Synthesis and characterization of a bimetallic iridium complex with a ten sp^2-carbon chain bridge†‡

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Received 8th May 2007, Accepted 25th June 2007
First published as an Advance Article on the web 4th July 2007
DOI: 10.1039/b706900f

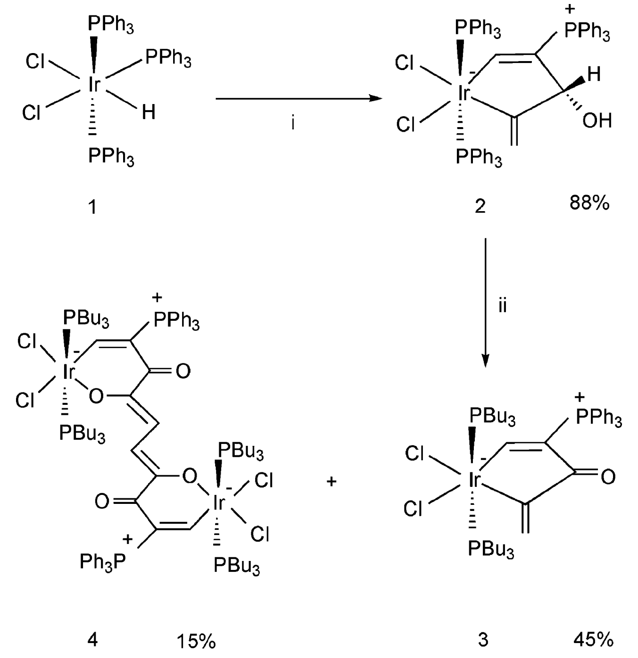
A special sp^2-carbon chain bridged bimetallic iridium complex has been synthesized and characterized; the compound has excellent air-stability, thermo-stability and electrochemical properties.

Organic compounds having conjugated π-systems can act as electronic bridges between transition metal atoms. Numerous experimental and theoretical studies on dinuclear organometallic compounds with two metal centres linked by a conjugated organic bridge have been reported,[1–8] especially those of ruthenium,[1] iron,[2] rhenium,[3] and platinum.[4] In contrast, conjugated bimetallic iridium complexes[5] are rare up to now. Additionally, many conjugated dinuclear complexes with sp-carbon bridges: $–C_x–$[6] or mixed bridges such as $—(C\equiv C)_x–(C_6H_4)_y–(C\equiv C)_x–$ are known,[7] while those with pure sp^2-carbon bridges, such as $–(CH)_x–$ bridged complexes, are still few.[8]

During our investigation of the reactions of $HC\equiv CCH(OH)C\equiv CH$[9] with transition-metal compounds, we have isolated a novel bimetallic iridium complex from the reaction of $HC\equiv CCH(OH)C\equiv CH$ with *cis*-$IrHCl_2(PPh_3)_3$ (**1**).[10] The compound is made up of two iridium centres connected by a conjugated organic bridge of ten sp^2-carbons. Interestingly, it can also be considered as two planar six-membered rings containing iridium linked by a $–(CH)_2–$ bridge. The compound has excellent air-stability, thermo-stability and electrochemical properties. The building of stable bimetallic systems with unusual structure allowing communication is also important for practical applications.[11]

Treatment of *cis*-$IrHCl_2(PPh_3)_3$ (**1**) with $HC\equiv CCH(OH)C\equiv CH$ in dichloromethane led to the formation of the dark yellow compound **2** in high yield (Scheme 1), which has been characterized by solution NMR spectroscopy and X-ray diffraction.§ The X-ray structure shown in Fig. 1 indicates that **2** has a distorted octahedral geometry around iridium. The metal atom and four carbon atoms of the penta-1,4-dien-3-ol ligand constitute a partially unsaturated five-membered ring. The metallacycle is almost planar as reflected by the small mean RMS deviation (0.1108 Å) from the least-squares plane through the five atoms Ir1, C1, C2, C3 and C4.

Five-membered ringed metallacycles are numerous, many of them act as intermediates or precursors of transition-metal-assisted reactions.[12] At room temperature, **2** remains nearly unchanged over 3 h in solution. To examine the reaction activity and improve the solubility of **2**, we have tried to replace the triphenylphosphine ligand on the iridium with tri-n-butylphosphine. Treatment of **2** with PBu_3 in dichloromethane under nitrogen readily gave rise to a brown solution containing a mixture of **3** and another very unstable complex which could not be isolated. A green mixture was produced when the experiment was carried out under air. We have monitored the reaction and analyzed the final solution to draw the following conclusion: under air a mixture was generated after a slow and intricate process which may involve oxidative coupling and other reactions. Fortunately, we succeeded in separating the orange product **3** and another interesting green product **4**.



Scheme 1 *Reagents and conditions*: i) $HC\equiv CCH(OH)C\equiv CH$, CH_2Cl_2, RT; ii) excess PBu_3, CH_2Cl_2, O_2, RT.

3 could be regarded as a product formed by replacement of PPh_3 with PBu_3 and the dehydrogenation of CH(OH) in compound **2**. The structure of **3** has also been confirmed by X-ray diffraction§ and its ORTEP drawing is reproduced in Fig. 2. Unlike complex **2**, the five-membered metallacycle of **3** has perfect co-planarity, which is reflected by the very small mean RMS deviation (0.022 Å) from the least-squares plane through the eight atoms C1, C2, C3, C4, C5, O1, P3 and Ir1. Complex **3** also shows better air-stability and thermal stability. It remains nearly unchanged when heated at 100 °C in toluene for several hours.

The most interesting product isolated from the reaction is complex **4**. The structure of **4** has been confirmed by a single

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† CCDC reference numbers 633228–633230. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b706900f

‡ Electronic supplementary information (ESI) available: Synthesis and characterization of all compounds. See DOI: 10.1039/b706900f

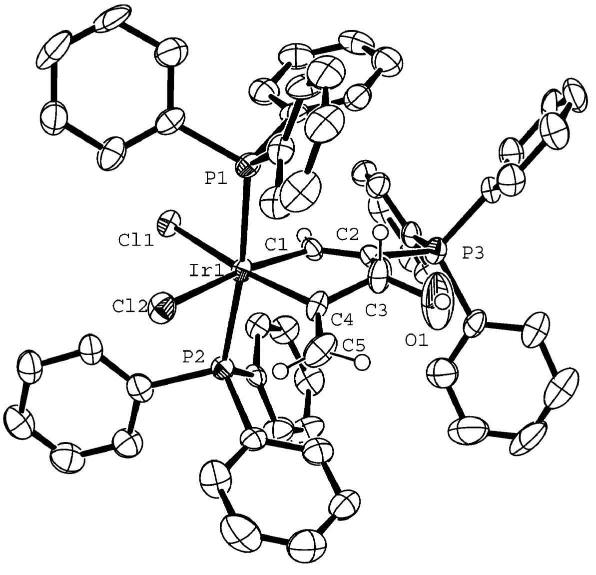

Fig. 1 An ORTEP plot of complex **2** with thermal ellipsoids at 50% probability levels. Two CH_2Cl_2 molecules and some of the hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [°]: Ir1–C1 1.986(11), Ir1–C4 2.026(11), C1–C2 1.326(16), C2–C3 1.482(18), C3–C4 1.502(18), C4–C5 1.281(18); C1–Ir1–C4 81.0(5), C1–C2–C3 115.4(11), C2–C3–C4 109.4(10), C3–C4–C5 118.3(12), C2–C3–O1 116.9(12), C4–C3–O1 119.9(13), C5–C4–Ir1 131.4(11), C3–C4–Ir1 110.5(8).

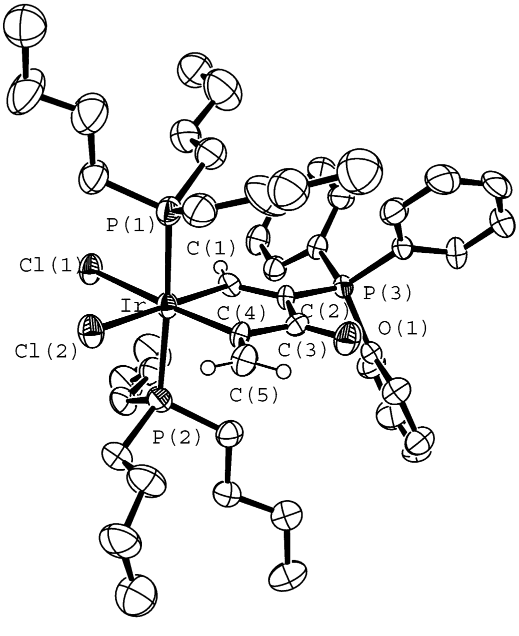

Fig. 2 An ORTEP plot of complex **3** with thermal ellipsoids at 50% probability levels. One diethyl ether molecule and some of the hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [°]: Ir1–C1 1.965(2), Ir1–C4 2.064(2), C1–C2 1.350(2), C2–C3 1.451(3), C3–C4 1.508(3), C4–C5 1.285(4); C1–Ir1–C4 81.8(1), C1–C2–C3 115.6(2), C2–C3–C4 113.4(2), C3–C4–C5 118.3(2), C2–C3–O1 124.0(2), C4–C3–O1 122.6(2), C5–C4–Ir1 131.2(2), C3–C4–Ir1 110.5(2).

crystal X-ray diffraction study.§ The ORTEP drawing is shown in Fig. 3. In this complex, the two iridium atoms are connected by a bridge consisting of a ten sp^2-carbon atom chain and a shorter bridge namely Ir1–O2–C4–C5–C5_3–C4_3–O2_3–Ir1_3. There is an inversion centre at the ten carbon chain linking the two Ir atoms. Atom Ir1 is linked across the inversion centre to Ir1_3 at $(-x, -y + 1, -z)$. Such a structure can also be viewed as two special six-membered iridacycles linked by a conjugated carbon bridge. Interestingly, the sixteen atoms of the rings and the bridge are almost co-planar, which is reflected by a deviation (0.0536 Å) from the RMS planes of the best fit. The exact mechanism for the formation of this novel complex is unclear at this moment.

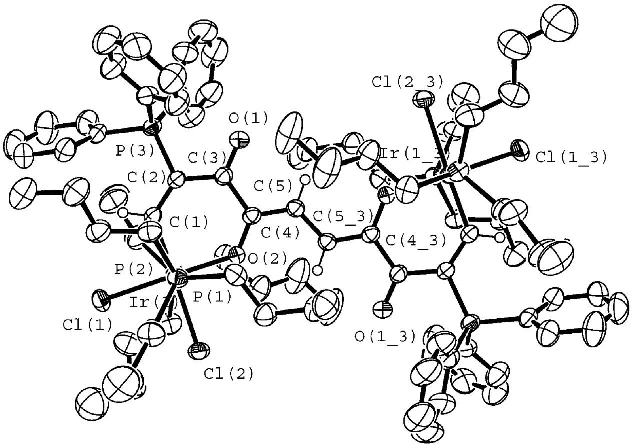

Fig. 3 An ORTEP plot of complex **4** with thermal ellipsoids at 50% probability levels. Three $CHCl_3$ molecules and some of the hydrogen atoms are omitted for clarity. Symmetry transformations used to generate equivalent atoms: _3 $-x, -y + 1, -z$. Selected bond distances [Å] and angles [°]: Ir1–C1 1.947(4), Ir1–O2 2.042(3), C1–C2 1.352(6), C2–C3 1.474(6), C3–C4 1.507(6), C4–C5 1.373(6), C3–O1 1.226(5); C5–C5_3 1.436(8); C1–Ir1–O2 91.68(15), C4–O2–Ir1 128.3(3), C2–C1–Ir1 127.3(3), C1–C2–C3 127.2(4), C2–C3–C4 120.5(4), C3–C4–C5 115.2(4), C2–C3–O1 117.8(4), C4–C3–O1 121.7(4), O2–C4–C5 121.0(4), O2–C4–C3 123.8(4), C4–C5–C5_3 123.4(5).

The NMR spectroscopic data are consistent with the X-ray structure. The room-temperature $^{13}C\{^1H\}$ NMR in $CDCl_3$ displayed a carbonyl signal at $\delta = 186.8$ ppm and an Ir–*C* signal at $\delta = 195.2$ ppm which is significantly downfield compared with chemical shifts of typical Ir–*C* signals (110–140 ppm).[13] The signal of C5 is observed at $\delta = 112.9$ ppm, which is comparable to those of CH groups of normal alkenes. Other signals of the bridging ligand were observed at 112.4 ppm (C2) and 156.9 ppm (C4). In the ^1H NMR (in $CDCl_3$) spectrum, the signals attributed to Ir–C*H* and bridgehead C*H* were observed at 13.8 ppm and 6.9 ppm. In addition, the highly symmetric structure could also be confirmed by the ^{31}P NMR spectrum: only two peaks at 17.5 ppm (t, J (PP) = 3.6 Hz, C*P*Ph$_3$) and −20.4 ppm (d, J(PP) = 3.6 Hz, Ir*P*Bu$_3$) were observed though there are six phosphorus atoms in the structure.

The electron-transfer properties of **4** have been studied in dichloromethane containing 0.10 M Bu_4NClO_4 by cyclic voltammetry. A representative voltammogram is shown in Fig. 4. Compound **4** exhibits two redox processes; $E_{1/2}$ of the first wave (A) at −0.14 V, $\Delta E\text{p} = 112$ mV, and $E_{1/2}$ of the second wave (B) at 0.61 V, $\Delta E\text{p} = 130$ mV, with a scan rate of 100 mV s^{-1}. The redox peak potential differences at 20 mV s^{-1} are 80 mV (A) and 90 mV (B). The differential pulse voltammogram also shows two signals, which have identical integrated areas, consistent with two one-electron-transfer processes.[14] The relative peak heights $i_{pa}/i_{pc}\approx 1$, and peak currents are found to be linear with the square root of scan rate ($\upsilon^{1/2}$) in the range from 20 to 200 mV s^{-1}, demonstrate

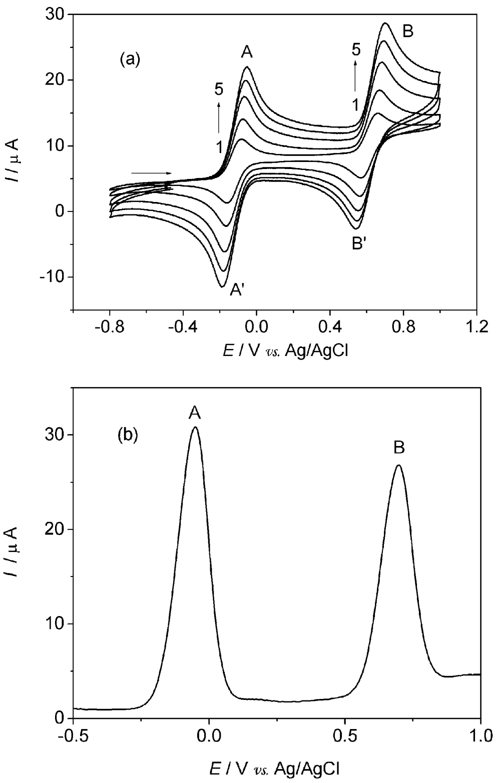

Fig. 4 Cyclic (a) and differential pulse (b) voltammograms of 1 mM compound **4** (*vs.* Ag/AgCl). The voltammograms were recorded in CH_2Cl_2 and Bu_4NClO_4 (0.1 M) as the supporting electrolyte, scan rate: (1) 20, (2) 50, (3) 100, (4)150, (5) 200 mV s^{-1}.

that the two quasi-reversible one-electron processes approach that of a reversible system on the cyclic voltammetric time scale. These two oxidation waves may be attributed to the formation of $\mathbf{4}^{+}$ and $\mathbf{4}^{2+}$, respectively. Observation of two oxidation waves for complex **4** imply that the transient intermediates of **4** are stable, probably dependent on conjugation and planarity, and there is some degree of electronic interaction between the two metal centers, due to a bridge consisting of a 10 sp^2 carbon atom chain or Ir1–O2–C4–C5–C5_3–C4_3–O2_3–Ir1_3 as the coupling medium.

As a result of the highly conjugated and planar structure, compound **4** is quite stable to air and is also thermally stable (the sample of **4** in toluene remains nearly unchanged when heated at 100 °C in air for several hours) as well as exhibiting excellent electrochemical properties. Additionally, there are active groups like chloride on the metal atoms, which enable **4** to be linked by polydentate ligands to form a polymer. Such a polymer may be a useful precursor for mixed-valence (MV), low-dimensional conductive (LDC) and non-linear optical (NLO) materials.[15]

We acknowledge with thanks the sponsorship of the program New Century Excellent Talents in Universities of China (NCET-04-0603) and the National Science Foundation of China (20572089).

Notes and references

§ Crystal data for **2**: $IrCl_2(CH{=}C(PPh_3)CH(OH)C({=}CH_2))(PPh_3)_2{\cdot}2CH_2Cl_2$, M_r = 1300.85, monoclinic, space group $P2(1)/n$, $Z = 4$, $a = 12.833(2)$ Å, $b = 32.704(5)$ Å, $c = 13.692(2)$ Å, $\alpha = 90$, $\beta = 111.703(2)$, $\gamma = 90°$, $V = 5339.1(17)$ Å^3; 38479 reflections, 8156 independent reflections ($R_{int} = 0.0693$); $R_1 = 0.0837$, $wR_2 = 0.1924$ for 619 parameters and 9407 reflections with $[I>2\sigma(I)]$. Crystal data for **3**: $IrCl_2(CH{=}C(PPh_3)CH(OH)C({=}CH_2))(PBu_3)_2{\cdot}Et_2O$, M_r = 1083.18, monoclinic, space group Cc, $Z = 4$, $a = 21.421(4)$ Å, $b = 14.267(3)$ Å, $c = 18.226(3)$ Å, $\alpha = 90$, $\beta = 106.765(3)$, $\gamma = 90°$, $V = 5333.5(17)$ Å^3; 20742 reflections, 8087 independent reflections ($R_{int} = 0.0294$); $R_1 = 0.0350$, $wR_2 = 0.0897$ for 473 parameters and 9151 reflections with $[I>2\sigma(I)]$. Crystal data for **4**: $[(\text{–}IrCl_2(PBu_3)_2CH{=}C(PPh_3)C(O)CO\text{–}){=}CH)\text{–}]_2{\cdot}3CHCl_3$, $M_r = 2644.94$, monoclinic, space group $P2(1)/n$, $Z = 2$, $a = 14.197(2)$, $b = 19.240(3)$, $c = 23.412(4)$ Å, $\alpha = 90$, $\beta = 99.442(3)$, $\gamma = 90°$, $V = 6308.5(18)$ Å^3. 48381 reflections, 10877 independent reflections ($R_{int} = 0.0278$); $R_1 = 0.0450$, $wR_2 = 0.1285$ for 557 parameters and 12382 reflections with $[I>2\sigma(I)]$.

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