

**A C-H activation / CO₂-carboxylation reaction sequence mediated by an
'Iridium(dppm)' species. Formation of the anionic ligand (Ph₂P)₂C-COOH.**

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Supporting information

General data.

All manipulations were carried out by using modified Schlenk techniques under an atmosphere of argon. Prior to use, thf, toluene and diethyl ether were dried and deoxygenated with a Innovative Technology Solvent Purification System. Acetone was dried with CaCl₂ and distilled before used. [Ir₂(μ-Cl)₂(coe)₄] was prepared according to a literature method.¹ Dppm was purchased from Aldrich and dcypm from STREM. CO₂ (99.999%) was purchased from Air Liquide and used without further purification.

Infrared spectra were recorded using a Perkin-Elmer Spectrum One spectrometer. Carbon and hydrogen analyses were performed with a Perkin-Elmer 2400 microanalyzer.

¹H, ¹³C{¹H} and ³¹P{¹H} NMR spectra were recorded on a Bruker Avance 400MHZ or 200MHz spectrometer. Chemical shifts are reported in parts per million and referenced to SiMe₄ using the residual signal of the deuterated solvent as reference and 85% phosphoric acid, respectively.

Synthesis of [IrCl (dppm)(H){(Ph₂P)₂C-COOH}] (2).

Dppm (102 mg, 0.27 mmol) in toluene (5 ml) was added to a stirred suspension of [Ir₂(μ-Cl)₂(coe)₄] (56 mg, 0.062 mmol) in toluene (5 ml). The initially red solution bleached to yellow and the argon atmosphere was replaced by CO₂ resulting in further bleaching to pale yellow and precipitation of a colourless solid. The reaction mixture was stirred for additional three hours. Afterwards the supernatant solution was decanted and the remaining white residue was washed with toluene (2 x 5 ml) and diethyl ether (2 x 5 ml). The obtained product 2*0.5toluene was dried in a vacuum. Yield 131 mg (96 %). Found: C, 60.3; H, 4.5%.

$C_{54.5}H_{48}IrClO_2P_4$ requires C, 60.25; H, 4.45%. $\nu_{\max}/\text{cm}^{-1}$ 2185w (Ir-H), 1580br (COO), 1270br (COO).

Similar results were obtained in thf, acetone or acetonitrile. **2** is insoluble in common organic solvents like toluene, diethyl ether, thf or acetone, and dissolves slowly and decomposes in chlorinated solvents like CHCl_3 and CH_2Cl_2 .

Suitable crystals of the composition $2 \cdot 3\text{acetone}$ for X-ray measurement were obtained directly from a reaction mixture in acetone.

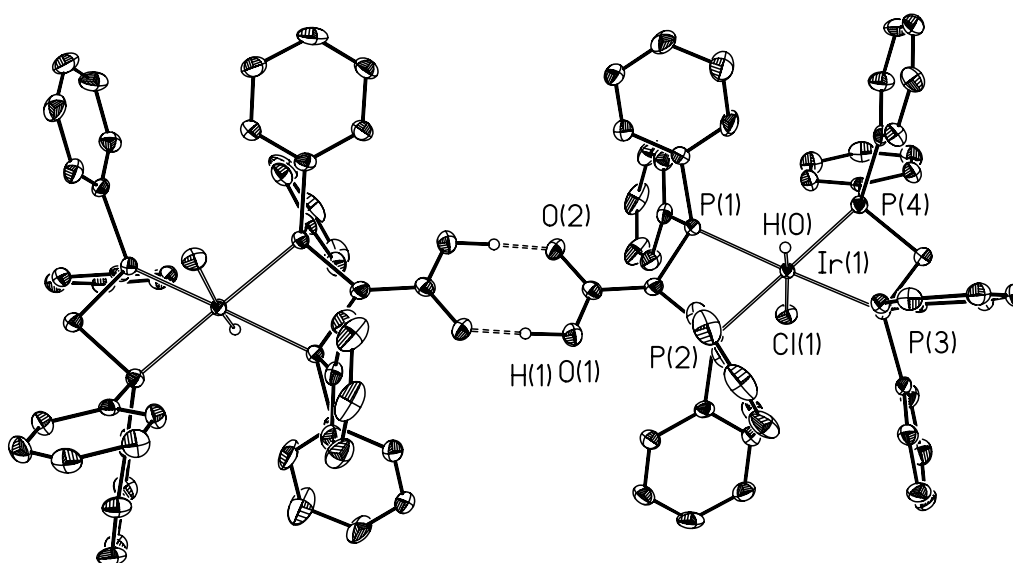


Figure 1. Dimeric unit of **2** as determined by X-ray diffraction (H atoms except H(0) and H(1) omitted for clarity).

Synthesis of $[\text{IrCl}(\text{dppm})_2(\text{H})]\text{PF}_6$ (**3**).

NH_4PF_6 (14.7 mg, 0.09 mmol) was added to a stirred suspension of **2** (77.2 mg, 0.066 mmol) in acetone (5 ml). Within 1 hour a clear colourless solution formed and the solvent was removed in a vacuum. The remaining solid was washed with diethyl ether (3 x 4ml) and dried in a vacuum. Yield: 97.4 mg (crude product, contains the excess of NH_4PF_6). As judged from the ^{31}P nmr, **3** is the only dppm containing product formed. The product can be further purified by recrystallisation from acetone. $\nu_{\max}/\text{cm}^{-1}$ 2198w (Ir-H). δ_{H} (400 MHz, CD_2Cl_2) - 16.39 (1H, q, J 12.1, Ir-H), 5.1-5.25 (2H, m, CHH'), 5.30-5.45 (2H, m, CHH'), 7.1-7.25 (32H, m, CH Ph), 7.35-7.45 (8H, m, CH Ph); δ_{C} (75 MHz, CD_2Cl_2) 50.1 (2C, q, J 15.6, $\text{P}-\text{CH}_2-\text{P}$), 128.0 (4C, q, J 15.5, $i\text{-C}$ Ph), 129.0 (8C, q, J 2.6, CH Ph), 129.5 (8C, q, J 2.6, CH Ph), 131.2 (4C, q, J 15.2, $i\text{-C}$ Ph), 132.1 (4C, s, $p\text{-CH}$ Ph), 132.5 (4C, s, $p\text{-CH}$ Ph), 133.0 (8C,

q, J 3.2, CH Ph), 133.4 (8C, q, J 2.9, CH Ph). δ_p (121.5 MHz, CD₂Cl₂) -55.2 (4P, s, dppm), -144.2 (1P, sept, J 711.3, PF₆⁻).

A related complex [IrCl(dppm)₂(H)]BF₄ has been previously reported.²

[Li{OOC-CH(PPh₂)₂}(tmeda)] 4

[Li{OOC-CH(PPh₂)₂}]³ was recrystallized from N,N,N',N'-tetramethylethylenediamine (tmeda). 4 was obtained as colourless needles.

δ_H (200 MHz, d8-THF) 2.14 (12H, s, CH₃ tmeda), 2.30 (4H, s, CH₂ tmeda), 4.10 (1H, t, J 3.0, CH), 7.0-7.1 (12H, m, CH Phenyl), 7.35-7.5 (4H, m, CH Ph), 7.5-7.65 (4H, m, CH Ph); δ_C (50.3 MHz, d8-THF) 46.1 (4C, s, CH₃ tmeda), 48.4 (1C, br, observed via HSQC, P₂CH), 58.8 (2C, s, CH₂ tmeda), 128.1 (2C, t, J 3.7, CH Ph), 128.20 (2C, t, J 3.6, CH Ph), 128.23 (1C, s, *p*-CH Ph), 128.4 (1C, s, *p*-CH Ph), 134.3 (2C, t, J 10.8, CH-Ph), 135.2 (2C, t, J 11.3 Hz, CH Ph), 140.2 (1C, t, J 5.4, *i*-C Ph), 141.0 (1C, t, J 5.0, *i*-C Ph), 174.7 (1C, br, COO); δ_p (81.0 MHz, d8-THF) -9.8 (s).

[Ir(dppm)₂]PF₆

[Ir(dppm)₂]PF₆ was prepared in analogy to [Ir(dppm)₂]OTf.⁴

δ_H (400 MHz, d6-acetone) 5.22 (4H, br, PCH₂P), 7.3-7.6 (40H, m, Ph); δ_p (162.0 MHz, d6-acetone) -35.7 (4P, s, dppm), -144.0 (1P, sept, J 711, PF₆)

Synthesis of [Ir(dcpm)₂]Cl·2thf

A solution of bis(dicyclohexylphosphino)methane (160 mg, 0.39 mmol) in thf (5 ml) was added to a stirred orange solution of [Ir₂(μ -Cl)₂(coe)₄] (75 mg, 0.084 mmol) in thf (5 ml). The solution turned immediately to red and an orange red precipitate was formed within seconds. The resulting suspension was stirred for 30 min. Afterwards the solid (120 mg) was isolated by filtration and dried in a vacuum. A second crop was obtained from the mother liquor. Therefore, the mother liquor was reduced to dryness and ether (5 ml) was added to the residue with rapid stirring. After standing for two days at rt, the supernatant solution was decanted and the remaining orange red solid (55 mg) was washed with ether (5 ml) and dried in a vacuum. Yield: 175 mg (88 %). δ_H (400 MHz, d6-dmsO) 1.2-1.4 (48H, m, Cy), 1.68 (8H, br, Cy), 1.78 (8H, br, CH₂ thf), 1.79-1.88 (16H, br, Cy), 1.89 (8H, br t, J 10.4, CH Cy), 2.1-2.2 (8H, br, Cy), 3.60 (12H, m, 4 × OCH₂ thf + 2 × PCH₂P); δ_C (50.3 MHz, d6-dmsO) 24.8 (4C, s, CH₂ thf), 25.2 (8C, br s, CH₂ Cy), 26.1 (8C, br m, CH₂ Cy), 26.5 (8C, br m, CH₂ Cy), 27.4

(8C, br s, CH₂ Cy), 28.7 (8C, br s, CH₂ Cy), 30.6 (2C, br m, PCH₂P, observed via HSQC), 36.3 (8C, t, *J* 6.5, CH Cy), 66.7 (4C, s, OCH₂ thf); δ_P (81.0 MHz, d₆-dmsO) -26.5 (s).

References

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