

# C–H and C–C bonds activation by iridium clusters: Synthesis and solid state structure of $[\text{Ir}_6(\text{CO})_{14}(\mu_3\text{-}\eta^1:\eta^2:\eta^1\text{-C}_7\text{H}_8)]$

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## Abstract

The reaction between norbornene ( $\text{C}_7\text{H}_{10}$ ) and  $\text{Ir}_6(\text{CO})_{16}$  in refluxing toluene yields the substituted cluster  $[\text{Ir}_6(\text{CO})_{14}(\text{C}_7\text{H}_8)]$ . In the solid state, the six iridium atoms define an octahedral metal cage, and one face is capped by the  $\text{C}_7\text{H}_8$  ligand, coordinated through a 1,2-vinylidene unit. The loss of two hydrogen atoms from the olefin is, presumably, the result of a double oxidative addition of its C–H bonds, followed by elimination of a hydrogen molecule from the cluster. The bonding parameters of the organic fragment, as well as the architecture of the carbonyl ligands, closely match those found in the alkyne-substituted  $[\text{Ir}_6(\text{CO})_{14}(\text{PhCCPh})]$  complex.

The cluster  $[\text{Ir}_6(\text{CO})_{14}(\text{C}_7\text{H}_8)]$  was characterized through  $^1\text{H}$ -,  $^{13}\text{C}$ - and bidimensional COSY NMR.  
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**Keywords:** Carbonyl cluster compounds; Iridium;  $^{13}\text{C}$  NMR spectroscopy; Alkyne ligands

Carbonyl clusters, substituted by organic fragments, have raised wide interest in the past since, in the context of the well-known cluster-surface analogy [1], they were believed to be useful models of the interactions between surface metal atoms and reactive fragments in heterogeneous catalysis. For many years, several mechanisms of surface reactions have been inferred from the reactivity of molecular models [2]. The obvious consideration that ligand-stabilized clusters are much less reactive than clean metallic surfaces led to a critical revision of the theory; on the other hand, the much higher stability

allows detailed structural and spectroscopic characterizations, that are much more difficult on transient intermediates in real catalytic conditions. For this reason, the assignments of spectroscopic data to different chemisorbed fragments are frequently based on molecular models [3]. More recently different application fields have been explored for organometallic clusters, for example for the preparation of functional materials.

Stable metallic cages and functionalized organic ligands can be combined in the same molecule, opening the way to metal–organic frameworks [4] or to metal-based molecular devices [5]. Metal clusters can find their own application in the construction of nets, because they offer building blocks of imposed geometry, and a large variety of ligand–metal–ligand angles, other than those available from mononuclear complexes [6].

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Multiple interactions between metal and carbon atom are particularly suited for this purpose, since they reinforce both the metal–metal and metal–ligand bonds, preventing ligand loss or cluster fragmentation [7].

The overall stability allows further reactions of the organic fragments, which can be derivatized or used for anchoring on a support [8]. Additionally, resistance toward fragmentation and multiple coordinating ability, make these species good candidates for homogeneous cluster catalysis [9].

Only a few large iridium clusters, substituted by hydrocarbons, have been isolated so far: they include the cycloheptatriene derivatives  $[\text{Ir}_6(\text{CO})_{13}(\text{C}_7\text{H}_8)]$   $[\text{Ir}_6(\text{CO})_{12}(\text{C}_7\text{H}_7)]^-$  and  $[\text{Ir}_6(\text{CO})_{12}(\text{C}_7\text{H}_8)]^{2-}$  [10], the alkyne-substituted  $[\text{Ir}_6(\text{CO})_{14}(\mu_3\text{-}\eta^2\text{-PhCCPh})]$ ,  $[\text{Ir}_6(\text{CO})_{12}(\mu_3\text{-}\eta^2\text{-PhCCPh})_2]$  [11] and the polysubstituted  $[\text{Ir}_7(\text{CO})_{12}(\text{C}_8\text{H}_{12})(\text{C}_8\text{H}_{11})(\text{C}_8\text{H}_{10})]$ , showing stages of cyclooctadiene dehydrogenation [12]. Iridium substrates are of special value in this kind of chemistry, because they are able to promote peculiar reactions, among which we can list: insertion of C–C triple bond into a Ir–H bond [13], C–C coupling [14], removal/addition of hydrogen atoms [10].

When coordinated by cluster complexes, olefins easily undergo oxidative addition reactions, producing  $\sigma$ , $\eta$ -alkenyl ligands [15]. Seminal studies on this subject have been performed on tri- and tetra-osmium clusters by Deeming et al. [16], Shapley et al. [17], Johnson, Lewis et al. [18]. More recent examples of this behavior are the oxidative additions of alkenes on  $\text{Re}_2(\text{CO})_{10}$ , under UV irradiation [19], and on  $\text{Re}_2(\text{CO})_8(\text{THF})_2$  [20]. As a result, cluster compounds containing  $\eta^2$ -bound olefins are rather uncommon [21], and are usually stable at low temperature and in the presence of excess olefin [22].

We report here the synthesis of  $[\text{Ir}_6(\text{CO})_{14}(\text{C}_7\text{H}_8)]$ , obtained by the direct reaction between  $\text{Ir}_6(\text{CO})_{16}$  and norbornene ( $\text{C}_7\text{H}_{10}$ ). The multicoordination of the olefin is accompanied by hydrogen loss, which is a further example of multiple activation of C–H and C–C bonds. Full details of NMR characterization of the cluster are reported.

## 1. Results

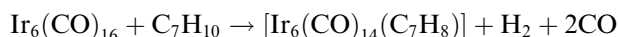
### 1.1. The synthesis of $[\text{Ir}_6(\text{CO})_{14}(\text{C}_7\text{H}_8)]$

The neutral derivative  $[\text{Ir}_6(\text{CO})_{14}(\text{C}_7\text{H}_8)]$  was obtained by carbonyl substitution, suspending  $\text{Ir}_6(\text{CO})_{16}$  [23] and a large excess of  $\text{C}_7\text{H}_{10}$  in toluene and heating the mixture to reflux for about 8 h. The unsubstituted reactant is totally insoluble in toluene, the product is moderately soluble. Therefore, the formation of the new product is confirmed by the darkening of the solution. The reaction time decreases if the starting material is freshly prepared, in agreement with aging of solid

$\text{Ir}_6(\text{CO})_{16}$ . The crude product can be crystallized from THF/2-propanol.

Having isolated and characterized  $[\text{Ir}_6(\text{CO})_{14}(\text{C}_7\text{H}_8)]$ , and having ruled out, by  $^1\text{H}$  NMR spectroscopy, the presence of hydride ligands, some questions were born in mind, regarding the mechanism of formation. As a matter of fact, two hydrogen atoms were abstracted from the ligand, but did not remain on the cluster. Therefore, we presume that the coordination of the organic unit proceeds through a double oxidative addition of the vinylic C–H bonds. Analogously,  $\text{Ru}_3(\text{CO})_{12}$  and  $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$  react with norbornene, yielding the dihydride clusters  $\text{Ru}_3(\text{CO})_9(\text{H})_2(\text{C}_7\text{H}_8)$  [24] and  $\text{Os}_3(\text{CO})_9(\text{H})_2(\text{C}_7\text{H}_8)$  [25]. The corresponding  $[\text{Ir}_6(\text{CO})_{13}(\text{H})_2(\text{C}_7\text{H}_8)]$  is presumably unstable, and undergoes reductive elimination of hydrogen, scavenging CO from the solution. However, owing to the heavy conditions employed, none of the intermediate species could be observed; on the contrary, the formation of  $\text{Os}_3(\text{CO})_9(\text{H})_2(\text{C}_7\text{H}_8)$ , performed at a lower temperature proceeds via several steps, with isolable  $\sigma$ -alkyl, hydride intermediates [25].

The overall stoichiometry, therefore, can be represented by the following equation:



The formula of the compound is in full agreement with the expected number of Cluster Valence Electrons (86 C.V.Es) [26], considering the  $\text{C}_7\text{H}_8$  moiety as a four electrons donor.

### 1.2. The solid state structure

The solid state structure of the cluster  $[\text{Ir}_6(\text{CO})_{13}(\mu\text{-CO})(\mu_3\text{-}\eta^2\text{-C}_7\text{H}_8)]$  is shown in Fig. 1; relevant structural parameters are listed in Table 1. The six metal atoms define an octahedral cage, one face of it being bridged by the organic moiety. The cluster lays on a crystallographic plane of symmetry; therefore, crystallographic and molecular symmetry ( $C_s$ ) are coincident. Five metal vertices are bonded to two terminal carbonyl ligands, the remaining Ir4 site carries three terminal COs: a disposition matching exactly that found in the alkyne-substituted  $[\text{Ir}_6(\text{CO})_{14}(\text{PhCCPh})]$  [11]. As in that case, the bonding between the coordinated carbon atoms (C11) and iridium can be described by a combination of two  $\sigma(\text{Ir}2\text{--C}11)$  and one  $\pi(\text{Ir}1\text{--C}11)$  bonds. The coincidence of the bonding modes of the two ligands, derived by initially different  $\pi$ -electron systems, is not unexpected, considering that, after removal of the two hydrogen from  $\text{C}_7\text{H}_{10}$ , two orbitals for each C atoms are available for bonding to the metals. Table 2 compares the structural parameters in the two clusters.

The Ir–Ir distances are scattered in the 2.697(1)–2.808(1) Å range, which is typical for octahedral iridium clusters. The edges of the face carrying the  $\text{C}_7\text{H}_8$  ligand

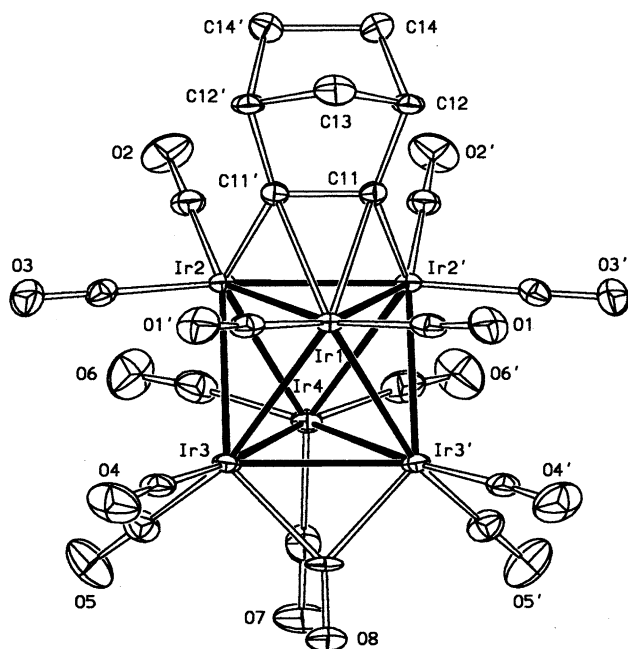


Fig. 1. The solid state structure of  $[\text{Ir}_6(\text{CO})_{14}(\text{C}_7\text{H}_8)]$ . Ellipsoid are drawn at the 30% probability level. The carbon atoms of the carbonyls are labeled as the oxygen to which they are attached.

are shorter than any other in the cluster, a feature in common with  $[\text{Ir}_6(\text{CO})_{14}(\text{PhCCPh})]$ . Also the Ir–C distances compare well in the two clusters, with the  $\sigma$  bonds (Ir2–C11, 2.01(1) Å) being shorter than the  $\pi$  bond (Ir1–C11, 2.18(1) Å). The most relevant differences can be observed around the C11 carbon atom: the C11–C11' distance is 1.44(1) Å, being intermediate between that of a single and a double C–C bond. Even the C12–C11–C11' angle of 107.1(6)° is an indication of a  $\text{sp}^3$  hybridization of carbon, probably as a consequence of the strain of the ring.

When adsorbed on Pt(111) surfaces, norbornene is bound to platinum through the C=C double bond and an agostic interaction with a C–H bond [27]; the latter is suggested by spectroscopic and structural evidences also in  $\text{Ru}_3(\text{CO})_9(\text{H})_2(\text{C}_7\text{H}_8)$  [24] and  $\text{Os}_3(\text{CO})_9(\text{H})_2(\text{C}_7\text{H}_8)$  [25]. In the present compound any relevant interaction between metal and hydrogen can be excluded considering that the (calculated) Ir–H distances are longer than 3.1 Å.

### 1.3. NMR spectroscopy

The  $^1\text{H}$  NMR spectrum of  $[\text{Ir}_6(\text{CO})_{14}(\text{C}_7\text{H}_8)]$  was recorded in  $\text{THF-}d^8$ ; no signals were detected in the hydride zone, ruling out the presence of such ligands. Four signals were clearly detected at  $\delta = 3.70(\text{s}, 2\text{H})$ , 2.13(d, 3H), 1.15(d, 1H) and 1.04(dd, 2H) ppm, one less than those expected for five non-equivalent sites. To achieve the full assignment  $^{13}\text{C}$  and correlated NMR analyses were performed. The following discussion

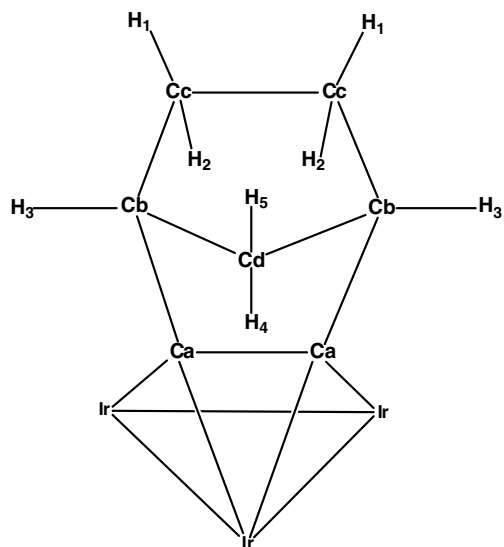
Table 1  
Selected interatomic distances (Å) and angles (°) for  $[\text{Ir}_6(\text{CO})_{14}(\text{C}_7\text{H}_8)]$ , with estimated standard deviations (e.s.d.s) in parentheses

Ir1–Ir2	2.697(1)
Ir1–Ir3	2.809(1)
Ir2–Ir2'	2.739(1)
Ir2–Ir3	2.778(1)
Ir2–Ir4	2.808(1)
Ir3–Ir4	2.767(1)
Ir3–Ir3'	2.774(1)
Ir1–C1	1.904(7)
Ir2–C2	1.823(7)
Ir2–C3	1.892(7)
Ir3–C4	1.888(7)
Ir3–C5	1.887(7)
Ir3–C8	2.065(8)
Ir4–C6	1.918(8)
Ir4–C7	1.869(12)
Ir1–C11	2.184(7)
Ir2–C11	2.010(7)
C11–C11'	1.44(1)
C11–C12	1.53(1)
C12–C13	1.58(1)
C12–C14	1.57(1)
C14–C14'	1.63(1)
C1–O1	1.15(1)
C2–O2	1.14(1)
C3–O3	1.17(1)
C4–O4	1.14(1)
C5–O5	1.13(1)
C6–O6	1.15(1)
C7–O7	1.14(1)
C8–O8	1.16(1)
Ir1–C11–Ir2	89.9(3)°
Ir1–C11–C12	130.7(4)
Ir2–C11–C11'	107.8(5)
Ir2–C11–C12	139.3(5)
C11'–C11–C12	107.1(6)
Ir3–C8–O8	137.8(2)

Table 2  
Comparison between average bond lengths (in Å) and angles in  $[\text{Ir}_6(\text{CO})_{14}(\text{C}_7\text{H}_8)]$  and in  $[\text{Ir}_6(\text{CO})_{14}(\text{PhCCPh})]$  [11]

	$[\text{Ir}_6(\text{CO})_{14}(\text{C}_7\text{H}_8)]$	$[\text{Ir}_6(\text{CO})_{14}(\text{PhCCPh})]$ [11]
Ir–Ir	2.770	2.766
Ir–CO (term)	1.89	1.87
Ir–CO (bridge)	2.07	2.06
C–O (term)	1.15	1.16
Ir–C ( $\sigma$ bond)	2.01	2.07
Ir–C ( $\pi$ bond)	2.18	2.21
C=C	107.1(6)°	126°

refers to the numbering Scheme 1. The  $^{13}\text{C}$  spectrum shows four signals, at  $\delta = 134, 56, 49$  and 27 ppm. The signal at 49 ppm was assigned to  $\text{C}_b$  (the CH groups) from a INEPT experiment, the remaining absorptions were assigned through a bidimensional heterocorrelated spectrum. Both the signals at low frequencies show cross peaks with two H signals, and are therefore due to the  $\text{CH}_2$  units; the less intense peak at 56 ppm was



Scheme 1. The numbering scheme of the hydrogen and carbon atoms of the  $C_7H_8$  ligand.

attributed to the unique  $C_d$  methylene carbon and the other at 27 ppm to the ethylene  $C_c$  atoms. The peak at 134 ppm is therefore unambiguously assigned to the quaternary  $C_a$  carbon atoms.

In the absence of a  $^{13}C$  CO labelled compound, the carbonyl portion of the  $^{13}C$  spectrum was not examined.

Having assigned the  $^{13}C$  peaks, the attributions in the  $^1H$  spectrum are straightforward:  $H_1$  and  $H_5$  (coincident at 2.13 ppm), resonate at higher frequencies than  $H_2$  (1.04 ppm) and  $H_4$  (1.15 ppm) that are closer to the Ir metals and are therefore more shielded. The similarity of their chemical shifts is a further convincing evidence against any agostic Ir–H interaction. The remaining peak, at 3.7 ppm is due to  $H_3$ . The geminal [ $^2J(H_4-H_5) = 9.4$  Hz,  $^2J(H_1-H_2) = 8.1$  Hz] and vicinal [ $^3J(H_1-H_3) = 2.4$  Hz] coupling constants were measured.

## 2. Experimental

All the solvents were purified and dried by conventional methods and stored under nitrogen. All the reactions were carried out under oxygen-free nitrogen atmosphere using the Schlenk-tube technique [28].  $[Ir_6(CO)_{16}]$  [23] was prepared by literature methods. Infrared spectra in solution were recorded on a Nicolet Avatar 1600 FT-IR spectrophotometer, using calcium fluoride cells previously purged with  $N_2$ . Elemental analyses were carried out by the staff of Laboratorio di Analisi of the Dipartimento di Chimica Inorganica, Metallorganica e Analitica. NMR spectra were recorded on a Bruker 300 spectrometer.

### 2.1. Synthesis of $[Ir_6(CO)_{14}(C_7H_8)]$

$[Ir_6(CO)_{16}]$  (0.30 g; 0.2 mmol) and norbornene (0.3 ml, 3 mmol) were suspended in 15 ml of toluene. The mixture was refluxed for 7 h, and the resulting dark brown solution was allowed to cool overnight to room temperature. The solid residue was eliminated by filtration, the solvent was evaporated in vacuum and the residue was dissolved in the minimum amount of THF. Crystals were grown by layering of 2-propanol. Low yields (10%) are mainly due to incomplete conversion of aged  $[Ir_6(CO)_{16}]$  and residual solubility in the crystallization mixture.

Anal. Calc. for  $C_{21}H_8Ir_6O_{14}$ : C, 15.4; H, 0.4. Found: C, 15.7; H, 0.9%.

$\nu(CO)$  in THF solution: 2093m, 2047vs, 2039s, 2000sh, 1835m  $cm^{-1}$ .

### 2.2. X-ray data collections and structure determinations

Crystal data are summarized in Table 3; other experimental details are listed in the supporting information.

Table 3  
Crystallographic data

Compound	$[Ir_6(CO)_{14}(C_7H_8)]$
Formula	$C_{21}H_8Ir_6O_{14}$
M	1637.49
Colour	Black
Crystal system	Orthorhombic
Space group	$Pnma$
$a$ (Å)	15.446(2)
$b$ (Å)	15.059(1)
$c$ (Å)	11.710(1)
$\alpha$ (°)	90
$\beta$ (°)	90
$\gamma$ (°)	90
$V$ (Å <sup>3</sup> )	2723.8(4)
Z	4
$T$ (K)	223
Crystal dimensions (mm)	$0.15 \times 0.21 \times 0.39$
$\mu$ (Mo K $\alpha$ ) ( $cm^{-1}$ )	291.6
Maximum and minimum transmission factors	1.000–0.327
Scan mode	$\omega$
Frame width (°)	0.30
Time per frame (s)	25
Number of frames	1206
Detector–sample distance (cm)	4.00
$\theta$ -Range (°)	3–28
Reciprocal space explored	hemisphere
Number of reflections (total, independent)	14139, 4253
$R_{int}$	0.046
Final $R_2$ and $R_{2w}$ indices $^a(F^2, \text{all reflections})$	0.054, 0.056
(Conventional $R_1$ index $I > 2\sigma(I)$ )	0.029
Reflections with $I > 2\sigma(I)$	3137
Number of variables	194
Goodness-of-fit <sup>b</sup>	1.04

<sup>a</sup>  $R_2 = [\sum(|F_o^2 - kF_c^2|)/\sum F_o^2]$ ,  $R_{2w} = [\sum w(F_o^2 - kF_c^2)^2/\sum w(F_o^2)^2]^{1/2}$ .

<sup>b</sup>  $[\sum w(F_o^2 - kF_c^2)^2/(N_o - N_v)]^{1/2}$ , where  $w = 4F_o^2/\sigma(F_o^2)^2$ ,  $\sigma(F_o^2) = [\sigma^2(F_o^2) + (0.02F_o^2)^2]^{1/2}$ ,  $N_o$  is the number of observations and  $N_v$  the number of variables.

The diffraction experiment was carried out on a Bruker SMART CCD area-detector diffractometer at 223 K, using Mo K $\alpha$  radiation ( $\lambda = 0.71073$ ). No crystal decay was observed, so that no time-decay correction was needed. The collected frames were processed with the software SAINT [29], and an empirical absorption correction was applied (SADABS) [30] to the collected reflections. The calculations were performed using the Personal Structure Determination Package [31] and the physical constants tabulated therein [32]. The structure was solved by direct methods (SHELXS) [33] and refined by full-matrix least-squares using all reflections and minimizing the function  $\sum w(F_o^2 - kF_c^2)^2$  (refinement on  $F^2$ ). All the non-hydrogen atoms were refined with anisotropic thermal factors. The hydrogen atoms were placed in their ideal positions (C–H = 0.97 Å), with the thermal parameter  $B$  1.10 times that of the carbon atom to which they are attached, and not refined. In the final Fourier map, the maximum residual was 2.78(44) e Å<sup>-3</sup> at 0.79 Å from Ir(2).

### 3. Supporting information available

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 271175. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK, fax (int code): +44 1223 336 033 or e-mail deposit@ccdc.cam.ac.uk or www:<http://www.ccdc.cam.ac.uk>.

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