



# Structures, relative energies, and ligand dissociation energies of iridium carbonyl phosphine clusters



Shengjie Zhang<sup>a</sup>, Alexander Katz<sup>b</sup>, Bruce C. Gates<sup>c</sup>, David A. Dixon<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, The University of Alabama, Tuscaloosa, AL 35487, United States

<sup>b</sup> Department of Chemical and Biomolecular Engineering, University of California at Berkeley, Berkeley, CA 94720, United States

<sup>c</sup> Department of Chemical Engineering and Materials Science, University of California at Davis, Davis, CA 95616, United States

## ARTICLE INFO

### Article history:

Received 27 May 2015

Received in revised form 20 June 2015

Accepted 21 June 2015

Available online 4 July 2015

### Keywords:

Iridium carbonyl phosphine complexes

Electronic structure calculations

Ligand dissociation energies

Coupled cluster (CCSD(T)) theory

Density functional theory

Catalysis

## 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  $\sim 30$  to  $\sim 60$  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  $\sigma$ -electron donors, and there is a trend of an increase in carbonyl ligand dissociation energies as more phosphines are substituted in the small clusters.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

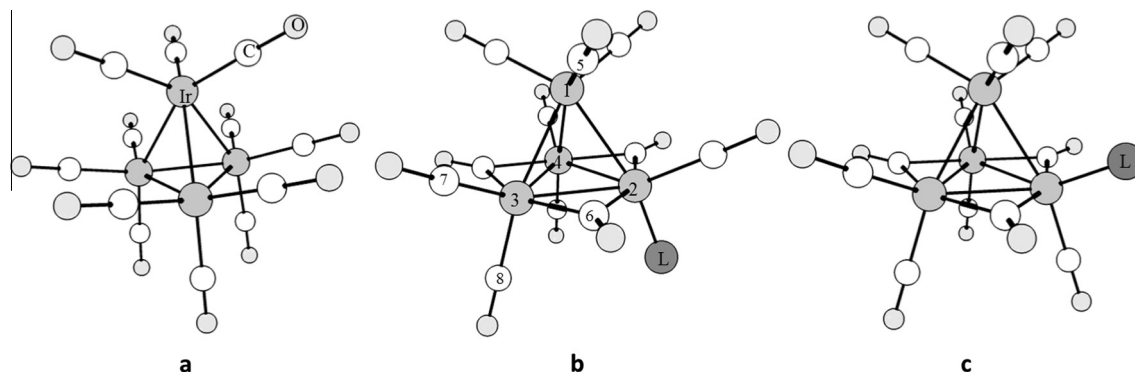
Iridium clusters catalyze a wide range of reactions, including oxidation, hydrogenation, C–H bond activation, cycloaddition, cycloisomerization [1,2], and ring-opening [3]. Iridium complexes play important roles in oxidation (e.g., of alcohols [4–6], phenols [7–9], and amines [10,11]), hydrogenation [12,13], C–H activation [14–16], cycloaddition (e.g., [2 + 2 + 2] [17–19], [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 [26–28] 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  $\sim 200$  K [26,27]. The tetra-iridium cluster framework is one of the simplest structures presenting neighboring 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 [29–32]. 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 (Fig. 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 [35–37]. 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  $\text{Ir}$  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** (Fig. 1) if the phosphine

\* Corresponding author.

E-mail address: [dadixon@ua.edu](mailto:dadixon@ua.edu) (D.A. Dixon).



**Fig. 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**.

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  $\sigma$ -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 neighboring 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) [44–46] and coupled cluster theory (CCSD(T)) [47–50] 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.

## 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- $\zeta$  (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:  $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}4f^{14}$ . The active electrons in the self-consistent field calculations for the Ir atom are the  $5s^25p^66s^25d^7$ . In the valence CCSD(T) and MP2 calculations, the  $5s^25p^6$  are in the core together with the 1s on C and O and the  $1s^22s^22p^6$  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 [65–67], PBE [68,69],  $\omega\text{B97X}$  [70], and  $\omega\text{B97X-D}$  [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  $\omega\text{B97X}$  are hybrid functionals with long-range corrections; and  $\omega\text{B97X-D}$  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 [72–74]. The open shell MP2 calculations were done at the RMP2 level [75].

Ligand dissociation energies (LDEs) were calculated from Eq. (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  $\Delta H(0\text{ K})$ .

Download English Version:

<https://daneshyari.com/en/article/5393156>

Download Persian Version:

<https://daneshyari.com/article/5393156>

[Daneshyari.com](https://daneshyari.com)