

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

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### Experimental Section

All manipulations were carried out at room temperature under a nitrogen atmosphere using standard Schlenk techniques, unless otherwise stated. Solvents were distilled under nitrogen from sodium benzophenone (ether, hexane), methanol (molecular sieves) or calcium hydride (dichloromethane).

### Preparation details and characterization data of $\text{IrCl}_2(\text{CH}=\text{C}(\text{PPh}_3)\text{CH}(\text{OH})\text{C}(\text{=CH}_2))(\text{PPh}_3)_2$ (**2**)

A mixture of  $\text{IrHCl}_2(\text{PPh}_3)_3$  (1.00 g, 0.95 mmol) and  $\text{HC}\equiv\text{CCH}(\text{OH})\text{C}\equiv\text{CH}$  (83.8 mg, 1.05 mmol) in  $\text{CH}_2\text{Cl}_2$  (15 mL) was stirred at room temperature for ca. 5 min to give a brown-yellow solution. The volume of the mixture was reduced to produce a dark yellow solid, which was collected by filtration, washed with ether (3×5 mL) and dried under vacuum. Yield: 0.95 g, 88%. Anal. Calcd for  $\text{C}_{59}\text{H}_{50}\text{Cl}_2\text{OP}_3\text{Ir}$  : C, 62.65; H, 4.46. Found: C, 62.29; H, 4.93.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 121.5 MHz) :  $\delta$  12.3 (t,  $J(\text{PP})$  3.8 Hz,  $\text{C}(\text{PPh}_3)$ ), -8.4 (d,  $J(\text{PP})$  3.8 Hz,  $\text{Ir}(\text{PPh}_3)$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300.1 MHz):  $\delta$  10.4

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(d,  $J(\text{PH})$  19.8 Hz, 1H, IrCH), 6.9~8.0 (m, 45H, PPh<sub>3</sub>), 4.7 (s, 1H, IrCCH<sub>2</sub>), 4.4 (s, 1H, IrCCH<sub>2</sub>), 4.1(d,  $J(\text{PH})$  6.8 Hz, 1H, CHOH), 1.1 (d,  $J(\text{PH})$  6.8 Hz, 1H, OH).  
<sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 75.5 MHz) :  $\delta$  183.4 (t,  $J(\text{PC})$  7.5 Hz, IrCCH<sub>2</sub>), 146.9 (dt,  $J(\text{PC})$  17.1 Hz, 7.5 Hz, IrCH), 120.6~135.9 (m, PPh<sub>3</sub>), 116.9 (dt,  $J(\text{PC})$  71.6 Hz,  $J(\text{PC})$  2.5 Hz, IrCHC(PPh<sub>3</sub>)), 113.6 (br, IrCCH<sub>2</sub>), 88.9 (d,  $J(\text{PC})$  16.8 Hz, CHOH).

**Preparation details of IrCl<sub>2</sub>(CH=C(PPh<sub>3</sub>)CH(OH)C(=CH<sub>2</sub>))(PBu<sub>3</sub>)<sub>2</sub> (**3**) and [(-IrCl<sub>2</sub>(PBu<sub>3</sub>)<sub>2</sub>CH=C(PPh<sub>3</sub>)C(O)CO-) =CH-]<sub>2</sub> (**4**)**

To a suspension of IrCl<sub>2</sub>(CHC(PPh<sub>3</sub>)CH(OH)CCH<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub> (**2**) (1.00 g, 0.88 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was added PBu<sub>3</sub> (0.90 ml, 3.46 mmol). The mixture was stirred at room temperature in air for ca. 2~3 days to give a green solution. The volume of the mixture was dried under vacuum. Separate **3** and **4** from the mixture by column chromatography (neutral alumina, eluent: hexane/dichloromethane). **3**: Yield: 0.40 g, 45%. **4**: Yield: 0.16 g, 15%.

**Characterization data of IrCl<sub>2</sub>(CH=C(PPh<sub>3</sub>)CH(OH)C(=CH<sub>2</sub>))(PBu<sub>3</sub>)<sub>2</sub> (**3**)**

Anal. Calcd for C<sub>47</sub>H<sub>73</sub>Cl<sub>2</sub>OP<sub>3</sub>Ir: C, 55.88; H, 7.28. Found: C, 55.49, H, 6.98. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 121.5 MHz) :  $\delta$  12.7 (t,  $J(\text{PP})$  3.6Hz, CPh<sub>3</sub>), -24.8 (d,  $J(\text{PP})$  3.6Hz, IrPBu<sub>3</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300.1 MHz):  $\delta$  13.2 (d,  $J(\text{PH})$  15.9Hz, 1H, IrCH), 7.0~7.6 (m, 15H, PPh<sub>3</sub>), 6.9 (s, 1H, IrCCH<sub>2</sub>), 6.1 (s, 1H, IrCCH<sub>2</sub>), 0.7~1.7 (m, 54H, PBu<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 75.5 MHz) :  $\delta$  217.9 (t,  $J(\text{PC})$  5.3 Hz, IrCCH<sub>2</sub>), 209.4 (d,  $J(\text{PC})$  15.9 Hz, CO), 138.6 (dt,  $J(\text{PC})$  16.6 Hz, 7.5 Hz, IrCH), 120.2~134.7 (m,

PPh<sub>3</sub>), 117.4 (d, *J*(PC) 81.5 Hz IrCHC(PPh<sub>3</sub>)), 123.0 (s, IrCCH<sub>2</sub>), 13.9~25.5 (m, PBu<sub>3</sub>).

**Characterization data of [(-IrCl<sub>2</sub>(PBu<sub>3</sub>)<sub>2</sub>CH=C(PPh<sub>3</sub>)(CO)CH(O)=CH)-]<sub>2</sub> (4)**

Anal. Calcd for C<sub>94</sub>H<sub>142</sub>Cl<sub>4</sub>O<sub>4</sub>P<sub>6</sub>Ir<sub>2</sub>: C, 55.12; H, 6.99. Found: C, 55.04; H, 6.87.

<sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 121.5 MHz) : δ 17.5 (t, *J*(PP) 3.6Hz, CPh<sub>3</sub>), -20.4 (d, *J*(PP) 3.6 Hz, IrPBu<sub>3</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300.1 MHz): δ 13.8 (d, *J*(PH) 24.6 Hz, 2H, IrCHCPh<sub>3</sub>), 7.4~7.6 (m, 30H, PPh<sub>3</sub>), 6.9 (s, 2H, IrOCCH), 0.7~1.9 (m, 108H, PBu<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 75.5 MHz) : δ 195.2 (s, IrCHC(PPh<sub>3</sub>)), 186.8 (s, C(PPh<sub>3</sub>)CO), 156.9 (s, IrOC), 122.4~133.6 (m, PPh<sub>3</sub>), 112.9 (s, IrOCCH), 112.4 (d, *J*(PC) 76.3 Hz, IrCC(PPh<sub>3</sub>), 13.7~24.8 (m, PBu<sub>3</sub>).

**Electrochemistry experiments details for [(-IrCl<sub>2</sub>(PBu<sub>3</sub>)<sub>2</sub>CH=C(PPh<sub>3</sub>)C(O)CO)=CH)-]<sub>2</sub> (4)**

Cyclic and differential pulse voltammeteries for **4** were performed at room temperature (25 °C) under N<sub>2</sub> atmosphere in freshly distilled CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 mol / L Bu<sub>4</sub>NClO<sub>4</sub> (TBAP), using a CHI660 voltammetric analyzer. A three electrode system in a single-compartment cell with resistance compensation was used throughout. The working electrode was glassy carbon disk whose diameter was 3 mm. This electrode was carefully polished with 1 μm, 0.3 μm, 0.05 μm alumina powder respectively and ultrasonically rinsed with distilled water and ethanol before each run. The auxiliary electrode was a platinum sheet and the reference electrode was Ag / AgCl in CH<sub>2</sub>Cl<sub>2</sub>

with 0.1 mol / L TBAP. The ferrocene / ferrocenium redox couple was located at 0.39 V under our experimental conditions.

X-ray	Crystal	Structure	Determination	for
		$\text{IrCl}_2(\text{CH}=\text{C}(\text{PPh}_3)\text{CH}(\text{OH})\text{C}(\text{=CH}_2))(\text{PPh}_3)_2$	(2) · 2	$\text{CH}_2\text{Cl}_2$ ,
		$\text{IrCl}_2(\text{CH}=\text{C}(\text{PPh}_3)\text{CH}(\text{OH})\text{C}(\text{=CH}_2))(\text{PBu}_3)_2$	(3) · 1	$\text{Et}_2\text{O}$ and
		$[(-\text{IrCl}_2(\text{PBu}_3)_2\text{CH}=\text{C}(\text{PPh}_3)\text{C}(\text{O})\text{CO}-)=\text{CH}-]_2$	(4) · 3	$\text{CHCl}_3$ .

Crystals of **2** and **4** suitable for X-ray diffraction were grown from a solution in  $\text{CH}_2\text{Cl}_2$  layered with diethyl ether and  $\text{CHCl}_3$  layered with hexane, respectively, while those for **3** were grown from a solution in diethyl ether. A yellow blocked crystal of **2**, an orange blocked crystal of **3** and a brown-green prismatic crystal of **4** were mounted on glass fibers and data collection was performed on a Bruker Apex CCD Area Detector at 223K. Intensity data were collected on a Bruker SMART CCD Area Detector with graphite-monochromated MoK radiation at temperature of 223 K. The structures were solved by direct methods, expanded by difference Fourier syntheses, and refined by full-matrix least-squares methods on  $F^2$  by using the Bruker SHELXTL (Version 6.10) program package. All non-hydrogen atoms were refined anisotropically. CCDC-633228, 633229 and 633230 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). In addition, compared with the collected data

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of **3** and **4**, that of **2** was relatively poor (R value of 8.37%) due to its stability (The sample of **2** only remains nearly unchanged within 3 hours in the solution).

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