166		
$r(\text{C-O})$ (<i>eq</i> , Å)		1.162	1.168		1.170	
$r(\text{Ir-C})$ (<i>ax</i> , Å)	1.901	1.874		1.867		
$r(\text{Ir-C})$ (<i>eq</i> , Å)		1.892	1.879		1.858	
LDE(CO) (<i>ax</i> , kcal/mol)	28.3	30.6		31.6		
LDE(CO) (<i>eq</i> , kcal/mol)		28.5	31.8		35.6	
$r(\text{Ir-P})$ (<i>ax</i> , Å)		2.316	2.285	2.300	2.270	2.254
$r(\text{Ir-P})$ (<i>eq</i> , Å)					2.281	
LDE (PH_3) (<i>ax</i> , kcal/mol)		25.3	23.7	22.2	23.1	24.0
LDE (PH_3) (<i>eq</i> , kcal/mol)					21.8	

^a All bond distances, frequencies, and NBO charges are calculated at the SVWN5 level.

^b All LDEs are calculated by CCSD(T) at the SVWN5 optimized geometries

Table 4

Table 4. Relative Energies of $\text{Ir}_2(\text{PH}_3)_y(\text{CO})_z$ Isomers in kcal/mol, predicted by various electronic structure methods.^a

Molecule	BP86	PBE	PW91	B3LYP	CAM-B3LYP	B97-D	B98	ω B97X	ω B97X-D	M06	MP2	CCSD(T)
$\text{Ir}_2(\text{CO})_7$ 2b	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$\text{Ir}_2(\text{CO})_7$ 2a	7.2	6.6	6.7	10.7	11.5	12.1	10.0	12.2	11.7	8.3	5.7	11.2
$\text{Ir}_2(\text{CO})_7$ 2c	29.9	29.8	29.7	29.5	29.7	24.0	29.5	29.7	29.5	30.4	29.0	28.0
$\text{Ir}_2\text{PH}_3(\text{CO})_7$ 2f	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$\text{Ir}_2\text{PH}_3(\text{CO})_7$ 2d	-2.2	-2.7	-2.5	1.3	1.8	5.7	0.6	2.5	1.6	0.0	1.9	2.7
$\text{Ir}_2\text{PH}_3(\text{CO})_7$ 2e	-0.9	-1.1	-1.1	1.3	2.2	4.2	1.3	2.6	1.9	0.0	3.9	3.0
$\text{Ir}_2\text{PH}_3(\text{CO})_6$ 2i	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$\text{Ir}_2\text{PH}_3(\text{CO})_6$ 2j	1.7	0.9	1.2	7.2	8.5	6.7	6.3	9.2	8.2	7.5	3.0	8.3
$\text{Ir}_2\text{PH}_3(\text{CO})_6$ 2h	4.7	3.9	4.1	8.9	9.8	9.6	8.2	10.7	9.9	6.6	4.3	10.0
$\text{Ir}_2\text{PH}_3(\text{CO})_6$ 2g	9.4	8.9	9.2	15.1	16.3	13.4	14.4	16.8	16.1	19.4	1.6	14.9
$\text{Ir}_2\text{PH}_3(\text{CO})_6$ 2k	29.6	29.7	29.6	30.1	31.0	23.6	30.4	31.9	31.2	32.7	29.8	30.0
$\text{Ir}_2(\text{PH}_3)_2(\text{CO})_6$ 2l	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$\text{Ir}_2(\text{PH}_3)_2(\text{CO})_6$ 2o	3.1	4.0	3.8	0.1	0.6	-4.5	0.9	0.9	1.4	3.6	-0.6	0.0
$\text{Ir}_2(\text{PH}_3)_2(\text{CO})_6$ 2m	2.2	2.7	2.6	0.8	1.7	-1.2	1.6	1.5	1.7	1.6	2.4	1.2
$\text{Ir}_2(\text{PH}_3)_2(\text{CO})_6$ 2n	12.6	12.3	12.3	15.5	17.1	13.0	15.1	17.6	16.5	13.5	9.1	14.9
$\text{Ir}_2(\text{PH}_3)_2(\text{CO})_5$ 2r	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$\text{Ir}_2(\text{PH}_3)_2(\text{CO})_5$ 2t	12.0	13.4	12.9	6.6	10.6	4.1	9.5	12.9	12.5	5.3	14.4	12.8
$\text{Ir}_2(\text{PH}_3)_2(\text{CO})_5$ 2s	11.5	11.8	11.6	12.0	17.0	10.8	13.8	19.3	17.7	6.9	15.4	18.7
$\text{Ir}_2(\text{PH}_3)_2(\text{CO})_5$ 2q	12.4	12.7	12.5	12.2	16.7	11.2	14.1	18.9	17.6	7.4	17.2	18.8
$\text{Ir}_2(\text{PH}_3)_2(\text{CO})_5$ 2p	18.4	19.0	18.8	18.7	23.1	15.7	20.6	25.2	24.1	18.7	13.8	23.7

^a All energies are single-point energies from SVWN5 optimized geometries.

Table 5

Table 5. Ir₂(PH₃)_y(CO)_z LDEs in kcal/mol, predicted by various electronic structure methods.^a

Reaction	Leaving Ligand	BP86	PBE	PW91	B3LYP	CAM- B3LYP	B97-D	B98	ωB97X	ωB97X -D	M06	MP2	CCSD(T)
1	PH ₃	21.2	23.8	24.1	18.2	23.8	23.5	22.5	27.7	28.4	18.7	36.3	28.6
2	PH ₃	12.7	15.6	16.0	7.5	11.9	12.9	11.7	15.4	16.3	10.4	28.6	17.1
3	PH ₃	41.7	44.2	44.6	38.3	43.8	41.1	42.6	47.7	47.7	40.9	61.5	48.1
4	CO <i>bri</i>	32.4	34.9	35.3	27.8	31.6	30.2	31.2	32.7	34.0	32.5	31.3	30.8
5	CO <i>ter</i>	27.7	29.9	30.1	21.6	25.1	26.4	25.1	26.6	27.7	19.8	34.0	25.8
6	CO	21.7	24.5	24.6	12.7	15.0	18.3	16.1	15.8	17.5	13.1	27.8	15.6
7	CO	50.4	53.0	53.1	44.1	48.2	46.1	47.8	50.3	50.6	45.8	61.5	48.6
8	PH ₃	18.9	21.5	21.9	16.2	22.2	21.3	20.4	26.4	26.8	17.3	34.5	27.4
9	PH ₃	12.0	14.9	15.3	6.5	10.7	13.0	10.6	14.3	15.2	9.1	27.9	16.2
10	PH ₃	3.3	6.3	6.8	-1.0	3.8	5.4	3.4	7.5	8.6	4.7	24.2	10.9
11	PH ₃	40.7	43.3	43.6	37.3	42.8	39.8	41.7	46.7	46.7	39.8	60.6	47.5
12	CO <i>bri</i>	34.2	36.9	37.3	30.0	34.0	31.9	33.4	35.5	36.8	35.3	32.4	33.2
13	CO <i>ter</i>	28.2	30.7	31.0	23.5	27.6	27.5	26.9	29.3	30.3	24.0	35.9	28.3
14	CO	26.0	28.0	28.4	22.7	25.9	28.7	25.3	27.8	28.6	22.4	33.5	27.1
15	CO <i>bri</i>	3.2	5.6	6.1	-4.2	-6.2	3.3	-2.3	-7.2	-3.8	3.1	9.0	-5.3
16	CO <i>ter</i>	14.7	17.4	17.8	7.8	10.8	14.1	11.5	12.0	13.9	10.0	25.0	13.4
17	CO	24.7	27.3	27.6	17.8	20.9	24.9	21.3	22.3	23.7	18.4	33.7	22.4

^a All energies are single point energies from SVWN5 optimized geometries. Reaction numbering from Figure 3.

Table 6Table 6. Calculated NBO Charges on Ir,^a Average C-O Stretching Frequencies ($\nu_{\text{C-O}}$),^a Ir-Ir Bond Energies (BDE),^b Bond Distances (r)^a, and LDEs for $\text{Ir}_2(\text{PH}_3)_y(\text{CO})_z$.^b

Property	$\text{Ir}_2(\text{CO})_8 \text{C}_{2v}$	$\text{Ir}_2\text{PH}_3(\text{CO})_7$ (2d)	$\text{Ir}_2(\text{PH}_3)_2(\text{CO})_6$ (2l)
Ir NBO charge	0.22	0.23 ^c , 0.06 ^d	0.07
Ir NBO 5d	8.21	8.20 ^c , 8.33 ^d	8.32
$r(\text{Ir-Ir})$ (Å)	2.774	2.760	2.744
BDE(Ir-Ir) (kcal/mol)	45.7	52.7	57.2
Average $\nu_{\text{C-O}}$ (cm^{-1})	2026	2002	1972
$r(\text{C-O})$ (<i>ter</i> , Å)	1.152	1.154	1.156
$r(\text{C-O})$ (<i>bri</i> , Å)	1.180	1.186	1.193
$r(\text{Ir-C})^c$ (<i>ter</i> , Å)	1.927	1.925 ^c , 1.916 ^d	1.914
$r(\text{Ir-C})^c$ (<i>bri</i> , Å)	2.090	2.106 ^c , 2.061 ^d	2.075
LDE(<i>ter</i> CO) (kcal/mol)		25.8	28.3
LDE(<i>bri</i> CO) (kcal/mol)		30.8	33.2
$r(\text{Ir-P})$ (Å)		2.309	2.300
LDE(PH_3) (kcal/mol)		28.6	27.4

^a All bond distances, frequencies, and NBO charges are calculated at the SVWN5 level.^b All BDEs and LDEs are calculated by CCSD(T) at the SVWN5 optimized geometries.^c Ir not bonded to PH_3 .^d Ir bonded to PH_3 .

Table 7

Table 7. Relative Energies of unsaturated Ir₄(PH₃)_y(CO)_z Isomers in kcal/mol at the ωB97x-D level.^a

Ir ₄ (CO) ₁₁	3a	3b	3c	3d	3e														
Rel. Energies	13.2	3.3	1.1	0.7	0.0														
Ir ₄ PH ₃ (CO) ₁₀	5a	5b	5c	5d	5e	5f	5g	5h	5i	5j	5k	5l	5m	5n	5o	5p	5q	5r	5s
Rel. Energies	24.9	25.9	35.9	29.5	26.3	21.4	22.2	35.0	33.1	27.6	0.0	42.9	29.5	26.0	23.8	36.9	26.5	24.1	20.3
Ir ₄ (PH ₃) ₂ (CO) ₉	7a	7b	7c	7d	7e	7f	7g	7h	7i	7j	7k	7l	7m	7n	7o	7p			
Rel. Energies	19.9	26.5	34.2	25.9	29.5	35.5	33.4	0.0	25.6	24.6	36.6	23.9	22.7	20.3	20.4	23.6			
Ir ₄ (PH ₃) ₃ (CO) ₈	9a	9b	9c	9d	9e	9f	9g	9h	9i	9j	9k	9l	9m	9n	9o	9p	9q	9r	
Rel. Energies	18.0	18.0	25.5	39.7	30.8	34.5	20.9	23.9	31.2	21.4	21.8	38.6	32.9	2.3	23.5	27.3	0.0	21.3	
Ir ₄ (PH ₃) ₄ (CO) ₇	11a	11b	11c	11d	11e	11f	11g	11h	11i	11j									
Rel. Energies	23.1	9.8	36.5	22.6	19.5	34.8	24.6	0.0	20.5	6.1									

^a **3a – 11j** are the isomers shown in Figure 4.

Table 8

Table 8. Average Ir NBO Charges,^a ΔNBO, and Relative Energies (ΔE, kcal/mol)^b for Ir₄(PH₃)_y(CO)_z Isomers, y + z = 12.

Property/Molecule	C _{3v}				T _d	
Ir ₄ (CO) ₁₂						
Ave NBO charge	0.10				0.08	
ΔNBO	-0.02				0.00	
ΔE	2.8				0.0	
Ir ₄ PH ₃ (CO) ₁₁	4a	4b	4c	4d	4e	
Ave NBO charge	0.07	0.07	0.06	0.09	0.06	
ΔNBO	0.01	0.01	0.02	-0.01	0.02	
ΔE	0.3	1.1	10.0	1.5	0.0	
Ir ₄ (PH ₃) ₂ (CO) ₁₀	6a	6b	6c		6d	6e
Ave NBO charge	0.05	0.04	0.05		0.03	0.03
ΔNBO	0.03	0.04	0.03		0.05	0.05
ΔE	0.0	8.2	1.1		0.8	0.6
Ir ₄ (PH ₃) ₃ (CO) ₉	8a	8b	8c		8d	8e
Ave NBO charge	0.02	0.00	0.00		-0.01	-0.04
ΔNBO	0.06	0.08	0.08		0.09	0.12
ΔE	0.1	0.0	6.8		3.4	2.4
Ir ₄ (PH ₃) ₄ (CO) ₈	10a	10b	10c		10d	
Ave NBO charge	-0.02	-0.02	-0.03		-0.04	
ΔNBO	0.10	0.10	0.11		0.12	
ΔE	0.0	0.1	7.4		2.6	

^a All NBO charges are calculated at the SVWN5 level.
^b All relative energies are calculated at the ωB97x-D level at the SVWN5 optimized geometries.

Table 9

Table 9. PH_3 and CO LDEs for $\text{Ir}_x(\text{PH}_3)_y(\text{CO})_z$ clusters in kcal/mol at the $\omega\text{B97x-D}$ level.^a

Molecule	$\text{C}_{3v} \text{ eq}$	$\text{C}_{3v} \text{ ax}$	$\text{C}_{3v} \text{ api}$	$\text{C}_{3v} \text{ bri}$	C_{3v} H-trans	T_d	T_d H-trans
PH_3							
$\text{Ir}_4\text{PH}_3(\text{CO})_{11}$	50.8(4a)	40.2(4b)	37.1(4d)	29.1(4c)		38.0(4e)	
$\text{Ir}_4(\text{PH}_3)_2(\text{CO})_{10}$	49.4(6a)	40.7(6a)	33.8(6b)	30.0(6b)		37.8(6d)	
		39.8(6c)				34.1(6e)	
$\text{Ir}_4(\text{PH}_3)_3(\text{CO})_9$	49.7(8a)	41.5(8a)	32.7(8c)	29.2(8c)		34.9 ^b (8d)	
	51.1(8b)					33.6 ^b (8e)	
$\text{Ir}_4(\text{PH}_3)_4(\text{CO})_8$	48.5(10a)	35.4(10b)	32.0(10a)	28.3(10c)		32.7(10d)	
	45.2(10c)						
CO							
$\text{Ir}_4(\text{CO})_{12}$	52.6	42.7	40.1	40.5		39.4	
$\text{Ir}_4\text{PH}_3(\text{CO})_{11}$	53.5(4a)	47.1(4a) 43.9(4a)	42.5(4a)	43.5(4a)		42.1(4e)	
	51.9(4b)		38.3(4b)	39.1(4b)		38.2(4e)	
$\text{Ir}_4\text{PH}_3(\text{CO})_{11}$	50.9(4c)		41.1(4c) 35.6(4c)		8.0 (4c)		
	53.3(4d)	43.0(4d)	46.0(4d)	42.5(4d) 40.3(4d)			
$\text{Ir}_4(\text{PH}_3)_2(\text{CO})_{10}$	53.5(6a)	48.9(6a)	39.2(6a)	45.9(6a)	11.2(6b)	41.2 ^c (6d)	
	36.8 ^b (6b)		44.6(6b)			38.9(6d)	
	54.9(6c)		42.9(6c)	41.0(6c)		39.2 ^c (6e) 42.4 ^c (6e)	
$\text{Ir}_4(\text{PH}_3)_3(\text{CO})_9$	59.4(8a)	50.5(8a)	37.7(8a)	45.2(8a)	15.2(8c)	43.6(8d)	
		50.9(8b)	40.7(8b)	43.7(8b)		38.7(8e)	17.4(8e)
	36.5 ^b (8c)		45.9(8c)				
$\text{Ir}_4(\text{PH}_3)_4(\text{CO})_8$	60.3(10a)		47.0(10a)		33.6(10a)		
$\text{Ir}_4(\text{PH}_3)_4(\text{CO})_8$	58.6(10b)		46.4(10b)	43.3(10b)			27.4(10d)
	36.9 ^b (10c)		41.0(10c)		16.4(10c)		

^a Letters in parentheses correspond to structures in Figure 4. ^b A bridging PH_3 changes into a equatorial one after the ligand dissociation.^c Isomers turn into C_{3v} structure after ligand dissociation