

# Binuclear cyclopentadienyliridium hydride chemistry: Terminal versus bridging hydride and cyclopentadienyl ligands



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## ABSTRACT

The cyclopentadienyliridium hydrides  $\text{Cp}_2\text{Ir}_2\text{H}_n$  ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ;  $n = 6, 4, 2, 0$ ), and  $\text{CpIrH}_n$  ( $n = 4, 2$ ) related to the experimentally known pentamethyl cyclopentadienyliridium hydrides  $\text{Cp}^*\text{Ir}_2\text{H}_n$  ( $\text{Cp}^* = \eta^5\text{-Me}_5\text{C}_5$ ;  $n = 6, 2$ ) and  $\text{Cp}^*\text{IrH}_4$  have been investigated by density functional theory. The lowest energy  $\text{Cp}_2\text{Ir}_2\text{H}_n$  ( $n = 6, 4, 2$ ) structures are predicted to have terminal Cp rings with the central  $\text{Ir}_2$  unit bridged by two hydrogen atoms. For the hexahydride  $\text{Cp}_2\text{Ir}_2\text{H}_6$ , such doubly bridged  $\text{Cp}_2\text{Ir}_2(\mu\text{-H})_2\text{H}_4$  structures are bent, leading to *trans* and *cis* structures of similar energies with an unbridged  $\text{Cp}_2\text{Ir}_2\text{H}_6$  isomer lying only  $\sim 4$  kcal/mol above the bridged structures. This suggests fluxional behavior consistent with experimental data on the temperature dependence of the proton NMR spectrum of the closely related  $\text{Cp}^*\text{Ir}_2\text{H}_6$ . The tetrahydride  $\text{Cp}_2\text{Ir}_2\text{H}_4$  is predicted to undergo slightly exothermic disproportionation into  $\text{Cp}_2\text{Ir}_2\text{H}_6 + \text{Cp}_2\text{Ir}_2\text{H}_2$  and thus not be a viable species. This is consistent with the failure to find any  $\text{Cp}^*\text{Ir}_2\text{H}_4$  in the  $\text{Cp}^*\text{Ir}_2\text{H}_n$  systems. The doubly bridged dihydride  $\text{Cp}_2\text{Ir}_2(\mu\text{-H})_2$  is a particularly favorable species since it lies more than 18 kcal/mol in energy below any other isomer. Higher energy  $\text{Cp}_2\text{Ir}_2\text{H}_n$  ( $n = 4, 2$ ) structures have one or two bridging Cp rings and exclusively terminal hydrogen atoms. Related structures are the lowest energy structures for the hydride-free  $\text{Cp}_2\text{Ir}_2$ . A higher energy  $\text{Cp}_2\text{Ir}_2$  structure consists of two CpIr units linked solely by an Ir–Ir bond. Analysis of the frontier molecular orbitals indicates this Ir–Ir bond to be the quadruple bond required to give each iridium atom the favored 18-electron configuration. However, this quadruple bond is a  $2\sigma + 2\pi$  bond with no  $\delta$  components and thus differs from the  $\sigma + 2\pi + \delta$  quadruple bond found in the long-known  $\text{Re}_2\text{Cl}_8^{2-}$ .

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## 1. Introduction

A characteristic of the third row transition metals, particularly rhenium, osmium, and iridium, is their ability to form relatively stable metal hydride derivatives. Rhenium even forms the unusual binary hydride anion  $\text{ReH}_2^-$  upon reduction of perrhenate with electropositive metals in protic solvents [1,2]. Other hydrides of the third row transition metals are ternary species stabilized by additional ligands such as CO, cyclopentadienyl (Cp), and phosphines.

The formulas of the stable ternary hydrides of the third row transition metals containing pentamethylcyclopentadienyl ( $\text{Cp}^*$ )

ligands follow a systematic pattern. The stoichiometries of the stable mononuclear derivatives  $\text{Cp}^*\text{MH}_n$  ( $\text{M} = \text{Re}$  [3,4],  $n = 6$ ;  $\text{M} = \text{Os}$  [5],  $n = 5$ ;  $\text{M} = \text{Ir}$  [6],  $n = 4$ ) follow the 18-electron rule [7–11]. The stoichiometries of the stable binuclear derivatives  $\text{Cp}^*\text{M}_2\text{H}_n$  ( $\text{M} = \text{Re}$  [3,4],  $n = 6$ ;  $\text{M} = \text{Os}$  [5],  $n = 4$ ;  $\text{M} = \text{Ir}$  [12],  $n = 2$ ) also follow a systematic pattern. However, the experimental structures of these three species  $\text{Cp}^*\text{M}_2\text{H}_n$  are not analogous. The rhenium and iridium derivatives are  $\text{Cp}^*\text{M}_2(\mu\text{-H})_2\text{H}_{n-2}$  structures with two bridging hydrogen atoms and  $n-2$  terminal hydrogen atoms (Fig. 1). However, in the osmium derivative  $\text{Cp}^*\text{Os}_2(\mu\text{-H})_4$  all four hydrogen atoms bridge the Os–Os bond. In fact,  $\text{Cp}^*\text{Os}_2(\mu\text{-H})_4$ , as well as its iron and ruthenium congeners, are rare examples of stable binuclear complexes with four ligands bridging a metal–metal bond. In terms of electron counting in these binuclear  $\text{Cp}^*\text{M}_2\text{H}_n$  derivatives, each bridging hydrogen contributes one electron to one of the metal atoms in addition to the electrons provided by the metal–metal multiple bonding. In addition to  $\text{Cp}^*\text{Ir}_2(\mu\text{-H})_2$ , the hydrogen-richer

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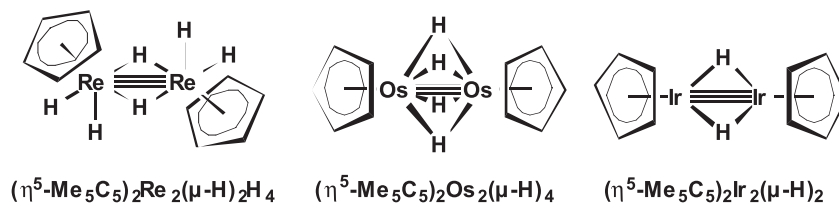


Fig. 1. Structures of the stable  $\text{Cp}_2\text{M}_2\text{H}_n$  experimentally known species. The methyl groups of the  $\text{Cp}^*$  ligand are omitted for clarity.

species  $\text{Cp}_2^*\text{Ir}_2\text{H}_6$  has been synthesized but not characterized structurally [6,13].

This paper reports a systematic density functional theory study of the cyclopentadienyliridium hydrides  $\text{CpIrH}_n$  ( $n = 4, 2$ ) and  $\text{Cp}_2\text{Ir}_2\text{H}_n$  ( $n = 6, 4, 2$ ) as well as the hydride-free  $\text{Cp}_2\text{Ir}_2$ . The mononuclear  $\text{CpIrH}_4$ , but not the other species, was studied theoretically some time ago by Lin and Hall [14]. These cyclopentadienyl iridium hydride systems have been used as bases for the reversible deprotonation of acidic organic compounds and catalysts for C–C bond cleavage of aromatic 1,2-diols [15]. In addition,  $\text{Cp}_2^*\text{Ir}_2(\mu\text{-H})_2$  has been used for the activation of C–H bonds in phosphorus derivatives and sulfoxides [16]. The hexahydride  $\text{Cp}_2^*\text{Ir}_2\text{H}_6$  has been shown to hydrodesulfurize thiophene to give butadiene and butane [13].

## 2. Theoretical methods

All calculations were performed using the Gaussian 09 program package [17]. Two density functional theory (DFT) methods were used in this study. One is the BP86 method, which is a pure DFT method that combines Becke's 1988 exchange functional with Perdew's 1986 correlation functional [18,19]. The other is the MPW1PW91 method [20], which is a second generation functional [21] combining the modified Perdew–Wang exchange functional with Perdew–Wang's 1991 correlation functional [22]. The MPW1PW91 method has been found to be more suitable for geometry optimization of the second and third row transition metal systems [23,24], while the BP86 method usually provides better vibrational frequencies.

The large numbers of electrons in the third row transition metals increases exponentially the required computational resources. In order to reduce the cost, effective core potential (ECP) relativistic basis sets were employed. The SDD (Stuttgart–Dresden ECP plus DZ) [25] ECP basis set was used for the iridium atoms whereas double- $\zeta$  plus polarization (DZP) basis sets were used for the carbon and hydrogen atoms. Thus, for carbon, one set of pure spherical harmonic d functions with orbital exponent  $\alpha_d(\text{C}) = 0.75$ , was added to the Huzinaga–Dunning standard contracted DZ sets, designated as (9s5p1d/4s2p1d) [26,27]. Similarly, for hydrogen, a set of p polarization functions ( $\alpha_p(\text{H}) = 0.75$ ) was added to the Huzinaga–Dunning DZ sets [28].

The geometries of all structures were fully optimized using the two selected DFT methods. The harmonic vibrational frequencies were obtained at the same levels by evaluating analytically the second derivatives of the energy with respect to the nuclear coordinates. The fine grid (75, 302) was the default for numerical evaluation of the integrals [29]. The finer grid (120, 974) was used for more precise resolution of the small imaginary vibrational frequencies. The tight ( $10^{-8}$  hartree) designation was the default for the self-consistent field (SCF) convergence.

Unsubstituted Cp derivatives were used for this study as models for the experimentally richer  $\text{Cp}^*$  chemistry in order to make most effective use of the computational resources. However, in order to observe effects of the methyl substituents the experimentally known [6,13]  $\text{Cp}_2^*\text{Ir}_2\text{H}_6$  system was also investigated. The optimized

$\text{CpIrH}_n$  ( $n = 2, 4$ ) and  $\text{Cp}_2\text{Ir}_2\text{H}_n$  ( $n = 0, 2, 4, 6$ ) structures are depicted in Figs. 2–7. Structures are designated according to the number of hydrogen atoms and relative energy ordering. For example, the singlet energetically lowest-lying  $\text{Cp}_2\text{Ir}_2\text{H}_2$  structure is designated as **2H-1**. The triplet spin state structures are not included in this paper because of their significantly higher energies relative to the singlet spin state structures. The bond distances in the Figures were determined by the MPW1PW91 (upper) and BP86 (lower) methods, respectively.

## 3. Results

### 3.1. $\text{CpIrH}_n$ ( $n = 2, 4$ ) structures

The low energy  $\text{CpIrH}_4$  structure **H4** exhibits  $C_s$  symmetry with one pentahapto  $\eta^5\text{-Cp}$  ring and four terminal hydrogen atoms, just like a four-legged piano-stool (Fig. 2 and Table 1). Structure **H4** corresponds to the experimental structure for the corresponding pentamethylcyclopentadienyl derivative  $\text{Cp}^*\text{IrH}_4$  [6]. The predicted Ir–H distances in structure **H4** are 1.575 Å (MPW1PW91) or 1.590 Å (BP86), 1.569 Å (MPW1PW91) or 1.582 Å (BP86) and 1.572 Å (MPW1PW91) or 1.586 Å (BP86). Unfortunately, the reported X-ray crystal structure on  $\text{Cp}^*\text{IrH}_4$  could not locate the hydrogen atoms so no experimental information on Ir–H distances in this type of structure is available.

The  $\text{CpIrH}_2$  structure **H2** is predicted to be a  $C_s$  structure with one pentahapto  $\eta^5\text{-Cp}$  ring and two hydrogen atoms (Fig. 2 and Table 1). The Ir–H distances are 1.591 Å (MPW1PW91) or 1.604 Å (BP86) and the H–Ir–H angle is 78.8° (MPW1PW91) or 79.2° (BP86).

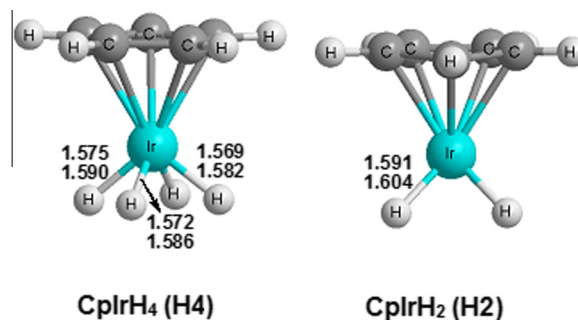


Fig. 2. Optimized geometries (bond lengths in Å) at the MPW1PW91/DZP (the upper) and BP86/DZP (the lower) levels of theory for the  $\text{CpIrH}_n$  structures ( $n = 4, 2$ ).

Table 1

Total energies ( $E$ , in hartree) and Ir–H distances (Å) for the lowest energy  $\text{CpIrH}_n$  ( $n = 2, 4$ ) structures. Neither structure has any imaginary vibrational frequencies.

		<b>H4</b> ( $C_s$ )	<b>H2</b> ( $C_s$ )
MPW1PW91	$E$	–300.225843	–298.993966
	Ir–H	1.575, 1.572, 1.569	1.591
BP86	$E$	–300.371150	–299.137921
	Ir–H	1.590, 1.586, 1.582	1.604

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