Supporting information for

*Dehydrogenation of Formic Acid by Ir-bisMETAMORPhos Complexes: Experimental and Computational Insight into the Role of a Cooperative Ligand*

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General information

General procedures: All reactions were carried out in dry glassware under nitrogen atmosphere using standard Schlenk techniques unless stated otherwise. THF, dioxane, toluene, pentane were distilled from sodium under dinitrogen, CH₂Cl₂ and diethylether were collected from an MB SPS-800. Deuterated solvents were degassed by four freeze-pump-thaw cycles and dried over molecular sieves (4Å). NMR spectra were measured on a Bruker AMX 400 (¹H: 400.1 MHz, ¹³C: 100.6 MHz and ³¹P: 162.0 MHz) or on a Varian Mercury 300 (¹H: 300.1 MHz) spectrometer at 298 K unless noted otherwise. High resolution mass spectra were recorded on a JEOL JMS SX/SX102A four sector mass spectrometer; for FAB-MS 3-nitrobenzyl alcohol was used as matrix. ESI (electrospray ionization) mass spectra were obtained on a time-of-flight JEOL AccuTOF LC-plus mass spectrometer (JMS-T100LP) equipped with a CSI or ESI source. Calculated spectra were obtained with JEOL Isotopic Simulator (version 1.3.0.0).

Materials: All reagents were purchased from commercial suppliers and used without further purification: Dichlorophenylphosphine (Sigma Aldrich), diethylamine (Sigma Aldrich), 9,9-dimethyl-xanthene (Sigma Aldrich), TMEDA (Sigma Aldrich), nBuLi (Acros organics), phosphorus trichloride (Sigma Aldrich), 4-butylbenzene-1-sulfonamide (ABCR GmbH), 4-(trifluoromethyl)benzenesulfonamide (ABCR GmbH), 2,4,6-tris(isopropyl)benzenesulfonamide (ABCR GmbH), Ir(acac)(COD) (Strem Chemicals), formic acid (Acros organics).

Catalytic dehydrogenation experiments
Catalyst 2a, 2b or 2c (5.0 µmol) was added to toluene (1 mL) in a Schlenk equipped with a condenser and connected to a water replacement set-up. The reaction mixture was heated to the required temperature and stirred for 10 minutes. Formic acid was added to the reaction mixture (188.6 µL, 5 mmol) and the evolved gas was collected. The set-up was calibrated with a Brooks flow-meter type 1054-3C and evolved gases were analyzed with a G·A·S Compact GC (Rt-MSieve 5A 20 m × 0.32 mm + Rt-Q-bond 2 m × 0.32 mm). The amounts of mol converted were determined from the volumes of gas collected using equation 1a and 1b.

Determination of molecular volume of H₂ and CO₂

\[
V_{H_2} = \frac{RT}{p} + b - \frac{a}{RT} = 24.49 \frac{L}{mol} \tag{1a}
\]

\[
R: 8.3145 \text{ m}^3 \text{ Pa}^{-1} \text{ mol}^{-1} \text{ K}^{-1}
\]

\[
T: 298.15 \text{ K}
\]

\[
p: 101325 \text{ Pa}
\]

\[
b: 26.7 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}
\]

\[
a: 2.49 \times 10^{-10} \text{ Pa}^{-1} \text{ m}^3 \text{ mol}^{-2}
\]

\[
V_{CO_2} = \frac{RT}{p} + b - \frac{a}{RT} = 24.42 \frac{L}{mol} \tag{1b}
\]

\[
R: 8.3145 \text{ m}^3 \text{ Pa}^{-1} \text{ mol}^{-1} \text{ K}^{-1}
\]

\[
T: 298.15 \text{ K}
\]

\[
p: 101325 \text{ Pa}
\]
b: $42.7 \times 10^{-6} \text{ m}^3\text{mol}^{-1}$
a: $36.5 \times 10^{-10} \text{ Pa}\text{m}^3\text{mol}^{-2}$

Computational details:
Geometry optimizations were carried out with the Turbomole program package\textsuperscript{52}, coupled to the PQS Baker optimizer\textsuperscript{53} via the BOpt package\textsuperscript{54}, at the spin unrestricted ri-DFT level using the BP86 functional\textsuperscript{55}, the resolution-of-identity (ri) method\textsuperscript{56}, and the def2-TZVP basis set\textsuperscript{57} for the geometry optimizations. Energy profiles are shown below and all structure are conveniently added as separate .xyz and .pdb files.

Synthesis and characterization.

\begin{align*}
&\begin{array}{c}
\text{(9,10-dihydroanthracene-1,8-diyl)bis(phenylphosphine oxide) (a)} \\
\end{array}
\end{align*}

To a solution of dichlorophenylphosphine (6.98 g, 5.29 mL, 39.0 mmol) in Et\textsubscript{2}O (150 mL) at 0 °C was added diethylamine (5.73 g, 8.08 mL, 78.38 mmol) dropwise under vigorous stirring. A white precipitate formed while the reaction mixture was allowed to warm up to room temperature and stirred for 16 hours. The reaction mixture was filtered, concentrated and N,N-(diethylamino)chlorophenylphosphine was obtained as a yellow oil, which was used immediately for follow-up synthesis due to its instability. \textsuperscript{31}P{\textsuperscript{1}H} NMR (162.0 MHz, Et\textsubscript{2}O unlocked): $\delta = 138.96$.

To a solution of 9,9-dimethylxanthene (4.0 g, 19.02 mmol) and TMEDA (4.53 g, 5.85 mL, 39.0 mmol) in diethylether (150 mL) was added a solution of nBuLi (15.3 mL, 2.5 M in hexane, 38.24 mmol) at 0 °C and a deep purple/brown solution was obtained. The reaction mixture was allowed to warm up to room temperature and stirred overnight. N,N-(diethylamino)chlorophenylphosphine (39.0 mmol) in diethylether (75 mL) was added dropwise to the reaction mixture and a clear yellow suspension was obtained and stirred for 16 hours. \textsuperscript{31}P{\textsuperscript{1}H} NMR (162.0 MHz, Et\textsubscript{2}O unlocked): $\delta = 52.55$ (s), 51.74 (s), [racemic mixture of diastereomers (RR/SS, SR/RS) of the phosphinamine]. The reaction mixture was carefully quenched with a 2 M HCl solution (100 mL) and stirred for 1 hour. The phases were separated and the aqueous phase was extracted with ethylacetate (3x). The organic phases were combined and concentrated. Azeotropic drying with toluene (2x) and stripping with
diethylether (3×) yielded a white foam. Purification by column chromatography (SiO\(_2\)/H\(_2\)O 8:2, eluens Et\(_2\)O/MeOH 97:3, deposited in CH\(_2\)Cl\(_2\)) yielded a as a racemic mixture of diastereomers (RR/SS, RS/SR) as a white foam (4.11 g, 47% yield).

\(^{31}\)P\(\{^1\)H\} NMR (162 MHz, CDCl\(_3\)): \(\delta = 11.76\) (s), 11.28 (s);

\(^{31}\)P NMR (162 MHz, CDCl\(_3\)): \(\delta = 11.76\) (dq, \(J = 506.8, 14.2\) Hz), 11.28 (dq, \(J = 506.2, 14.1\) Hz);

\(^1\)H NMR (400 MHz, CD\(_2\)Cl\(_2\)): \(\delta = 8.22\) (d, \(J = 506.8, 4\)H, PH), 8.16 (d, \(J = 506.2, 4\)H, PH), 7.83-7.45 (m, 56H), 7.30 (m, 8H), 1.76 (s, 6H, CH\(_3\)-Xanthene), 1.74 (s, 12H, CH\(_3\)-Xanthene), 1.67 (s, 6H, CH\(_3\)-Xanthene);

\(^{13}\)C\(\{^1\)H\} NMR (100 MHz, CD\(_2\)Cl\(_2\)): \(\delta = 150.90\) (d, \(J = 3.1\) Hz), 150.78 (d, \(J = 3.16\) Hz), 132.80 (d, \(J = 2.86\) Hz), 132.68 (d, \(J = 2.90\) Hz), 132.12 (d, \(J = 25.62\) Hz), 131.83 (d, \(J = 2.14\) Hz), 131.76 (d, overlapping), 131.73 (d, overlapping), 131.66 (d, \(J = 1.85\)), 331.11 (s), 130.61 (s), 130.55 (s), 129.24 (d, \(J = 6.47\) Hz), 129.11 (d, \(J = 6.47\) Hz), 124.64 (d, \(J = 11.01\) Hz), 124.52 (d, \(J = 11.01\) Hz), 120.0 (d, \(J = 23.56\) Hz), 119.04 (d, \(J = 23.56\) Hz), 34.46 (s), 33.71 (s), 32.90 (s), 31.98 (s), 31.76 (s), 31.67 (s), 31.09 (d, \(J = 25.93\) Hz), 131.04 (s), 130.61 (s), 130.55 (s), 129.24 (d, \(J = 6.47\) Hz), 129.11 (d, \(J = 6.47\) Hz), 124.64 (d, \(J = 11.01\) Hz), 124.52 (d, \(J = 11.01\) Hz), 120.0 (d, \(J = 23.56\) Hz), 119.04 (d, \(J = 23.56\) Hz), 34.46 (s), 33.71 (s), 32.90 (s), 31.98 (s);

HR MS (FAB\(^{+}\)): \(m/z\) calcd. for C\(_{27}\)H\(_{25}\)O\(_3\)P\(_2\) [M+H]\(^{+}\): 459.1279, observed: 459.1275.

(9,9-dimethyl-9H-xanthene-4,5-diyl)bis(chloro(phenyl)phosphine) (b)

Compound a (1.39 g, 3.03 mmol) was dissolved in neat PCl\(_3\) (5 mL) at 0 °C and heated to 60 °C for 14 hours, during which time a yellow/orange suspension was obtained. The reaction mixture was cooled to room temperature, concentrated, dissolved in 10 mL toluene and evaporated (3×) to leave a yellow foam. Compound b (stereo-isomers RR, SS, RS, SR) is unstable and should be used immediately.

\(^{31}\)P\(\{^1\)H\} NMR (162.0 MHz, THF unlocked): \(\delta = 73.71\) (s), 73.65 (s).

\(\text{N,N’-((9,9-dimethyl-9H-xanthene-4,5-diyl)bis(phenylphosphinediyl))bis(4-butylbenzenesulfonamide) (La)}\)

Commercially available 4-butylbenzene-1-sulfonamide (1.30 g, 6.08 mmol) was dissolved in 10 mL of toluene and azeotropically dried. The compound was dissolved in THF (25 mL) and nBuLi (2.55 mL, 2.5 M in hexane, 6.36 mmol) was added dropwise at 0 °C, resulting in a white/grey slurry. Compound b (3.04 mmol) was dissolved in THF (30 mL) and slowly added to the slurry to give a clear yellow solution that was stirred at room temperature for 14 hours. The reaction mixture was concentrated and purified by column chromatography (SiO\(_2\), eluens toluene/ethyl acetate 9:1, deposited in CH\(_2\)Cl\(_2\)). Fractions
were combined and concentrated, stripping with Et₂O (3×) yielded La as a white foam (0.9 g, 1.06 mmol, 35% yield). Compound La was obtained pure in its mesomeric form (RS/SR) and this species exists in two tautomeric forms La₁ and La₂, with a ratio of 1 : 0.4, respectively, according to ¹H and ³¹P NMR integrations.

³¹P[¹H] NMR (162 MHz, CD₂Cl₂): δ = 26.92 (s, La₁), 23.24 (d, J = 39.1 Hz, Lb₁), -6.13 (d, J = 39.1 Hz, La₂);
³¹P NMR (162 MHz, CD₂Cl₂): δ = 26.92 (s), 23.24 (d, J = 39.1 Hz), -6.13 (dd, J = 518.2, 39.1 Hz);
¹H NMR: (400 MHz, CD₂Cl₂): Major tautomer La₁: δ = 7.76 (dt, J = 7.23, 1.09 Hz, 2H), 7.49 (br m, 4H), 7.37 (br m, 2H), 7.21 (br m, 8H), 5.96 (br s, 2H, NH), 2.56 (t, J = 7.93 Hz, 4H, (C₃H₇)-CH₂-Ar), 1.57 (s, 3H, CH₃-Xanthene), 1.56-1.49 (m, 4H, (C₂H₅)-CH₂-CH₂-Ar), 1.47 (s, 3H, CH₂-Xanthene), 1.38-1.26 (m, 4H, CH₂(CH₂)-(C₂H₄)-Ar), 0.91 (t, J = 7.3 Hz, 6H, CH₃-(C₃H₆)-Ar) Minor tautomer La₂: δ = 8.68 (dd, J = 518.4, 5.6 Hz, 0.4H, Ph) remaining signals are overlapped by tautomer La₁;
¹³C{¹H} NMR (101 MHz, CD₂Cl₂): δ = 151.57 (d, J = 16.8 Hz, d, La₁), 148.08 (s, m, La₁), 138.91 (s, p, La₁), 130.77 (s), 130.56 (s), 130.16 (s), 130.06 (d, J = 8.55 Hz), 129.05 (s), 128.73 (s), 128.35 (s), 128.30 (s), 128.63 (s), 123.80 (s), 122.74 (d, J = 18.0 Hz, h/i, La₁), 35.43 (s, q, La₁), 34.22 (s, b, La₁), 33.33 (s, a/a’,La₁), 33.14 (s, r, La₁), 32.61 (s, a/a’,La₁), 22.25 (s, s, La₁), 13.63 (s, t, La₁);
HR MS (FAB⁺): m/z calcd. for C₄₇H₅₁N₂O₅P₂S₂: 849.2715, observed: 849.2662;

N,N’-(9,9-dimethyl-9H-xanthene-4,5-diyl)bis(phenylphosphinediyl))bis(4-trifluoromethylbenzenesulfonamide) (Lb)
Commercially available 4-(trifluoromethyl)benzenesulfonamide (0.459 g, 2.04 mmol) was dissolved in 4 mL of toluene and azeotropically dried. The compound was dissolved in THF (15 mL) and nBuLi (0.86 mL, 2.5 M in hexane, 2.14 mmol) was added dropwise at 0 °C, resulting in a white slurry. Compound b (1.02 mmol) was dissolved in THF (10 mL) and slowly added to the slurry to give a clear yellow solution that was stirred at room temperature for 16 hours. The reaction mixture was concentrated and purified by column chromatography (SiO₂, eluens toluene/ethyl acetate 9:1, deposited in CH₂Cl₂). Fractions were combined and concentrated, stripping with Et₂O (3×) yielded Lb as a white foam (0.258 g, 0.3 mmol, 29% yield). Compound Lb was obtained pure in its mesomeric form (RS/ SR) and this species exists in two tautomeric forms Lb₁, Lb₂ and Lb₃ with a ratio of 1 : 1.8 : 0.2, respectively, according to ¹H and ³¹P NMR integrations.

³¹P[¹H] NMR (162 MHz, CD₂Cl₂): δ = 27.07 (s, Lb₁), 24.07 (d, J = 40.7 Hz, Lb₂), -4.10 (s, Lb₃), -6.07 (d, J = 40.7 Hz, Lb₂);
$^{31}$P NMR (162 MHz, CD$_2$Cl$_2$) δ 27.07 (s), 24.07 (d, $J = 40.7$ Hz), -4.10 (d, $J = 526.5$ Hz), -6.07 (d, $J = 520.7$ Hz);

$^1$H NMR: (400 MHz, CD$_2$Cl$_2$): Major tautomer Lb2: δ = 8.76 (dd, $J = 520.5$, 5.8 Hz, 1H, PH), 7.98 – 7.92 (m, 2H), 7.73 (d, $J = 8.2$ Hz, 2H), 7.62 (d, $J = 8.3$ Hz, 2H), 7.55 (d, $J = 8.2$ Hz, 2H), 7.49 (d, $J = 8.1$ Hz, 2H), 7.38 – 7.33 (m, 2H), 7.30 – 7.17 (m, 10H), 7.09 (t, $J = 7.4$ Hz, 2H), 6.33 (d, $J = 4.4$ Hz, 1H, NH), 1.67 (s, 3H, CH$_3$-Xanthene), 1.47 (s, 3H, CH$_3$-Xanthene);

Tautomer Lb1 δ = 6.21 (s, 1H, NH), 1.50 (s, 3H, CH$_3$-Xanthene), 1.40 (s, 3H, CH$_3$-Xanthene), remaining signals are overlapped by tautomer Lb2/3;

$^{13}$C{$_1^1$H} NMR (101 MHz, CD$_2$Cl$_2$): δ = 152.08 (d, $J = 16$ Hz), 151.89 – 151.77 (m), 151.59 (d, $J = 20.9$ Hz), 149.18 (s), 145.54 (s), 145.43 (s), 136.24 – 136.04 (m), 135.90 (d, $J = 10.0$ Hz), 134.37 (s), 134.01 (d, $J = 7.5$ Hz), 133.66 (s), 133.63 (s), 133.52 (s), 133.31 (s), 132.45 (s), 132.38 (s), 132.33 (s), 132.15 (s), 131.80 (s), 131.68 (s), 131.43 (s), 131.39 (s), 131.21 (s), 131.19 (s), 131.01 (s), 130.83 (s, c/c’, Lb1/ Lb2), 130.50 (s, c/c’, Lb1/ Lb2), 130.46 (s, c/c’, Lb1/ Lb2), 130.27 (s), 130.12 (s), 129.93 (s), 129.79 (s), 129.79 (s), 129.46 (s), 129.32 (s), 129.13 (s), 129.07 (s), 128.92 (s), 128.78 (s), 128.73 (s), 127.76 (d, $J = 13.5$ Hz), 127.62 (s), 126.82 (s), 126.68 - 126.46 (m), 126.41 – 126.18 (m), 126.04 – 125.79 (m), 125.35 (s), 125.07 (s), 124.45 (s), 124.47 (s), 124.35 (m, i’h’, Lb1), 123.28 (d, $J = 18.3$ Hz, i’h’, Lb2), 122.47 (m, q/q’, Lb2 / Lb3), 113.03 (s, i/h, Lb2), 111.97 (s, i/h, Lb2), 34.85 (s, b, Lb2), 34.66 (s, b, Lb1), 34.53 (s, b, Lb3), 33.68 (s, a/a’, Lb2), 33.42 (s, a/a’, Lb3), 32.65 (s, a/a’, Lb1), 32.01 (s, a/a’, Lb3), 29.88 (s, a/a’, Lb1), 29.56 (s, a/a’, Lb2).

$^{19}$F NMR (282 MHz, CD$_2$Cl$_2$) δ -63.25 (m);

HR MS (ESI$^+$): m/z calcd. for C$_{57}$H$_{70}$N$_2$O$_5$P$_2$S$_2$ [M+H]$^+$: 873.1210, observed: 873.1234;

Anal. Calcd. for C$_{41}$H$_{32}$F$_6$N$_2$O$_5$P$_2$S$_2$: C, 56.42; H, 3.70; N, 3.21, found: C, 56.62; H, 3.72, N, 3.17.

\[ \text{N,N'}-((9,9\text{-dimethyl-9H-xanthene-4,5-diyl})\text{bis(phenylphosphinediyi)})\text{bis(2,4,6-triisopropylbenzenesulfonylamide)} \ (\text{Lc}) \]

Commercially available 2,4,6-triisopropylbenzenesulfonyamide (1.73 g, 6.10 mmol) was dissolved in 8 mL of toluene and azeotropically dried. The compound was dissolved in THF (25 mL) and nBuLi (2.56 mL, 2.5 M in hexane, 6.4 mmol) was added dropwise at 0 °C, resulting in a white slurry. Compound b (3.05 mmol) was dissolved in THF (20 mL) and slowly added to the slurry to give a clear yellow solution that was stirred at room temperature for 16 hours. The reaction mixture was concentrated and purified by column chromatography (SiO$_2$, eluents toluene/ethyl acetate 100:2 to 100:6, deposited in CH$_2$Cl$_2$). Fractions were combined and concentrated, stripping with Et$_2$O (3×) yielded Lc as a white foam (1.15 g, 1.16 mmol, 38% yield). Compound Lc was obtained pure in its mesomeric form (RS/RS) and this species exists in two tautomeric forms Lc1, Lc2 and Lc3 with a ratio of 1 : 1.9 : 0.1, respectively, according to $^1$H and $^{31}$P NMR integrations.
Commercially available Ir(acac)(COD) (6 mg, 0.015 mmol) was dissolved in CH₂Cl₂ (1 mL) together with ligand La (12.8 mg, 0.015 mmol). The reaction mixture turned bright orange instantly and was stirred for 15 minutes. Evaporation of solvent and volatiles left an orange solid in near-quantitative yield.

**Complex 1a**

Commercially available Ir(acac)(COD) (6 mg, 0.015 mmol) was dissolved in CH₂Cl₂ (1 mL) together with ligand La (12.8 mg, 0.015 mmol). The reaction mixture turned bright orange instantly and was stirred for 15 minutes. Evaporation of solvent and volatiles left an orange solid in near-quantitative yield.

**Complex 1b**

Commercially available Ir(acac)(COD) (6 mg, 0.015 mmol) was dissolved in CH₂Cl₂ (1 mL) together with ligand Lb (13.1 mg, 0.015 mmol). The reaction mixture turned bright orange instantly and was stirred for 15 minutes. Evaporation of solvent and volatiles left an orange solid in near-quantitative yield.
H NMR: (400 MHz, CD₂Cl₂): δ = 13.53 (bs, s, 1H), 7.83 (dd, J = 21.3, 11.3, 7.5 Hz, 3H), 7.68 (d, J = 8.1 Hz, 3H), 7.52 (m, J = 15.4 Hz, 7H), 7.39 (dd, J = 7.6, 1.2 Hz, 3H), 7.26 (m, J = 8.3 Hz, 5H), 7.17 (dd, J = 14.3, 6.6 Hz, 3H), 1.83 (s, 3H), 1.56 (s, 3H).

**Complex 1c**
Commercially available Ir(acac)(COD) (6 mg, 0.015 mmol) was dissolved in CH₂Cl₂ (1 mL) together with ligand Lc (14.8 mg, 0.015 mmol). The reaction mixture turned bright orange instantly and was stirred for 15 minutes. Evaporation of solvent and volatiles left an orange solid in near-quantitative yield.

**3¹P[¹H] NMR**: (162 MHz, CD₂Cl₂): δ = 36.04;

**¹H NMR**: (400 MHz, CD₂Cl₂): δ = 11.14 (bs, s, 1H), 7.76 - 766 (m, 4H), 7.46 - 7.27 (m, 6H), 7.17 - 7.07 (m, 4H), 6.90 (s, 4H), 4.44 - 4.37 (m, 2H), 3.94 - 3.85 (m, 4H), 1.89 (s, 3H), 1.50 (s, 3H), 1.22 (dd, J = 6.9, 1.8 Hz, 12H), 0.93 (d, J = 6.7 Hz, 12H), 0.70 (d, J = 6.6 Hz, 12H).

**Complex 2a**
Complex 1a was stirred at room temperature in CH₂Cl₂ (1 mL) for 30 hours, during which time a color change from orange to bright yellow, reaction mixture was concentrated. Complex 2a was formed quantitatively as a diastereomeric mixture.

**3¹P[¹H] NMR**: (162 MHz, CD₂Cl₂, offset @ -10 ppm, with ratios): δ = 27.20 (d, J = 19.7 Hz, 1.0), 26.18 (d, J = 20.6 Hz, 0.2), 14.49 (d, J = 19.8 Hz, 1.0), 14.25 (d, J = 7.4 Hz, 0.45), 13.35 (d, J = 20.0 Hz, 0.2), 9.16 (d, J = 7.5 Hz, 0.45), 7.43 (d, J = 20.3 Hz, 0.4), 6.57 (d, J = 20.4 Hz, 0.8), 1.78 (d, J = 21.3 Hz, 0.4), 0.12 (d, J = 21.3 Hz, 0.8);

**¹H NMR**: (400 MHz, CD₂Cl₂): δ = 8.01 – 7.93 (m), 7.88 – 7.79 (m), 7.74 – 7.63 (m), 7.59 – 7.42 (m), 7.40 – 7.21 (m), 7.20 – 7.11 (m), 7.11 – 7.06 (m), 7.06 – 6.95 (m), 6.95 – 6.84 (m), 6.84 – 6.74 (m), 6.65 (d, J = 9.2 Hz, 1H), 2.65 – 2.51 (m), 2.14 (s), 2.11 (s), 2.08 (s), 2.03 (s), 1.92 (s), 1.74 (s), 1.59 – 1.49 (m), 1.50 (s), 1.39 – 1.23 (m), 0.99 – 0.93 (m), 0.93 – 0.86 (m), -22.65 (t, J = 21.0 Hz, 0.2), -22.74 (t, J = 21.7 Hz, 1.0), -24.76 (t, J = 25.1 Hz, 0.8) -24.99 (t, J = 25.7 Hz, 0.8), -28.66 (t, J = 22.0 Hz, 1H, 0.45); **HR MS (FAB⁺)**: m/z calcd. for C₄₇H₅₀Ir₅N₂O₄P₂S₂ [M+H]⁺: 1041.2266, observed: 1041.2256; **Anal. Calcd.** for C₄₇H₅₀Ir₅N₂O₄P₂S₂: C, 54.27; H, 4.75; N, 2.69, found: C, 54.05; H, 4.89, N, 2.73.

**Complex 2b**
Complex 1b was stirred at room temperature in toluene (1 mL) for 30 hours, during which time a color change from orange to yellow, reaction mixture was concentrated. Complex 2b was formed quantitatively as a diastereomeric mixture.

**3¹P[¹H] NMR**: (162 MHz, CD₂Cl₂, offset @ -10 ppm, with ratios): δ = 28.70 (d, J = 19.8 Hz, 1.0), 27.73 (d, J = 20.5 Hz, 0.2), 15.42 (d, J = 17.4 Hz, 0.1), 14.95 (d, J = 19.8 Hz, 1.0), 13.61 (d, J = 20.3 Hz, 0.2), 9.96 (d, J = 16.7 Hz, 0.1);

**¹H NMR**: (400 MHz, CD₂Cl₂, hydride region with ratios): δ = 8.29 (d, J = 8.2 Hz, 8.24 (d, J = 8.1 Hz), 7.82 (dt, J = 16.6, 8.3 Hz), 7.70 (d, J = 7.8 Hz), 7.58 (t, J = 7.6 Hz), 7.55 – 7.35 (m), 7.33 – 7.19 (m), 7.19 – 7.06 (m), 7.06 – 6.98 (m), 6.98 – 6.87 (m), 6.84 – 6.77 (m), 6.63 – 6.53 (m), 1.92 (s), 1.54 (s), -22.56 (t, J = 21.5 Hz, 0.2), -22.64 (t, J = 22.0 Hz, 1.0), -28.76 (t, J = 22.1 Hz, 0.1); **¹³F NMR** (282 MHz, CD₂Cl₂) δ = -63.22 (s), -63.52 (s); **HR MS (CSI⁺)**: m/z calcd. for C₄₅H₃₇F₇Ir₅N₂O₄P₂S₂ [M+H]⁺: 1065.0761, observed: 1065.0805; **Anal. Calcd.** for C₄₅H₃₇F₇Ir₅N₂O₄P₂S₂: C, 46.28; H, 2.94; N, 2.63, found: C, 46.01; H, 3.04, N, 2.69.

**Complex 2c**
Complex 1c was stirred at room temperature in CH$_2$Cl$_2$ (1 mL) for 16 hours at room temperature, during which time a color change from orange to light yellow, reaction mixture was concentrated. Complex 2c was formed quantitatively as a diastereomeric mixture.

$^{31}$P[$^1$H] NMR (162 MHz, CD$_2$Cl$_2$, offset @ -10 ppm, with ratios): $\delta = 29.74$ (d, $J = 18.1$ Hz, 1.0), 28.35 (d, $J = 19.3$ Hz, 0.5), 19.77 (d, $J = 18.2$ Hz, 1.0), 17.61 (d, $J = 19.2$ Hz, 0.5);

$^1$H NMR: (400 MHz, CD$_2$Cl$_2$, hydride region with ratios): 7.86 – 7.73 (m), 7.64 (d), 7.60 – 7.51 (m), 7.49 (d, $J = 7.6$ Hz), 7.43 (d, $J = 15.3$ Hz), 7.35 (ddd, $J = 14.3, 7.6, 2.0$ Hz), 7.28 – 7.16 (m), 7.14 (s), 7.12 (s), 7.06 – 7.03 (m), 7.03 (s), 6.95 (s), 6.94 (s), 6.91 – 6.81 (m), 6.77 – 6.69 (m), 6.58 (dd, $J = 15.5, 7.6$ Hz), 6.00 (s), 5.55 (s), 4.47 – 4.31 (m), 3.94 – 3.81 (m), 3.25 (m), 2.87 (m), 2.03 (s), 2.01 (s), 1.90 (s), 1.57 (s), 1.30 – 1.18 (m), 1.19 – 1.12 (m), 1.06 (d, $J = 6.6$ Hz), 1.00 (dd, $J = 6.7, 4.8$ Hz), 0.94 (d, $J = 6.6$ Hz), -21.87 (t, $J = 21.5$ Hz, 1.0), -22.93 (t, $J = 21.1$ Hz, 0.5); HR MS (CSI$^+$): m/z calcd. for C$_57$H$_{69}$Ir$_2$N$_2$O$_5$P$_2$S$_2$ [M+H]$^+$: 1181.3830, observed: 1181.3726; Anal. Calcd. for C$_57$H$_{69}$Ir$_2$N$_2$O$_5$P$_2$S$_2$: C, 58.00; H, 5.89; N, 2.37, found: C, 57.82; H, 5.93, N, 2.31.

VT-NMR of diastere-pure complex 2a

S1. Temperature dependence of $^{31}$P NMR of complex 2a (diastere-pure) in CD$_2$Cl$_2$. 
VT-NMR of diastereo-pure complex 2a with 1eq. HCOOH

S2. VT $^{31}$P NMR of complex 2a (diastereo-pure) with 1eq. of HCOOH in CD$_2$Cl$_2$.

S3. VT $^1$H NMR of complex 2a (diastereo-pure) with 1eq. of HCOOH in CD$_2$Cl$_2$. 
Crystal structure of 2c

C_{37}H_{71}IrN_{2}O_{6}P_{2}S_{2} \cdot CH_{2}Cl_{2} \cdot 0.5(C_{4}H_{10}O), \ Fw = 1320.40, colourless needle, 0.52 \times 0.12 \times 0.11 \text{ mm}^3, \text{triclinic, } P \overline{1} (no. 2), a = 11.6106(3), b = 17.2668(6), c = 18.6161(4) \ \text{Å}, \alpha = 113.198(2), \beta = 95.475(2), \gamma = 105.211(1)^\circ, \ V = 3226.02(16) \ \text{Å}^3, Z = 2, D_x = 1.359 g/cm^3, \mu = 2.31 \text{ mm}^{-1}. \text{The crystal appeared to crack into two fragments and was consequently integrated with two orientation matrices using the Eval15 software.} \ 50934 \text{ Reflections were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (}\lambda = 0.71073 \ \text{Å}) \text{ up to a resolution of } (\sin \theta/\lambda)_{\text{max}} = 0.65 \ \text{Å}^{-1} \text{ at a temperature of 150(2) K. Absorption correction and scaling based on multiple measured reflections was performed with TWINABS (0.59-0.75 correction range).} \ 14853 \text{ Reflections were unique (}R_{\text{int}} = 0.018\text{), of which 14073 were observed [I>2}\sigma(I)]. \text{The structure was solved with the program SHELXT and refined with SHELXL-2013 against F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms of the metal complex were located in difference-Fourier maps, and in the solvent molecules included in calculated positions. All hydrogen atoms were refined with a riding model. The diethyl ether molecule was refined with partial occupancy. 718 Parameters were refined with 30 restraints (for displacement parameters in the partially occupied diethyl ether). R1/wR2 [I > 2}\sigma(I)]: 0.0273 / 0.0777. R1/wR2 [all refl.]: 0.0293 / 0.0788. S = 1.073. Residual electron density between -1.14 and 3.46 e/Å^3. Geometry calculations and checking for higher symmetry was performed with the PLATON program.} \n
CCDC 1020151 contains 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.
Figure S4: Displacement ellipsoid plot of 2c in the crystal (50% probability level). Dichloromethane and diethyl ether solvent molecules and C-H hydrogen atoms in the metal complex are omitted for clarity.
Diastereomeric structure used in calculations

![Diastereomeric structure](image)

$\text{R} = \text{phenyl}$

Energies and imaginary frequencies of calculated structures

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Energy profiles of structures 3I and 4I

![Energy profiles diagram]

Figure S5. Potential energy surfaces (DFT, BP86, def2-TZVP) for dehydrogenation of formic acid by 3I and 4I ($\Delta G_{298K}^{\circ}$ in kcal mol$^{-1}$).
Figure S6. Potential energy surfaces (DFT, BP86, def2-TZVP) for dehydrogenation of formic acid by 5I and 6I ($\Delta G_{298K}^\circ$ in kcal mol$^{-1}$).
Energy profile of structure 7I

Rearrangement of HCOOH in 7I to orient the substrate in the right position for direct hydride-transfer to yield structure 7II was found to be endergonic by 23.5 kcal mol\(^{-1}\). The transition state (7III) of the direct hydride-transfer toward the dihydride structure 7IV was found to be significantly higher (29.9 kcal mol\(^{-1}\)) than for the axial structures 5III and 6III. Similar to the transition states previously found (5III and 6III) hydrogen-bonding interactions were also observed in 7III. The release of H\(_2\) has been described above, for complete energy profile of 7I see supporting information. Starting from complex 8I, rearrangement of HCOOH to enable direct hydride-transfer led to an unstable species and no transition state could be identified.

![Potential energy surfaces](image)

Figure S7. Potential energy surfaces (DFT, BP86, def2-TZVP) for dehydrogenation of formic acid by 7I (\(\Delta G_{298K}^\circ\) in kcal mol\(^{-1}\)).
Energy profile with CF$_3$ and CH$_3$ substituents

Figure S8. Potential energy surfaces (DFT, BP86, def2-TZVP) for dehydrogenation of formic acid by with CF$_3$ and CH$_3$ substituents ($\Delta G^{\circ}_{\text{298K}}$ in kcal mol$^{-1}$).
$^{31}$P NMR ligand La
$^1$H NMR ligand La
$^{13}$C NMR ligand La
$^{31}$P NMR ligand Lb
\(^1\text{H NMR ligand Lb}\)
$^{13}$C NMR ligand Lb
$^{19}\text{F NMR ligand Lb}$
$^1$H NMR ligand Le
$^{13}$C NMR ligand Lc
$^{31}$P NMR 2a
\(^{31}\text{P NMR 2b}\)
$^{1}H$ NMR 2b
$^{19}$F NMR 2b
"\(^1\)H NMR 2c"
References


