

Note

Synthesis and crystal structure of $\text{Ir}(\text{C}_2\text{H}_4)_2(\text{C}_5\text{H}_7\text{O}_2)$

V.A. Bhirud^a, A. Uzun^a, P.W. Kletnieks^b, R. Craciun^c, J.F. Haw^b, D.A. Dixon^c,
M.M. Olmstead^d, B.C. Gates^{a,*}

^a Department of Chemical Engineering and Materials Science, University of California, Davis, CA 95616, USA

^b Department of Chemistry, University of Southern California, Los Angeles, CA 90086, USA

^c Chemistry Department, University of Alabama, Shelby Hall, P.O. Box 870336, Tuscaloosa, AL 35487-0336, USA

^d Department of Chemistry, University of California, Davis, CA 95616, USA

Received 13 November 2006; received in revised form 6 January 2007; accepted 7 January 2007

Available online 17 January 2007

Abstract

We report a new synthesis and characterization of $\text{Ir}(\text{C}_2\text{H}_4)_2(\text{C}_5\text{H}_7\text{O}_2)$ [(acetylacetonato)-bis(η^2 -ethene)iridium(I)], prepared from $(\text{NH}_4)_3\text{IrCl}_6 \cdot \text{H}_2\text{O}$ in a yield of about 45%. The compound has been characterized by X-ray diffraction crystallography, infrared, Raman, and NMR spectroscopies and calculations at the level of density functional theory. $\text{Ir}(\text{C}_2\text{H}_4)_2(\text{C}_5\text{H}_7\text{O}_2)$ is isostructural with $\text{Rh}(\text{C}_2\text{H}_4)_2(\text{C}_5\text{H}_7\text{O}_2)$, but there is a substantial difference in the ethylene binding energies, with Ir–ethylene having a stronger interaction than Rh–ethylene; two ethylenes are bound to Ir with a binding energy of 94 kcal/mol and to Rh with a binding energy of 70 kcal/mol. © 2007 Elsevier B.V. All rights reserved.

Keywords: Acetylacetonate; Ethylene; Iridium complex

1. Introduction

Volatile transition metal β -diketonate complexes have been widely investigated as precursors for low-temperature CVD materials [1] and electroluminescent devices [2], with much of the effort focused on complexes of alkaline earth and lanthanide metals and only little on complexes of noble metals. The latter are attracting increasing interest as precursors of supported metal-complex catalysts, especially those with uniform, site-isolated structures [3]. For example, $\text{Au}(\text{CH}_3)_2(\text{C}_5\text{H}_7\text{O}_2)$ was used to synthesize supported cationic gold catalysts for CO oxidation [4], and recent work [5,6] illustrates opportunities for making catalytic intermediates on metal oxides or zeolites from $\text{Rh}(\text{C}_2\text{H}_4)_2(\text{C}_5\text{H}_7\text{O}_2)$.

$\text{Ir}(\text{C}_2\text{H}_4)_2(\text{C}_5\text{H}_7\text{O}_2)$ [7] [(acetylacetonato)-bis(η^2 -ethene)iridium(I)] is similarly a potential catalyst precursor, but the reported synthesis has, in our hands, been less than

optimal, and there is no definitive report of its structure. Thus, we developed a new synthesis of $\text{Ir}(\text{C}_2\text{H}_4)_2(\text{C}_5\text{H}_7\text{O}_2)$ and investigated its structure, by X-ray crystallography and IR, Raman, and NMR spectroscopies and calculations at the level of density functional theory (DFT).

2. Experimental and computational

Solvents used in the synthesis of $\text{Ir}(\text{C}_2\text{H}_4)_2(\text{C}_5\text{H}_7\text{O}_2)$ were reagent grade and deaerated by sparging of N_2 immediately before use. Each synthesis step was carried out with standard air-exclusion techniques. The reagents and solvents included the precursor $(\text{NH}_4)_3\text{IrCl}_6 \cdot \text{H}_2\text{O}$ (39% Ir) (Strem), diethyl ether (absolute), methanol, heptane, and isopropanol (EMD Chemicals) and 2,4-pentanedione (Hacac) (99+%, Sigma–Aldrich) and cyclooctene (95%, Acros).

$[\text{IrCl}(\text{C}_8\text{H}_{14})_2]_2$ was synthesized from 2.0 g of $(\text{NH}_4)_3\text{IrCl}_6 \cdot \text{H}_2\text{O}$ [8] in a round-bottom flask, to which were added 10 mL of deaerated isopropanol and 20 mL of deaerated, deionized water, followed by 4 mL of cyclooctene. The

* Corresponding author. Fax: +1 530 752 1031.

E-mail address: bcgates@ucdavis.edu (B.C. Gates).

mixture was refluxed under argon for 4 h and cooled to room temperature, and the aqueous layer was separated from the oily residue, which was washed three times with 25-mL aliquots of ethanol, leading to $[\text{IrCl}(\text{C}_8\text{H}_{14})_2]_2$ as an orange-yellow solid.

$[\text{IrCl}(\text{C}_8\text{H}_{14})_2]_2$ (0.5 g) was placed in a Schlenk tube in a glovebox and sealed. With the Schlenk tube in an ice bath and attached to a vacuum line, 25 mL of cold, deaerated heptane was added, and the suspension was stirred for 5 min, becoming bright yellow. Ethylene was then bubbled through the solution at atmospheric pressure, leading to a lightening of the color within 5 min and the formation of an almost colorless solution (with a yellowish tinge) after 20 min. With a continuing ethylene flow, the solution was cooled to -80°C in a dry ice bath, and it was allowed to stand for 5 min without stirring, whereupon the supernatant liquid was removed by pipette. The remaining yellowish-gray precipitate was washed three times with 15 mL of deaerated ethylene-saturated heptane at dry-ice temperature. Approximately 0.4 g of KOH powder was then added to the tube under a blanket of flowing ethylene, with 0.4 g of Hacac followed by 20 mL of cold, deaerated diethyl ether saturated with ethylene, and stirring was started. After 15–20 min, the tube was removed from the dry-ice bath and placed into an ice bath, and after 5 min the color of the solution changed to orange-yellow; with stirring for an additional 30 min, yellow particles formed on the tube wall. To this mixture, 20 mL of water was added, and stirring continued for 15 min. The water layer was decanted and the ether removed by evaporation at 0°C . The resultant orange-yellow crystals were harvested and washed twice with 15 mL of water followed by 15 mL of methanol at 0°C . Most of the methanol was then removed by pipette, and the remainder by evaporation. The product crystals of $\text{Ir}(\text{C}_2\text{H}_4)_2(\text{C}_5\text{H}_7\text{O}_2)$ (230 mg) were dried under vacuum for 90 min, transferred to a vial, sealed under argon, and stored at room temperature in a glovebox. The yield was about 45%. An elemental analysis of the crystals was performed by Galbraith Laboratories, and the results were found to be in good agreement with the stoichiometric values. Anal. Calc. for $\text{Ir}(\text{C}_2\text{H}_4)_2(\text{C}_5\text{H}_7\text{O}_2)$: C, 31.11; H, 4.32; O, 9.22. Found: C, 31.35; H, 4.47%; O not determined.

When brought in contact with air, the compound was observed to change color slowly to brown and decompose.

Crystals of $\text{Ir}(\text{C}_2\text{H}_4)_2(\text{C}_5\text{H}_7\text{O}_2)$ were yellow blocks, $0.07 \times 0.11 \times 0.13$ mm in size, $\text{C}_9\text{H}_{15}\text{IrO}_2$, $f_w = 347.41$, orthorhombic, $Pnma$, $a = 7.6075(2)$, $b = 14.1739(4)$, $c = 9.0043(14)$ Å, $V = 970.92(5)$ Å³, $Z = 4$, $T = 90(2)$ K. The diffraction data were collected with a Bruker SMART 1000 diffractometer, graphite-monochromated Mo K α radiation, and a nitrogen cold stream provided by a CRYO Industries apparatus; $2\theta_{\text{max}} = 63^\circ$, Mo K α , $\lambda = 0.71073$ Å, ω scans, 10056 reflections measured, 1156 independent ($R_{\text{int}} = 0.0284$) and included in the refinement. A correction for absorption was applied by using the program SADABS 2.10 [9]. The structures were solved by direct methods (SHELXS-97) [10] and refined by full-matrix least-squares

on F^2 (SHELXL-97) for a total of 76 parameters [10]. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms on the ethylene molecule were located on a difference map and refined by using a C–H distance restraint of 0.99(1) Å. Other hydrogen atoms were added by geometry and refined by using a riding model. R_1 (1092 observed data based on F^2) = 0.0118, wR_2 (all data based on F^2) = 0.0291.

A Bruker IFS 66v spectrometer with a spectral resolution of 2 cm^{-1} was used to collect transmission IR spectra of $\text{Ir}(\text{C}_2\text{H}_4)_2(\text{C}_5\text{H}_7\text{O}_2)$ (128 scans), prepared by mixing a few tiny crystals (<1 mg) with approximately 5 mg of KBr in a dry box. Approximately 1–2 mg of this mixture was placed between a pair of KBr windows for optical optimization that allowed detection of minor peaks. A Raman spectrum of $\text{Ir}(\text{C}_2\text{H}_4)_2(\text{C}_5\text{H}_7\text{O}_2)$ was similarly measured with a Bruker RFS 100/S Spectrometer with a spectral resolution of 4 cm^{-1} .

Preparation of the $\text{Ir}(\text{C}_2\text{H}_4)_2(\text{C}_5\text{H}_7\text{O}_2)$ for ^{13}C MAS-NMR spectroscopy consisted of loading the sample in a powder form into a 7.5-mm zirconia MAS rotor. The spectrum was acquired with a Varian Infinity plus spectrometer at 300 MHz; the instrument was equipped with a modified Chemagnetics 7.5 mm MAS probe. External referencing was with respect to the methyl signal of hexamethylbenzene (17.35 ppm relative to TMS), which was also used to calibrate 90° flip for both carbon and proton. The spectrum was the signal-averaged result of 2000 scans taken with a pulse delay of 30 s at ambient temperature. The rotor spinning speed was 5.0 kHz.

^{13}C and ^1H NMR spectra of $\text{Ir}(\text{C}_2\text{H}_4)_2(\text{C}_5\text{H}_7\text{O}_2)$ dissolved in CDCl_3 solvent were obtained with a 400-MHz Bruker spectrometer. Single pulses were used for both the ^{13}C and ^1H spectra as well as 2-s pulse delays, except that proton decoupling was used for the ^{13}C spectrum. Both FIDs were processed with 2 Hz of line broadening to improve the appearance of the spectra.

The geometries of the Ir^+ complex with $\text{C}_5\text{H}_7\text{O}_2(\text{acac})$, the Ir^+ complex with two C_2H_4 molecules, and the Ir^+ complex with acac and two C_2H_4 molecules were optimized by using DFT with the B3LYP exchange-correlation functional [11]. The Stuttgart relativistic small core effective core potential and the associated basis set were used for Ir [12] and the aug-cc-pVDZ basis set [13] for the other atoms. Calculations of the NMR parameters were done with the B3LYP exchange-correlation functional in the GIAO formalism [14] and the Stuttgart small core basis set/ECP on Ir with two additional sets of f functions and an additional set of g functions [15]. For the other atoms in the NMR calculations, the Ahlrich's triple-zeta polarization basis sets were used [16]. All of the calculations were done with the computer program GAUSSIAN-03 [17] on the Cray XD-1 and SGI computers at the Alabama Supercomputer Center. Calculations were done for different spin states of the Ir^+ because the ground state of the Ir^+ is the quintet (^5F) followed by the triplet and then the singlet [18].

3. Results and discussion

The X-ray structure of $\text{Ir}(\text{C}_2\text{H}_4)_2(\text{C}_5\text{H}_7\text{O}_2)$ is shown in Fig. 1, with important bond lengths and angles in Table 1. The $\text{Ir}(\text{C}_2\text{H}_4)_2(\text{C}_5\text{H}_7\text{O}_2)$ molecule (Fig. 1) has crystallographic mirror symmetry, with the mirror passing through Ir1, C2, and H2 and bisecting the angle between the ethylenes. This structure is isostructural to the rhodium analogue [19], and their geometries are compared, together with calculated values, in Table 1. The Ir–C(ethylene) distances are essentially equal. Ignoring hydrogens, the acetylacetonate ligand is planar, with a mean deviation of 0.0018 Å from the plane defined by C1/O1/C5/C2/C5A/O1A/C1A. The ethylene line of C3 and C4 subtends an angle of 3.8° to the normal to this plane. Hydrogen atoms of the ethylene molecule are distinctly bent away from the Ir atom, emphasizing the loss of double bond character in the C3–C4 bond. The angle between the centroids of the ethylene carbon atoms and the central Ir atom is 96.0°.

The calculated geometry is in excellent agreement with the experimental values, with the calculated values giving Ir–C and Ir–O bond distances that are too long by 0.03 and 0.04 Å, respectively. The complex of two C_2H_4 molecules with Ir^+ has a metal–carbon bond distance that is 0.05 Å shorter than the ones in $\text{Ir}(\text{C}_2\text{H}_4)_2(\text{C}_5\text{H}_7\text{O}_2)$. The C=C bond distance in the ethylene increases from a calculated value of 1.335 Å in the isolated molecule to a value of 1.40 to 1.41 Å in the complexes. The C=O bonds increase in length from 1.247 Å in the $\text{C}_5\text{H}_7\text{O}_2^-$ ion to 1.295 Å in the $\text{Ir}(\text{C}_5\text{H}_7\text{O}_2)$ complex. The addition of two ethylenes to the $\text{Ir}(\text{C}_5\text{H}_7\text{O}_2)$ complex leads to a substantial increase in the Ir–O bond length, from 1.93 to 2.08 Å, coupled with a decrease of 0.014 Å in the length of the C=O bonds in the $\text{C}_5\text{H}_7\text{O}_2$ ligand. The C–H bonds are bent out of the plane by approximately 13.5° (trans $\angle\text{HCCH} = 153^\circ$) in the iridium complex, independent of whether the acac

ligand is present. In the rhodium complexes, the C–H bonds are bent out of the plane by about 11.5°, and again the angle is independent of whether the $\text{C}_5\text{H}_7\text{O}_2$ ligand is present. The calculations show that the optimized geometries of the rhodium and iridium complexes are quite similar. Furthermore, removal of the $\text{C}_5\text{H}_7\text{O}_2$ ligand does not lead to substantial changes in the metal–olefin geometry.

The Raman and IR spectra of the complex (assignments of the bands are given as supplementary material) are presented in Table 2. The calculated frequency (Table 2) for the symmetric C=O stretch of 1597 cm^{-1} is in good agreement with the experimental value of 1572 cm^{-1} , considering that the calculated value is a harmonic frequency. The prediction of the calculations is that the C–C–C asymmetric stretch is at 1561 cm^{-1} and of much higher intensity than the symmetric stretch at 1289 cm^{-1} . The calculated value for the asymmetric C–C–C stretch is in good agreement with the experimental assignment of 1531 cm^{-1} . The frequency of the symmetric C=O stretch in $\text{Ir}(\text{C}_2\text{H}_4)_2(\text{C}_5\text{H}_7\text{O}_2)$ is greater than the value in the $\text{Ir}(\text{C}_5\text{H}_7\text{O}_2)$ complex, predicted at 1524 cm^{-1} , but lower than the value of 1665 cm^{-1} predicted for the bare $\text{C}_5\text{H}_7\text{O}_2^-$ ion. The asymmetric C=O stretch characterizing $\text{Ir}(\text{C}_5\text{H}_7\text{O}_2)$ is predicted to be at 1414 cm^{-1} and that characterizing the bare anion at 1577 cm^{-1} , both substantially higher values than that characterizing $\text{Ir}(\text{C}_2\text{H}_4)_2(\text{C}_5\text{H}_7\text{O}_2)$. The C–C–C asymmetric stretch is predicted to be at 1551 cm^{-1} in $\text{Ir}(\text{C}_5\text{H}_7\text{O}_2)$ and at 1501 cm^{-1} in the $\text{C}_5\text{H}_7\text{O}_2^-$ ion, showing the increase resulting from complexation. The symmetric and asymmetric combinations of the C=C stretches are predicted to be at 1241 and 1227 cm^{-1} in $\text{Ir}(\text{C}_2\text{H}_4)_2(\text{C}_5\text{H}_7\text{O}_2)$. These values are substantially lower than the value of 1684 cm^{-1} predicted for free C_2H_4 .

The ^{13}C and ^1H NMR spectra of $\text{Ir}(\text{C}_2\text{H}_4)_2(\text{C}_5\text{H}_7\text{O}_2)$ in deaerated CDCl_3 solvent (Table 2) essentially match those reported [20]. The ^{13}C MAS-NMR spectrum of solid $\text{Ir}(\text{C}_2\text{H}_4)_2(\text{C}_5\text{H}_7\text{O}_2)$ (Fig. 2) is entirely consistent with its crystal structure. The comparison of the experimental chemical shifts with the calculated values discussed below for the $\text{C}_5\text{H}_7\text{O}_2$ ligand and with previously reported values for the ethylene ligands provides a strong confirmation of the crystallographic data identifying $\text{Ir}(\text{C}_2\text{H}_4)_2(\text{C}_5\text{H}_7\text{O}_2)$.

The characteristic shift of the ethylene ligands of $\text{Ir}(\text{C}_2\text{H}_4)_2(\text{C}_5\text{H}_7\text{O}_2)$ was reported [20] to occur at 40.9 ppm, which compares favorably with our experimental value of 39 ppm. The agreement between the experimental and theoretical results is good, as shown in Fig. 2. The methyl carbon value agrees within 1–2 ppm, the methine carbon values within 0–2 ppm, and the carbonyl carbon values within 8–9 ppm. The larger discrepancy in the chemical shifts for the ethylene ligands (about 20 ppm) is likely a consequence of additional relativistic effects because of the presence of Ir. Calculations modeling the analogous complex with Rh^+ instead of Ir^+ showed much better agreement with experiment for the ethylene carbon shifts when the same approach was used.

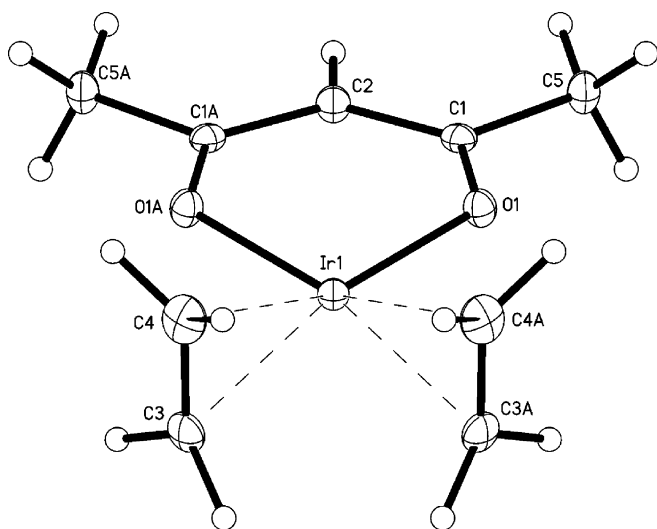


Fig. 1. Molecular structure of $\text{Ir}(\text{C}_2\text{H}_4)_2(\text{C}_5\text{H}_7\text{O}_2)$. Displacement parameters are drawn at the 50% probability level.

Table 1
Calculated and experimental (X-ray) geometric parameters with bond distances (d) in angstrom (Å) and bond angles (\angle) in degrees (°)

Parameter	Ir(C ₂ H ₄) ₂ (C ₅ H ₇ O ₂) (Calc.)	Ir(C ₂ H ₄) ₂ (C ₅ H ₇ O ₂) (X-ray)	Rh(C ₂ H ₄) ₂ (C ₅ H ₇ O ₂) (Calc.)	Rh(C ₂ H ₄) ₂ (C ₅ H ₇ O ₂) (X-ray) [19]
d (M–C)	2.135	2.107(2) 2.108(3)	2.148	2.129(5) 2.125(6)
d (M–O)	2.080	2.042(2)	2.071	2.051(4)
d (C=C)	1.415	1.404(4)	1.396	1.372(8)
d (C=O)	1.281	1.285(3)	1.278	1.279(6)
d (C–C)(acac)	1.407	1.402(3)	1.408	1.397(6)
\angle (OMO)	90.5	91.45(9)	90.7	90.9(2)

Table 2
IR and NMR spectroscopic data characterizing Ir(C₂H₄)₂(C₅H₇O₂)

Spectroscopic technique (units for representation of bands)	Bands	Reference
IR (cm ⁻¹) ^a	C–H str: 3115(w, broad), 3045(vs), 3030(w), 2981(s), 2935(w), 2906(w), 2879(s), HCH bends and rocks: 1572(sh), 1549(sh), 1531(vs), 1486(sh), 1424(m), 1400(m); 1361(s), 1276(s), 1212(s); 1200(s)	Expt. this work
IR (cm ⁻¹) ^b	C–H str: 3214(11), 3209(42), 3206(10), 3185(1), 3185(0), 3144(31), 3144(0), 3116(15), 3116(16), 3111(49), 3111(0), 3106(0), 3106(11), 3041(4), 3041(12) HCH bends and rocks: 1537(9), 1529(3), 1477(15), 1464(7), 1458(73), 1453(0), 1451(14), 1450(0), 1384(2), 1381(24), 1217(0), 1212(0) C=O sym: 1597 (497); C=O asym: 1421(142); C=C sym: 1241(27); C=C asym: 1227(27); C– C–C asym: 1561(344); C–C–C sym: 1289(47)	Calc. this work
IR (cm ⁻¹)	1576(sh), 1554(vs), 1538(vs), 1487(sh, w), 1430(m), 1368(s), 1281(s), 1216(s), 1205(s)	[20]
Raman (cm ⁻¹)	1537(w), 1483(w), 1438(m), 1364(s), 1280(s), 1210(vs)	This work
Raman (cm ⁻¹)	1542(m), 1524(w), 1486(m), 1436(m), 1364(s), 1282(vs), 1212(vs), 1203(s)	[20]
Liquid ¹³ C NMR (ppm)	δ CO (acac ring): 186.9; δ CH (acac ring): 101.1; δ C (ethylene): 40.7; δ CH ₃ (acac ring): 27.5	This work
Liquid ¹³ C NMR (ppm)	δ CO (acac ring): 186.7; δ CH (acac ring): 100.9; δ C (ethylene): 40.9; δ CH ₃ (acac ring): 27.4	[20]
Liquid ¹ H NMR (ppm)	δ CH (acac ring): 7.3; δ CH ₂ (ethylene): 5.8; δ CH ₃ (acac ring): 2.0	This work

vs = Very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder.

^a Assignments of the IR bands are given as [Supplementary material](#).

^b Values in parentheses are calculated IR intensities in km/mol.

The ground state of the atom is predicted to be the triplet, which is essentially degenerate with the quintet ($\Delta E = 3.3$ kcal/mol), and the singlet is 38.8 kcal/mol above the triplet. Considering that we have not included spin orbit effects and that our calculated value is a term average, we conclude that the calculated values are consistent with the experimental results [21]. Addition of the acac ($\Delta E_{ST} = 8.8$ kcal/mol) or two ethylene molecules ($\Delta E_{ST} = 11.1$ kcal/mol) leads to the lowest state being the singlet, by approximately 10 kcal/mol as compared to the triplet, a stabilization of the singlet attributed to complexation of approximately 50 kcal/mol as compared to the isolated ion. The full complex Ir(C₂H₄)₂(C₅H₇O₂) has the singlet more stable than the triplet by 44.3 kcal/mol. The fact that the singlet is the ground state is consistent with our ability to observe these species by NMR spectroscopy.

Jesse et al. [22] used differential scanning calorimetry to determine the enthalpies of reactions of the crystalline complexes, Ir(C₂H₄)₂(C₅H₇O₂) and Rh(C₂H₄)₂(C₅H₇O₂), with CO gas, concluding that although the bonding types are quite similar, the Ir–ethylene bond is stronger than the Rh–ethylene bond. This result was confirmed by IR spectra showing that the energies of the vibration bands of ν (C=C)

and δ (CH₂)_{scis} in Ir(C₂H₄)₂(C₅H₇O₂) are less than those of their counterparts in Rh(C₂H₄)₂(C₅H₇O₂), representing a stronger interaction for Ir–ethylene. The observed increase in metal–alkene bond strength on going from Rh to Ir was explained as evidence of stronger π - and σ -bonds in the iridium complexes. UV photoelectron spectra reported by van Dam et al. [23] are also in agreement with this conclusion, as the authors stated that σ bonding becomes more important in the iridium complexes than the π back-bonding. This conclusion is also consistent with the calculated total binding energy of two ethylene molecules to the M(C₅H₇O₂) complex, whereby, for M = Ir, the binding energy is 94.1 kcal/mol and for M = Rh is 69.8 kcal/mol. Thus, the binding energy characterizing the complex with the Ir bonded to a C₂H₄ molecule is 47 kcal/mol (roughly estimated as one-half of the total binding energy), vs. 35 kcal/mol for the rhodium complex. The energy of the reaction $M(C_5H_7O_2)C_2H_4 + C_2H_4 \rightarrow M(C_5H_7O_2)(C_2H_4)_2$ is -32.0 kcal/mol for M = Rh and -44.8 kcal/mol for M = Ir, consistent with the average values.

What is remarkable is that there is a substantial difference in the ethylene binding energies for the two isovalent metal complexes, although there is essentially no difference in the geometric parameters characterizing them. Examina-

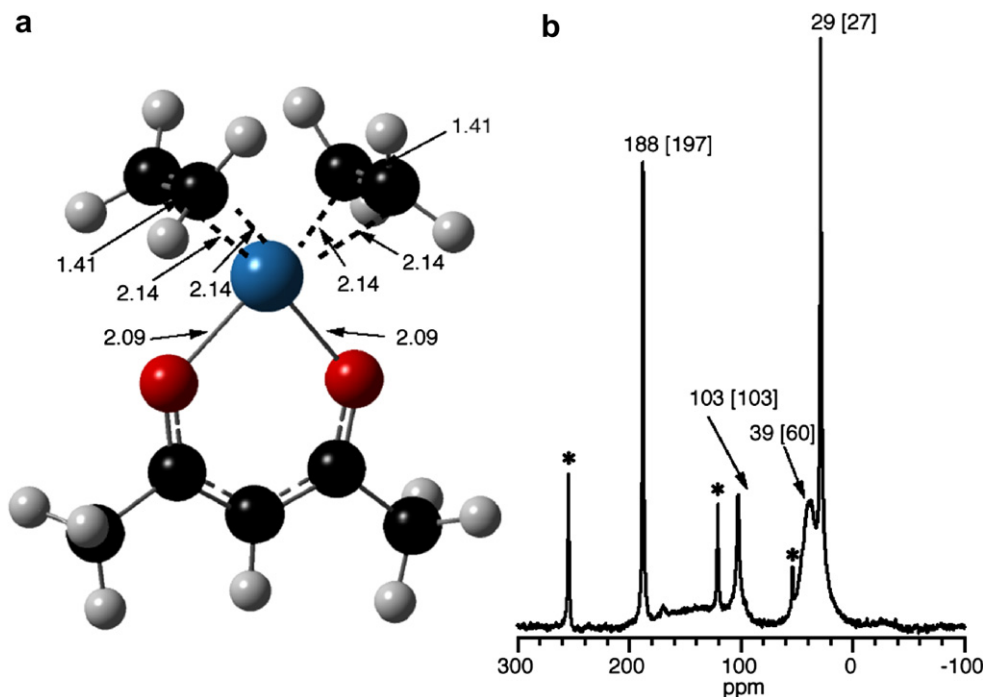


Fig. 2. (a) Optimized geometry of $\text{Ir}(\text{C}_2\text{H}_4)_2(\text{C}_5\text{H}_7\text{O}_2)$. Bond lengths are given in angstrom (\AA). (b) Solid-state ^{13}C NMR spectrum of $\text{Ir}(\text{C}_2\text{H}_4)_2(\text{C}_5\text{H}_7\text{O}_2)$. Experimental values are indicated for each peak with theoretical values appearing in square brackets (* denotes spinning sideband).

tion of the Mulliken charges shows that the Ir atom bears more negative charge than the Rh atom in either the acetylacetonate complex with one ethylene or that with two, with the respective charges being 0.16 and -0.06 e for the rhodium complexes with one and two ethylenes, respectively, and 0.00 and -0.22 e for the two respective iridium complexes. Thus, there is more charge density available on the Ir atom to interact with the two ethylenes than on the Rh atom, or, conversely, there is more donation from the ethylenes to the Ir atom than to the Rh atom. The latter statement is consistent with the charges on the carbon atoms in the ethylene molecules, which show more negative charge (-0.19 e) in the rhodium complex than the iridium complex (-0.15 e).

Consistent with the results characterization the charges, the HOMO is predicted to be more stable in $\text{Ir}(\text{C}_2\text{H}_4)_2(\text{C}_5\text{H}_7\text{O}_2)$ than in $\text{Rh}(\text{C}_2\text{H}_4)(\text{C}_5\text{H}_7\text{O}_2)$, with the respective values being 5.49 and 5.21 eV (Fig. 3). More important, the GAP defined as $|E(\text{HOMO}) - E(\text{LUMO})|$ is larger in the rhodium complex than in the iridium complex for both the monoethylene derivative and the diethylene derivative. The GAP characterizing $\text{Rh}(\text{C}_2\text{H}_4)(\text{C}_5\text{H}_7\text{O}_2)$ is 3.06 eV, and that characterizing $\text{Rh}(\text{C}_2\text{H}_4)_2(\text{C}_5\text{H}_7\text{O}_2)$ is 4.22 eV, with a difference of 1.16 eV, mostly a consequence of destabilizing the LUMO in the latter. The GAP characterizing $\text{Ir}(\text{C}_2\text{H}_4)(\text{C}_5\text{H}_7\text{O}_2)$ is much lower, 2.29 eV, and that characterizing $\text{Ir}(\text{C}_2\text{H}_4)_2(\text{C}_5\text{H}_7\text{O}_2)$ is 3.84 eV, a difference of 1.55 eV. The difference in the changes in the GAPs between Ir and Rh is 9 kcal/mol (0.39 eV), accounting for most of the difference in the C_2H_4 binding energies. The HOMO is always a d_{z^2} orbital but addition of the second C_2H_4

causes a change in the location of the LUMO from the metal–olefin region to the acac.

Åkermark et al. [24] reported limited CAS calculations with an effective polarized double zeta basis set representing the $\text{Rh}(1,3\text{-propanedionato})(\text{C}_2\text{H}_4)_2$ complex. They reported a binding energy of about 14 kcal/mol per ethylene, far smaller than our calculated value. This difference is probably a consequence primarily of their not including all of the d electrons in the CAS as well as their excluding the C–C σ - and π -occupied orbitals; a smaller part of the difference may be attributed to our consideration of acac rather than the simpler hydrogen derivative. Åkermark et al. [24] reported C–C bond distances similar to our values.

The analysis of the electron densities in the iridium complexes (Table 3) was done by use of the natural bond order analysis [25]. The addition of C_2H_4 to Ir^+ leads to a small increase in s character on C and a transfer of approximately 0.2 e/C to the Ir^+ , with most of the electron density being transferred to the d orbitals. Bonding of a second C_2H_4 does essentially the same in terms of the C orbitals, but most of the additional density is transferred to the valence s on Ir. Addition of acac to Ir^+ leads to an increase of about 0.1 e on the Ir. When a C_2H_4 is added to the $\text{Ir}(\text{acac})$ complex, less than 0.1 e is transferred to the Ir, and there is a transfer of density from the Ir d orbitals to the Ir s orbitals. Addition of a second C_2H_4 leads to similar small changes. As a result of the addition of acac to $\text{Ir}(\text{C}_2\text{H}_4)_2$, there is a transfer of density back into the ethylene π orbitals and an increase of about 0.1 e to both the Ir s and d orbitals.

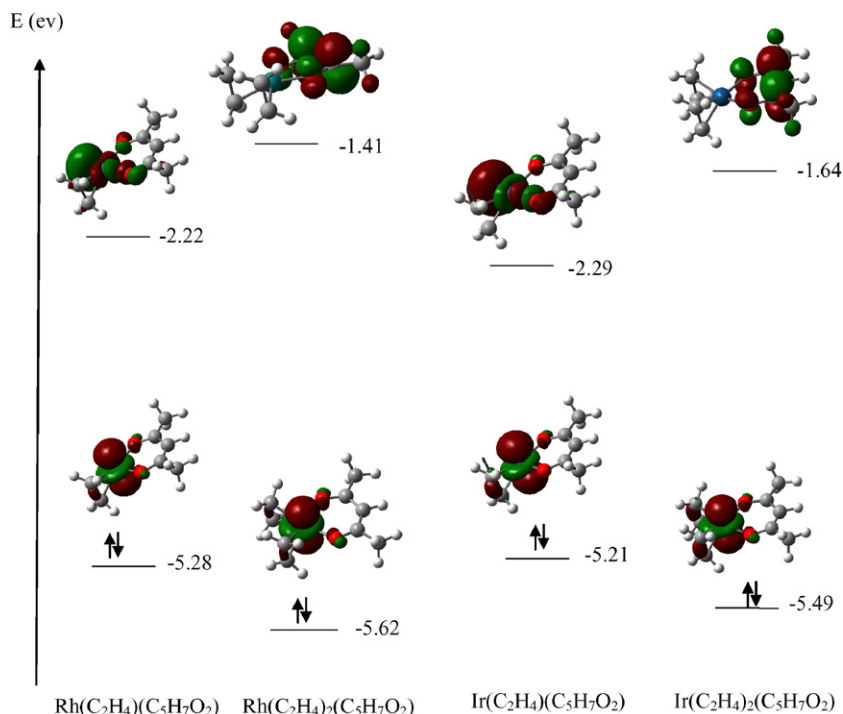


Fig. 3. Orbital energy diagram for the HOMOs and LUMOs (energies in eV).

Table 3
Natural electron populations for C from C₂H₄ and Ir

Molecule	C s	C p	Ir s	Ir d
C ₂ H ₄	1.16	3.46		
Ir(C ₂ H ₄)	1.20	3.23	0.09	8.31
Ir(C ₂ H ₄) ₂	1.20	3.23	0.37	8.48
Ir(C ₅ H ₇ O ₂)			0.34	8.75
Ir(C ₂ H ₄)(C ₅ H ₇ O ₂)	1.19	3.42	0.41	8.60
Ir(C ₂ H ₄) ₂ (C ₅ H ₇ O ₂)	1.18	3.37	0.47	8.58

4. Conclusions

Ir(C₂H₄)₂(C₅H₇O₂) was synthesized in approximately a 45% yield from (NH₄)₃IrCl₆ · H₂O, and its crystal structure was determined and complemented by IR, Raman, and NMR spectroscopies and calculations at the DFT level. The compound has a structure consistent with that of Rh(C₂H₄)₂(C₅H₇O₂), but the bonding strength of ethylene to an Ir atom in Ir(C₂H₄)₂(C₅H₇O₂) is greater than that to a Rh atom in Rh(C₂H₄)₂(C₅H₇O₂).

Acknowledgements

We thank Prof. S. Sen of the University of California, Davis, for help with the Raman spectroscopy. The research at the University of California; the University of Southern California; and the University of Alabama was supported, respectively, by the US Department of Energy (DOE), Grant DE-FG02-04ER15600; DOE Grant DE-FG02-04ER15598; and the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences,

DOE, under the catalysis center program, and by the Robert Ramsay Chair Foundation.

Appendix A. Supplementary material

CCDC 622328 contains the supplementary crystallographic data for the compound referred in this article. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2007.01.008](https://doi.org/10.1016/j.jorganchem.2007.01.008).

References

- [1] T. Maruyama, T. Shirai, *J. Mat. Sci.* 30 (1995) 5551.
- [2] M. Tiitta, L. Niimisto, *Chem. Vap. Deposition* 3 (1997) 167.
- [3] J.F. Goellner, B.C. Gates, G.N. Vayssilov, N. Rösch, *J. Am. Chem. Soc.* 122 (2000) 8056.
- [4] J. Guzman, B.C. Gates, *Angew. Chem., Int. Ed.* 42 (2003) 690.
- [5] V.A. Bhirud, J.O. Ehresmann, P.W. Kletnieks, J.F. Haw, B.C. Gates, *Langmuir* 22 (2006) 490.
- [6] A.J. Liang, V.A. Bhirud, J.O. Ehresmann, P.W. Kletnieks, J.F. Haw, B.C. Gates, *J. Phys. Chem. B* 109 (2005) 24236.
- [7] H.L.M. Van Gaal, A. Van der Ent, *Inorg. Chim. Acta* 7 (1973) 653.
- [8] A. Van der Ent, A.L. Onderdelinden, *Inorg. Synth.* 28 (1990) 90.
- [9] G.M. Sheldrick, *SADABS*; 2.10 ed., G.M. Sheldrick, University of Göttingen, Göttingen, Germany, 2003.
- [10] G.M. Sheldrick, *SHELXTL*; 5.1 ed., G.M. Sheldrick, Bruker Analytical X-ray Instruments, Inc.: Madison, Wisconsin, 1997.
- [11] A.D. Becke, *J. Chem. Phys.* 98 (1993) 5648; C. Lee, W. Yang, R.G. Parr, *Phys. Rev. B* 37 (1988) 785.

- [12] M. Küchle, H. Dolg, H. Stoll, H. Preuss, *J. Chem. Phys.* 100 (1994) 7535, and references therein;
W. Küchle, M. Dolg, H. Stoll, H. Preuss, Pseudopotentials of the Stuttgart/Dresden Group (1998) (Revision: Tue Aug 11, 1998). See World Wide Web: <<http://www.theochem.uni-stuttgart.de/pseudopotentiale>>.
- [13] R.A. Kendall, T.H. Dunning Jr., R.J. Harrison, *J. Chem. Phys.* 96 (1992) 6796.
- [14] K. Wolinski, J.F. Hinton, P. Pulay, *J. Am. Chem. Soc.* 112 (1990) 8251.
- [15] J.M.L. Martin, A. Sundermann, *J. Chem. Phys.* 114 (2001) 3408.
- [16] A. Schafer, H. Horn, R.F. Ahlrichs, *J. Chem. Phys.* 97 (1992) 2571.
- [17] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, GAUSSIAN 03, Revision b.05, Gaussian, Inc., Wallingford, CT, 2004.
- [18] See: <<http://physics.nist.gov/PhysRefData/Handbook/Tables/iridiumtable6.htm>>.
- [19] M. Bühl, M. Håkansson, A.H. Mahmoudkhani, L. Öhrström, *Organometallics* 19 (2000) 5589;
D.W. Price, M.G.B. Drew, K.K. Hii, J.M. Brown, *Chem. Eur. J.* 6 (2000) 4587.
- [20] A.C. Jesse, M.A.M. Meester, D.J. Stufkens, K. Vrieze, *Inorg. Chim. Acta* 26 (1978) 129.
- [21] C.E. Moore, Atomic energy levels as derived from the analysis of optical spectra, vol. III, Mo to La, Hf to Ac, US National Bureau of Standards Circular 467, US Department of Commerce, National Technical Information Service, COM-72-50283, Washington, DC, 1971.
- [22] A.C. Jesse, A. Baks, D.J. Stufkens, K. Vrieze, *Inorg. Chim. Acta* 29 (1978) 177.
- [23] H. Van Dam, A. Terpstra, D.J. Stufkens, A. Oskam, *Inorg. Chem.* 19 (1980) 3448.
- [24] B. Åkermark, M.R. Blomberg, J. Glaser, L. Öhrström, S. Whalberg, K. Wärnmark, K. Zetterberg, *J. Am. Chem. Soc.* 116 (1994) 3405.
- [25] A.E. Reed, L.A. Curtiss, F. Weinhold, *Chem. Rev.* 88 (1988) 899.