Supporting Information

for

A modular approach to neutral P,N-ligands:
synthesis and coordination chemistry

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Dedicated to the memory of Peter Hofmann.

Experimental procedures and analytical data

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1 General Information

All manipulations, except those indicated, were carried out under exclusion of air and moisture using standard Schlenk and glove box techniques. As inert gas, Argon 5.0, purchased from Messer Group GmbH, was used after drying over Granusic® phosphorus pentoxide granulate. Solvents were dried over activated alumina columns using a solvent purification system (M. Braun SPS 800) or according to standard literature-known methods and stored in glass ampules under an argon atmosphere [1]. Toluene was distilled from sodium, n-pentane from sodium/potassium alloy, tetrahydrofuran, benzene and n-hexane from potassium, and dichloromethane and chloroform from calcium hydride. The same procedures were used to dry the deuterated solvents. Degassed solvents were obtained by three successive freeze-pump-thaw-cycles. NMR spectra were recorded on Bruker Avance (400 MHz, 600 MHz) instruments. Chemical shifts (δ) are reported in parts per million (ppm) and are referenced to residual proton solvent signals or carbon resonances [2, 3]. H$_3$PO$_4$ ($^{31}$P) and CCl$_3$F ($^{19}$F) were used as external standards. The following abbreviations were used: s (singlet), d (doublet), dd (doublet of doublets), t (triplet), q (quartet), sept (septet), m (multiplet), br s (broad signal). High-resolution mass spectra were acquired on Bruker ApexQe hybrid 9.4 T FT-ICR (ESI, DART) and JEOL JMS-700 magnetic sector (FAB, EI, LIFDI) spectrometers at the mass spectrometry facility of the Institute of Organic Chemistry, of the University of Heidelberg. Elemental analyses were carried out in the Microanalysis Laboratory of the Heidelberg Chemistry Department on a vario MICRO cube (Elementar). All chemicals were obtained from commercial suppliers and were used without further purification. The formamidines 1a–c were prepared according to literature procedures [4–9]. Isobutyraldehyde 2,4,6-trimethylphenylimine 4 was synthesized following a standard condensation protocol [10, 11]. 2-(Diphenylphosphino)benzaldehyde 6 was obtained commercially from Sigma Aldrich (CAS 50777-76-9). Alternatively, 6 can be synthesized starting from commercially available 2-(2-bromophenyl)-1,3-dioxolane and chlorodiphenylphosphine through a lithiation, nucleophilic substitution, and deprotection sequence [12–14].
2 Synthetic Procedures and Analytical Data

2.1 Synthesis of Ligands 2a–c and 3a–c

Compounds 2a–c, 3a–c were synthesized following a general procedure.

General Procedure 1 (GP 1): To a solution of the formamidine (15.0 mmol, 1.0 equiv.) in 150 mL of THF at −78 °C was added dropwise a solution of t-butylium lithium in pentane (15.0 mmol, 1.0 equiv., 1.9 M). The reaction was left at this temperature for 30 min, warmed to r.t. and stirred for 1 h. This mixture was added to a solution of the chlorophosphine (15.0 mmol, 1.0 equiv.) in 150 mL of THF at −78 °C, stirred for 30 min at this temperature and warmed to r.t. over night. The solvent was removed under reduced pressure and the residue was taken up in 300 mL of toluene. The mixture was then filtered through a plug of Celite© and the solvent was evaporated in vacuo yielding the desired product as a colorless or yellow solid.

Preparation of Chiral Chlorophosphines: A procedure adapted from Cramer et al. was used [15]. A mixture of (S)-BINOL (10.0 mmol, 1.0 equiv.), freshly distilled PCl₃ (10 mL), and 3 drops of NMP was heated to reflux in 100 mL toluene for 10 min. The reaction mixture was concentrated in vacuo and the residue was distilled twice azeotropically with toluene to give the chiral chlorophosphine in quantitative yield. The product was used in GP 1 without further purification.
Compound 2a

yield: 4.80 g colorless solid (10.3 mmol, 97 %, GP 1).

$^1$H-NMR (399.89 MHz, THF-$d_8$): $\delta$ (ppm) = 1.92 (s, 6 H, H-13), 2.12 (s, 3 H, H-12), 2.16 (s, 6 H, H-7), 2.23 (s, 3 H, H-6), 6.65 (s, 2 H, H-10), 6.85 (s, 2 H, H-4), 7.34–7.45 (m, 6 H, H-16/H-17), 7.55–7.66 (m, 4 H, H-15), 7.82 (d, $J = 1.8$ Hz, 1 H, H-1).

$^{13}$C($^1$H)-NMR (100.55 MHz, THF-$d_8$): $\delta$ (ppm) = 19.07 (s, 2 C, C-13), 20.05 (d, $J = 1.2$ Hz, 2 C, C-7), 20.57 (s, 1 C, C-12), 20.76 (d, $J = 0.5$ Hz, 1 C, C-6), 128.45 (s, 2 C, C-9), 128.79 (s, 2 C, C-10), 129.19 (d, $J = 6.7$ Hz, 4 C, C-16), 129.86 (d, $J = 1.8$ Hz, 2 C, C-17), 130.27 (s, 2 C, C-4), 131.37 (s, 1 C, C-11), 133.85 (d, $J = 22.7$ Hz, 4 C, C-15), 136.95 (d, $J = 2.6$ Hz, 1 C, C-5), 137.00 (d, $J = 3.4$ Hz, 2 C, C-3), 139.28 (d, $J = 19.7$ Hz, 2 C, C-14), 139.83 (d, $J = 16.1$ Hz, 1 C, C-2), 147.91 (d, $J = 0.7$ Hz, 1 C, C-8), 152.80 (d, $J = 2.5$ Hz, 1 C, C-1).

$^{31}$P($^1$H)-NMR (161.88 MHz, THF-$d_8$): $\delta$ (ppm) = 49.70 (s, 1 P).

EA (C$_{31}$H$_{33}$N$_2$P): calcd. C: 80.14 %, H: 7.16 %, N: 6.03 %; found: C: 79.61 %, H: 7.33 %, N: 5.99 %.

HR-MS (DART+): [M+H]$^+$ = C$_{31}$H$_{34}$N$_2$P$^+$ calcd.: 465.2454 found: 465.2447.
Compound 2b

![Chemical Structure](image)

**Yield:** 6.75 g colorless solid (12.3 mmol, 90 %, GP 1).

**$^1$H-NMR (600.13 MHz, THF-$d_8$):** $\delta$ (ppm) = 0.96–1.08 (m, 18 H, H-7/H-13), 1.15–1.24 (m, 6 H, H-7/H-13), 2.94–3.06 (m, 2 H, H-12), 3.22–3.36 (m, 2 H, H-6), 6.81–6.88 (m, 1 H, H-11), 6.91–6.99 (m, 2 H, H-10), 7.15–7.21 (m, 2 H, H-4), 7.22–7.27 (m, 1 H, H-5), 7.35–7.44 (m, 6 H, H-16/H-17), 7.59–7.69 (m, 4 H, H-15), 7.82–7.91 (m, 1 H, H-1).

**$^{13}$C($^1$H)-NMR (150.90 MHz, THF-$d_8$):** $\delta$ (ppm) = 24.80 (s, 2 C, C-7/C-13), 24.89 (s, 4 C, C-7/C-13), 25.55 (s, 2 C, C-7/C-13), 28.08 (s, 2 C, C-12), 29.65 (s, 2 C, C-6), 123.55 (s, 2 C, C-10), 123.88 (s, 1 C, C-11), 125.06 (d, $J = 1.8$ Hz, 2 C, C-4), 128.94 (d, $J = 2.3$ Hz, 1 C, C-5), 129.64 (d, $J = 7.2$ Hz, 4 C, C-16), 130.86 (s, 2 C, C-17), 134.41 (d, $J = 23.7$ Hz, 4 C, C-15), 138.70 (d, $J = 20.1$ Hz, 2 C, C-14), 139.90 (d, $J = 18.6$ Hz, 1 C, C-2) 140.17 (s, 2 C, C-9), 147.75 (d, $J = 0.8$ Hz, 1 C, C-8), 148.19 (d, $J = 3.2$ Hz, 2 C, C-3), 153.84 (d, $J = 3.9$ Hz, 1 C, C-1).

**$^{31}$P($^1$H)-NMR (242.94 MHz, THF-$d_8$):** $\delta$ (ppm) = 47.51 (br s, 1 P).

**EA (C$_{37}$H$_{45}$N$_2$P):** calcd.: C: 80.98 %, H: 8.21 %, N: 5.11 %; found: C: 80.17 %, H: 8.01 %, N: 5.22 %.

**HR-MS (ESI+):** [M+H]$^+$ = C$_{37}$H$_{46}$N$_2$P$^+$ calcd.: 549.3393 found: 549.3396.
Compound 2c

yield: 7.50 g yellow oil (18.0 mmol, 84 %, GP 1).

$^1$H-NMR (600.13 MHz, THF-$d_8$): $\delta$ (ppm) = 6.72–6.78 (m, 2 H, H-7), 6.86–6.91 (m, 2 H, H-8), 6.96–6.99 (m, 2 H, H-4), 7.10–7.14 (m, 2 H, H-3), 7.38–7.43 (m, 6 H, H-Ar), 7.47–7.52 (m, 4 H, H-Ar), 8.07 (d, $J = 3.1$ Hz, 1 H, H-1).

$^{13}$C{${^1}$H}-NMR (150.90 MHz, THF-$d_8$): $\delta$ (ppm) = 115.44 (d, $J = 22.3$ Hz, 2 C, C-8), 115.46 (dd, $J = 22.6$ Hz, $J = 6.6$ Hz, 2 C, C-4), 122.43 (d, $J = 7.9$ Hz, 2 C, C-7), 128.94 (d, $J = 6.1$ Hz, 4 C, C-Ar), 130.03 (s, 2 C, C-Ar), 130.37–130.56 (m, 2 C, C-3), 132.76–133.03 (m, 4 C, C-Ar), 136.91 (d, $J = 16.6$ Hz, 2 C, C-10), 139.66 (m, 1 C, C-2), 147.57 (d, $J = 2.9$ Hz, 1 C, C-6), 154.53 (d, $J = 18.6$ Hz, 1 C, C-1), 160.12 (d, $J = 240.2$ Hz, 1 C, C-9), 161.41 (d, $J = 244.4$ Hz, 1 C, C-5).

$^{31}$P{${^1}$H}-NMR (242.94 MHz, THF-$d_8$): $\delta$ (ppm) = 60.64 (s, 1 P).

EA (C$_{25}$H$_{19}$F$_2$N$_2$P): calcd. C: 72.11 %, H: 4.60 %, N: 6.73 %; found: C: 71.49 %, H: 4.81 %, N: 6.66 %.

HR-MS (ESI+): [M+H]$^+$ = C$_{25}$H$_{20}$F$_2$N$_2$P$^+$ calcd.: 417.1327 found: 417.1337.
Compound 3a

yield: 9.50 g yellow solid (16.0 mmol, 92 %, GP 1).

$^1$H-NMR (600.13 MHz, THF-$d_8$): $\delta$ (ppm) = 1.84 (s, 6 H, H-13), 2.03 (s, 3 H, H-12), 2.29 (s, 3 H, H-7), 2.45 (s, 3 H, H-6), 2.62 (s, 3 H, H-7), 6.52 (s, 2 H, H-10), 6.99 (s, 1 H, H-4), 7.01 (s, 1 H, H-4), 7.17–7.23 (m, 2 H, H-20/H-21), 7.25–7.29 (m, 2 H, H-19/H-22), 7.35–7.39 (m, 1 H, H-20/H-21), 7.40 (d, $J =$ 1.5 Hz, 1 H, H-1), 7.41–7.45 (m, 1 H, H-20/H-21), 7.56 (d, $J =$ 8.6 Hz, 1 H, H-17), 7.68 (d, $J =$ 8.8 Hz, 1 H, H-17), 7.89 (d, $J =$ 8.4 Hz, 1 H, H-19/H-22), 7.96 (d, $J =$ 8.6 Hz, 1 H, H-19/H-22), 8.00 (d, $J =$ 8.6 Hz, 1 H, H-16), 8.08 (d, $J =$ 8.8 Hz, 1 H, H-16).

$^{13}$C{$^1$H}-NMR (150.90 MHz, THF-$d_8$): $\delta$ (ppm) = 19.10 (s, 2 C, C-13), 19.31 (d, $J =$ 3.8, 1 C, C-7), 19.81 (s, 1 C, C-7), 20.73 (s, 1 C, C-12), 21.16 (s, 1 C, C-6), 122.22 (s, 1 C, C-17), 122.31 (d, $J =$ 1.6 Hz, 1 C, C-17), 123.65 (d, $J =$ 2.4 Hz, 1 C, C-Ar), 124.99 (d, $J =$ 5.5 Hz, 1 C, C-Ar), 125.40 (d, $J =$ 5.5 Hz, 1 C, C-Ar), 125.95 (s, 1 C, C-20/C-21), 126.12 (s, 1 C, C-20/C-21), 127.32 (s, 1 C, C-20/C-21), 127.64 (s, 1 C, C-19/C-22), 128.12 (s, 2 C, C-9), 128.92 (s, 2 C, C-10), 128.96 (s, 1 C, C-11), 129.24 (s, 1 C, C-19/C-22), 129.43 (s, 1 C, C-19/C-22), 130.03 (m, 2 C, C-4), 131.51 (s, 1 C, C-16), 131.88 (d, $J =$ 1.3 Hz, 1 C, C-16), 132.18 (s, 1 C, C-Ar), 133.43 (d, $J =$ 1.0 Hz, 1 C, C-Ar), 133.69 (d, $J =$ 1.5 Hz, 1 C, C-Ar), 134.88 (d, $J =$ 18.6 Hz, 1 C, C-2), 138.05 (d, $J =$ 4.3 Hz, 1 C, C-Ar), 138.51 (d, $J =$ 2.9 Hz, 1 C, C-Ar), 138.75 (d, $J =$ 4.4 Hz, 1 C, C-Ar), 146.80 (s, 1 C, C-8), 148.25 (br s, 1 C, C-1), 149.20 (d, $J =$ 6.5 Hz, 1 C, C-Ar), 149.43 (s, 1 C, C-Ar).

$^{31}$P{$^1$H}-NMR (242.94 MHz, THF-$d_8$): $\delta$ (ppm) = 135.44 (s, 1 P).

EA (C$_{39}$H$_{45}$N$_2$O$_2$P): calcd. C: 78.77 %, H: 5.93 %, N: 4.71 %; found: C: 78.81 %, H: 6.16 %, N: 4.57 %.

HR-MS (ESI+): [M+H]$^+$ = C$_{39}$H$_{46}$N$_2$O$_2$P$^+$ calcd.: 595.2509 found: 595.2488.
yield: 10.8 g yellow solid (15.9 mmol, 91 %, GP 1).

$^1$H-NMR (600.13 MHz, THF-$d_8$): $\delta$ (ppm) = 0.86 (d, $J = 6.6$ Hz, 6 H, H-13), 1.07 (d, $J = 6.9$ Hz, 6 H, H-13), 1.27 (d, $J = 6.8$ Hz, 6 H, H-7), 1.40 (d, $J = 6.4$ Hz, 3 H, H-7), 1.43 (d, $J = 6.7$ Hz, 3 H, H-7) 2.89–3.03 (m, 2 H, H-12), 3.48 (sept, $J = 6.8$ Hz, 1 H, H-6), 3.62 (sept, $J = 6.8$ Hz, 1 H, H-6), 6.72–6.78 (m, 1 H, H-Ar), 6.80–6.86 (m, 2 H, H-Ar), 7.16–7.31 (m, 6 H, H-Ar), 7.30–7.34 (m, 2 H, H-Ar), 7.34–7.38 (m, 1 H, H-Ar), 7.40–7.46 (m, 1 H, H-17), 7.42 (d, $J = 1.1$ Hz, 1 H, H-1), 7.58 (d, $J = 8.8$ Hz, 1 H, H-17), 7.80 (d, $J = 8.2$ Hz, 1 H, H-20/H-21), 7.84 (d, $J = 8.8$ Hz, 1 H, H-19/H-22), 7.98 (d, $J = 8.3$ Hz, 1 H, H-16), 8.09 (d, $J = 8.8$ Hz, 1 H, H-16).

$^{13}$C$[^1$H$]$-NMR (150.90 MHz, THF-$d_8$): $\delta$ (ppm) = 23.96 (br s, 1 C, C-7), 24.43 (s, 2 C, C-13), 24.53 (s, 2 C, C-13), 24.72 (br s, 1 C, C-7), 25.59 (br s, 1 C, C-7), 26.14 (br s, 1 C, C-7), 28.29 (s, 2 C, C-12), 29.76 (s, 1 C, C-6), 29.81 (s, 1 C, C-6), 121.96 (s, 1 C, C-17), 122.28 (s, 1 C, C-17), 123.26 (s, 2 C, C-Ar), 123.64 (d, $J = 1.8$ Hz, 1 C, C-Ar), 124.08 (s, 1 C, C-Ar), 124.81 (s, 1 C, C-Ar), 125.16 (d, $J = 1.5$ Hz, 1 C, C-Ar), 125.23 (d, $J = 5.5$ Hz, 1 C, C-Ar), 126.05 (s, 1 C, C-Ar), 126.33 (s, 1 C, C-Ar) 127.41 (s, 1 C, C-Ar), 127.48 (s, 1 C, C-Ar), 127.67 (s, 1 C, C-Ar), 127.78 (s, 1 C, C-Ar), 129.26 (s, 1 C, C-20/C-21), 129.55 (s, 1 C, C-16), 129.97 (d, $J = 1.9$ Hz, 1 C, C-Ar), 132.12 (s, 1 C, C-Ar), 131.72 (br s, 1 C, C-19/C-22), 132.09 (s, 1 C, C-16), 132.12 (s, 1 C, C-Ar), 133.09 (s, 1 C, C-Ar), 133.09 (s, 1 C, C-Ar), 133.70 (d, $J = 1.0$ Hz, 1 C, C-Ar), 133.85 (d, $J = 1.5$ Hz, 1 C, C-Ar), 134.60 (d, $J = 16.0$ Hz, 1 C, C-Ar) 139.64 (s, 2 C, C-Ar), 146.91 (s, 1 C, C-Ar), 149.17–149.34 (m, 2 C, C-Ar), 149.46 (s, 1 C, C-Ar), 149.74 (d, $J = 6.7$ Hz, 1 C, C-Ar) 150.39 (br s, 1 C, C-1).

$^{31}$P$[^1$H$]$-NMR (242.94 MHz, THF-$d_8$): $\delta$ (ppm) = 136.34 (s, 1 P).

EA (C$_{45}$H$_{47}$N$_2$O$_2$P): calcd. C: 79.62 %, H: 6.98 %, N: 4.13 %; found: C: 78.98 %, H: 6.91 %, N: 4.10 %.

HR-MS (ESI+): [M+H]$^+$ = C$_{45}$H$_{47}$N$_2$O$_2$P$^+$ calcd.: 679.3448 found: 679.3454.
Compound 3c

yield: 8.32 g colorless solid (15.2 mmol, 87 %, GP 1).

$^1$H-NMR (600.13 MHz, CD$_2$Cl$_2$): δ (ppm) = 6.14–6.26 (m, 2 H, H-7), 6.54–6.68 (m, 2 H, H-8), 7.07–7.15 (m, 2 H, H-4) 7.28–7.41 (m, 6 H, H-Ar), 7.44 (d, $J = 8.4$ Hz, 1 H, H-13), 7.46–7.50 (m, 1 H, H-16/H-17), 7.52–7.56 (m, 1 H, H-16/H-17), 7.58 (d, $J = 8.8$ Hz, 1 H, H-13), 7.68 (d, $J = 1.8$ Hz, 1 H, H-1), 7.95–8.02 (m, 2 H, H-Ar), 8.02 (d, $J = 8.4$ Hz, 1 H, H-12), 8.06 (d, $J = 8.8$ Hz, 1 H, H-12).

$^{13}$C{$^1$H}-NMR (150.90 MHz, CD$_2$Cl$_2$): δ (ppm) = 115.26 (d, $J = 22.3$ Hz, 2 C, C-8), 116.33 (d, $J = 22.6$ Hz, 2 C, C-4), 120.81 (d, $J = 8.8$ Hz, 1 C, C-Ar), 121.31 (d, $J = 1.5$ Hz, 1 C, C-Ar), 121.63 (s, 1 C, C-Ar), 122.16 (d, $J = 8.1$ Hz, 2 C, C-7), 123.75 (d, $J = 2.1$ Hz, 1 C, C-Ar), 123.84 (d, $J = 5.1$ Hz, 1 C, C-Ar), 125.60 (s, 1 C, C-Ar), 125.73 (s, 1 C, C-Ar), 126.82 (s, 1 C, C-Ar), 126.93 (s, 1 C, C-Ar), 126.99 (s, 2 C, C-Ar), 128.40 (s, 1 C, C-Ar), 128.63 (s, 1 C, C-Ar), 128.65 (s, 1 C, C-Ar), 130.58 (dd, $J = 6.0$ Hz, $J = 8.8$ Hz, 2 C, C-3), 130.78 (s, 1 C, C-12), 131.16 (s, 1 C, C-12), 132.78 (d, $J = 1.2$ Hz, 1 C, C-Ar), 132.85 (d, $J = 1.2$ Hz, 1 C, C-Ar), 133.90 (dd, $J = 16.3$ Hz, $J = 2.9$ Hz, 1 C, C-2), 146.32 (dd, $J = 1.1$ Hz, $J = 2.6$ Hz, 1 C, C-6), 147.50 (d, $J = 4.2$ Hz, 1 C, C-Ar), 148.08 (d, $J = 1.8$ Hz, 1 C, C-Ar), 149.34 (d, $J = 6.6$ Hz, 1 C, C-1), 159.94 (d, $J = 241.9$ Hz, 1 C, C-9), 161.90 (d, $J = 246.9$ Hz, 1 C, C-5).

$^{31}$P{$^1$H}-NMR (242.94 MHz, CD$_2$Cl$_2$): δ (ppm) = 140.44 (s, 1 P).

EA (C$_{33}$H$_{21}$F$_2$N$_2$O$_2$P): calcd. C: 72.57 %, H: 3.87 %, N: 5.13 %; found: C: 71.99 %, H: 3.98 %, N: 5.34 %.

HR-MS (ESI+): [M+H]$^+$ = C$_{33}$H$_{22}$F$_2$N$_2$O$_2$P$^+$ calcd.: 547.1382 found: 547.1384.
2.2 Synthesis of Ligand 5

This compound was synthesized according to an adapted literature procedure [11]:

Isobutyraldehyde 2,4,6-trimethylphenylimine (2.01 g, 10.6 mmol, 1.0 equiv.) was dissolved in 50 mL of THF and cooled to −78 °C. A solution of t-butyl lithium (1.7 M in hexanes, 6.24 mL, 10.6 mmol, 1.0 equiv.) was added dropwise, the mixture was allowed to warm to r.t., and stirred for 1 h at this temperature. A solution of chlorodiphenylphosphine (2.34 g, 1.90 mL, 10.6 mmol, 1.0 equiv.) in 50 mL of THF was cooled to −78 °C and the lithiated imine was added dropwise. The mixture was stirred overnight and the volatiles were removed under reduced pressure. The residue was dried thoroughly, extracted with toluene and filtered through a plug of Celite®. The clear yellow filtrate was concentrated under reduced pressure, yielding an orange-brown oil (3.17 g, 8.48 mmol, 80%).

$^1$H-NMR (600.13 MHz, CDCl₃): $\delta$ (ppm) = 1.46 (d, $J = 13.4$ Hz, 6 H, H-9), 1.96 (s, 6 H, H-7), 2.21 (s, 3 H, H-6), 6.78 (s, 2 H, H-4), 7.30-7.31 (m, 6 H, H-Ar), 7.56-7.57 (m, 4 H, H-Ar), 7.61 (d, $J = 2.1$ Hz, 1 H, H-1).

$^{13}$C-NMR (150.90 MHz, CDCl₃): $\delta$ (ppm) = 18.70 (s, 2 C, C-7), 20.79 (s, 1 C, C-6), 24.32 (d, $J = 16.7$ Hz, 2 C, C-9), 40.89 (d, $J = 18.1$ Hz, 1 C, C-8), 127.22 (s, 2 C, C-3), 128.36 (d, $J = 6.8$ Hz, 4 C, C-12), 128.88 (s, 2 C, C-4), 129.06 (s, 2 C, C-13), 132.85 (s, 1 C, C-5), 134.72 (d, $J = 19.4$ Hz, 4 C, C-11), 135.23 (d, $J = 17.6$ Hz, 2 C, 10), 148.33 (s, 1 C, C-2), 171.94 (d, $J = 5.0$ Hz, 1 C, C-1).

$^{31}$P{$^1$H}-NMR (242.92 MHz, CDCl₃): $\delta$ (ppm) = 17.41 (s, 1 P).

HR-MS (ESI+): [M]$^+$ = C₂₅H₂₈NP$^+$ calcd.: 373.1954 found: 373.1932.
2.3 Synthesis of Ligand 7

This compound was synthesized according to a modified literature procedure [16–18]:

2-(Diphenylphosphino)benzaldehyde (2.09 g, 7.20 mmol, 1.0 equiv.) and mesitylamine (1.01 g, 7.44 mmol, 1.03 mmol) were dissolved in 40 mL toluene. The orange solution was heated to 135 °C for 20 h under a dropping funnel filled with molecular sieves. Evaporating the solvent \textit{in vacuo} yielded the product as a yellow solid, which was used in following syntheses without further purification (2.60 g, 6.38 mmol, 89 %).

$^1$H-NMR (600.13 MHz, CDCl$_3$): $\delta$ (ppm) = 1.84 (s, 6 H, H-7), 2.25 (s, 3 H, H-6), 6.81 (s, 2 H, H-4), 6.91–6.95 (m, 1 H, H-Ar), 7.19 (d, $J = 7.0$ Hz, 1 H, H-Ar), 7.23–7.31 (m, 5 H, H-Ar), 7.31–7.37 (m, 5 H, H-Ar), 7.39 (t, $J = 7.7$ Hz, 1 H, H-Ar), 7.50 (t, $J = 7.6$ Hz, 1 H, H-Ar), 8.90 (d, $J = 5.6$ Hz, 1 H, H-Ar).

$^{13}$C-NMR (150.90 MHz, CDCl$_3$): $\delta$ (ppm) = 18.02 (s, 2 C, C-7), 20.86 (s, 1 C, C-6), 127.22 (s, 2 C, C-3), 127.71 (d, $J = 4.7$ Hz, 1 C, C-10), 128.63 (s, 2 C, C-4), 128.79 (d, $J = 7.1$ Hz, 4 C, C-16), 129.07 (s, 2 C, C-17), 129.11 (s, 1 C, C-11), 131.06 (s, 1 C, C-12/C-13), 132.97 (s, 1 C, C-5), 133.47 (s, 1 C, C-12/C-13), 134.24 (d, $J = 20.1$ Hz, 4 C, C-15), 136.38 (d, $J = 10.0$ Hz, 2 C, C-14), 138.63 (d, $J = 19.9$ Hz, 1 C, C-9), 139.47 (d, $J = 17.5$ Hz, 1 C, C-8), 148.61 (s, 1 C, C-2), 161.40 (d, $J = 23.6$ Hz, 1 C, C-1).

$^{31}$P-NMR (242.94 MHz, CDCl$_3$): $\delta$ (ppm) = −14.63 (s, 1 P).

HR-MS (ESI+): [M]$^+$ = C$_{28}$H$_{26}$NP$^+$  calcd.: 407.1797  found: 407.1812.
2.4 Synthesis of Metal Complexes

All metal complexes were synthesized following General Procedures 3 and 4 (GP 2 top, GP 3 bottom). In GP 2 and GP 3 the following metal precursors were used: [Pd(cod)Cl$_2$], [Pd(allyl)Cl]$_2$, [Cp*RhCl$_2$]$_2$, [Cp*IrI$_2$]$_2$, [Rh(cod)$_2$]BF$_4$, [Ir(cod)Cl]$_2$.

General Procedure 2 (GP 2): A solution of the ligand (100 µmol, 1.0 equiv.) in 5 mL of DCM was added to the metal precursor [M]–X (100 µmol, 1.0 equiv.) and the mixture was stirred for 30 minutes. At this point, the product was either isolated by layering with toluene and pentane yielding the desired neutral product or AgBF$_4$ (100 µmol, 1.0 equiv.) was added to produce the cationic derivative. The suspension was then stirred in the dark for another 30 minutes, the solid residue was filtered off and the filtrate was layered with toluene and pentane, and stored at −40 °C. This procedure yielded a powder or in several cases single crystals suitable for X-ray diffraction. The solid was then washed with pentane and dried under high vacuum for several days to remove residual solvent.

General Procedure 3 (GP 3): A solution of the ligand (100 µmol, 1.0 equiv.) in 5 mL DCM was added to the metal precursor [M]–BF$_4$ (100 µmol, 1.0 equiv.). The mixture was stirred for 30 minutes, filtered, layered with toluene and pentane and stored at −40 °C. This procedure yielded a powder or in several cases single crystals suitable for X-ray diffraction. The solid was then washed with pentane and dried under high vacuum for several days to remove residual solvent.
**Compound [2a-PdCl₂]**

![Compound Structure](image)

**yield:** 350 mg light yellow solid (545 μmol, 78 %, GP 2).

**¹H-NMR (399.89 MHz, CD₂Cl₂):** δ (ppm) = 1.47 (s, 6 H, H-7), 2.23 (s, 3 H, H-6), 2.29 (s, 3 H, H-12), 2.42 (s, 6 H, H-13), 6.75 (s, 2 H, H-4), 6.94 (s, 2 H, H-10), 7.21 (d, J = 37.6 Hz, 1 H, H-1), 7.50–7.59 (m, 4 H, H-16), 7.66–7.75 (m, 2 H, H-17), 7.95–8.07 (m, 4 H, H-15).

**¹³C{¹H}-NMR (100.55 MHz, CD₂Cl₂):** δ (ppm) = 18.62 (s, 2 C, C-7), 19.46 (s, 2 C, C-13), 21.00 (s, 1 C, C-12), 21.12 (s, 1 C, C-6), 125.51 (d, J = 61.3 Hz, 2 C, C-14), 129.02 (s, 2 C, C-10), 129.35 (d, J = 12.4 Hz, 4 C, C-16), 130.55 (s, 2 C, C-4), 130.97 (d, J = 6.6 Hz, 1 C, C-2), 133.04 (s, 2 C, C-9), 134.16 (d, J = 2.7 Hz, 2 C, C-17), 137.42 (s, 1 C, C-11), 137.66 (s, 2 C, C-3), 135.87 (d, J = 13.5 Hz, 4 C, C-15), 140.77 (s, 1 C, C-5), 141.92 (s, 1 C, C-8), 166.31 (d, J = 19.6 Hz, 1 C, C-1).

**³¹P{¹H}-NMR (161.88 MHz, CD₂Cl₂):** δ (ppm) = 101.11 (s, 1 P).

**EA (C₃₁H₃₃N₂PPdCl₂):** calcd. C: 58.00 %, H: 5.18 %, N: 4.36 %; found: C: 57.52 %, H: 5.38 %, N: 4.11 %.

**MS (LIFDI+):** [M−Cl]⁺ = C₃₁H₃₃N₂PPdCl⁺  calcd.: 605.1  found: 603.8.
Compound \([2a-PdCl]_2(BF_4)_2\)

**yield:** 81.0 mg colorless solid (58.4 \(\mu\)mol, 75 %, GP 2).

The compound was isolated as a dimer in the solid state. At r.t. a dynamic equilibrium between monomeric and dimeric species was found in CDCl\(_3\) solution. Chemical shifts are provided for the average structure in CD\(_2\)Cl\(_2\). For a VT-NMR study of compound \([2a-PdCl]_2(BF_4)_2\) see Section 3.

\(^1\)H-NMR (600.13 MHz, CD\(_2\)Cl\(_2\)): \(\delta\) (ppm) = 1.01–2.62 (m, 18 H, H-6/H-7/H-12/H-13), 6.58-6.19 (m, 15 H, H-Ar/H-1).

\(^{13}\)C\(^{\text{1}}\)H-NMR (150.90 MHz, CD\(_2\)Cl\(_2\)): \(\delta\) (ppm) = 18.94 (br s, 4 C, C-7/C-13), 19.41 (br s, 4 C, C-7/C-13), 21.04 (br s, 2 C, C-6/C-12), 21.15 (br s, 2 C, C-6/C-12), 122.39 (d, \(J = 65.5\) Hz, 4 C, C-14), 128.65 (br s, 2 C, C-Ar), 129.77 (br s, 4 C, C-4/C-10), 130.49 (br s, 8 C, C-15/C-16) 131.02 (br s, 4 C, C-4/C-10), 133.23 (br s, 4 C, C-Ar), 135.36 (br s, 8 C, C-15/C-16), 136.37 (br s, 4 C, C-17), 137.46 (br s, 4 C, C-Ar), 139.61 (br s, 4 C, C-Ar), 142.10 (br s, 2 C, C-Ar), 168.10 (br s, 2 C, C-1).

\(^{31}\)P\(^{\text{1}}\)H-NMR (242.93 MHz, CD\(_2\)Cl\(_2\)): \(\delta\) (ppm) = 108.85 (br s, 2 P).

EA (C\(_62\)H\(_{66}\)Cl\(_2\)N\(_4\)P\(_2\)Pd\(_2\)B\(_2\)F\(_8\)): calcd. C: 53.71 %, H: 4.80 %, N: 4.04 %; found: C: 53.96 %, H: 4.79 %, N: 4.43 %.

HR-MS (ESI\(^+\)): \([2M-2BF_4]^{2+}\) = C\(_{62}\)H\(_{66}\)Cl\(_2\)N\(_4\)P\(_2\)Pd\(_2\)\(^{2+}\) calcd.: 606.1101 found: 606.1144.
Compound [2a-Pd(allyl)]BF$_4$

yield: 125 mg yellow solid (178 µmol, 83 %, GP 2).

$^1$H-NMR (600.13 MHz, CD$_2$Cl$_2$): $\delta$ (ppm) = 1.40 (s, 3 H, CH$_3$), 1.48 (s, 3 H, CH$_3$), 2.26 (s, 3 H, CH$_3$), 2.27 (s, 3 H, CH$_3$), 2.31 (s, 3 H, CH$_3$), 2.38 (s, 3 H, CH$_3$), 2.99 (d, $J = 12.6$ Hz, H-20), 3.83 (dd, $J = 10.2$ Hz, $J = 14.0$ Hz, 1 H, H-18), 4.04–4.13 (m, 2 H, H-18/H-20), 5.88–5.97 (m, 1 H, H-19), 6.80 (s, 1 H, H-4/H-10), 6.82 (s, 1 H, H-4/H-10), 6.97 (s, 1 H, H-4/H-10), 6.99 (s, 1 H, H-4/H-10), 7.50 (d, $J = 22.3$ Hz, 1 H, H-1), 7.50–7.63 (m, 6 H, H-15/H-17), 7.66–7.77 (m, 4 H, H-16).

$^{13}$C$^{[1]H}$-NMR (150.90 MHz, CD$_2$Cl$_2$): $\delta$ (ppm) = 18.49 (s, 1 C, CH$_3$), 18.58 (s, 1 C, CH$_3$), 19.20 (s, 2 C, CH$_3$), 20.93 (s, 1 C, CH$_3$), 21.04 (s, 1 C, CH$_3$), 55.79 (d, $J = 4.1$ Hz, 1 C, C-20), 82.28 (d, $J = 31.1$ Hz, 1 C, C-18), 123.66 (d, $J = 5.9$ Hz, 1 C, C-19), 126.80 (s, 1 C, C-Ar), 127.14 (d, $J = 19.0$ Hz, 1 C, C-Ar), 129.74 (s, 1 C, C-4/C-10), 129.79 (s, 1 C, C-4/C-10), 129.90 (s, 1 C, C-Ar), 129.97 (s, 2 C, C-Ar), 130.03 (s, 1 C, C-Ar), 130.06 (s, 1 C, C-Ar), 130.61 (s, 1 C, C-4/C-10), 130.68 (s, 1 C, C-4/C-10), 132.16 (d, $J = 6.7$ Hz, 1 C, C-Ar), 134.32 (s, 2 C, C-Ar), 134.94 (s, 1 C, C-Ar), 135.04 (s, 2 C, C-Ar), 135.16 (s, 2 C, C-Ar), 136.96 (s, 1 C, C-Ar), 137.59 (d, $J = 32.3$ Hz, 2 C, C-14), 140.79 (s, 1 C, C-Ar), 146.04 (s, 1 C, C-Ar), 166.78 (d, $J = 20.3$ Hz, 1 C, C-1).

$^{31}$P$^{[1]}$H-NMR (242.93 MHz, CD$_2$Cl$_2$): $\delta$ (ppm) = 98.88 (s, 1 P).

EA (C$_{34}$H$_{38}$N$_2$PdBF$_4$ + 0.5 CH$_2$Cl$_2$): calcd. C: 55.90 %, H: 5.30 %, N: 3.78 %; found: C: 56.33 %, H: 5.46 %, N: 3.82 %. The presence of half an equivalent of dichloromethane was accounted for.

HR-MS (ESI+): [M–BF$_4$]$^+$ = C$_{34}$H$_{38}$N$_2$Pd$^+$ calcd.: 613.1806 found: 613.1802.
Compound [2a-Rh(cod)]BF$_4$

yield: 137 mg yellow solid (182 μmol, 85 %, GP 3).

$^1$H-NMR (399.89 MHz, CD$_2$Cl$_2$): $\delta$ (ppm) = 1.34 (s, 6 H, H-7), 2.07 (s, 3 H, H-6), 2.08–2.34 (m, 8 H, H-19/H-20), 2.17 (s, 3 H, H-12), 2.29 (s, 6 H, H-13), 3.58–3.84 (m, 2 H, H-21), 4.46–4.72 (m, 2 H, H-18), 6.57 (s, 2 H, H-4), 6.87 (s, 2 H, H-10), 7.23 (dd, $J = 2.9$ Hz, $J = 29.2$ Hz, 1 H, H-1), 7.40–7.49 (m, 4 H, H-16), 7.52–7.62 (m, 2 H, H-17), 7.63–7.73 (m, 4 H, H-15).

$^{13}$C($^1$H)-NMR (100.55 MHz, CD$_2$Cl$_2$): $\delta$ (ppm) = 19.04 (s, 2 C, C-7), 19.21 (s, 2 C, C-13), 20.91 (s, 1 C, C-6/C-12), 20.99 (s, 1 C, C-6/C-12), 28.95 (s, 2 C, C-20), 31.68 (d, $J = 2.3$ Hz, 2 C, C-19), 83.47 (d, $J = 11.1$ Hz, C-21), 111.36 (dd, $J = 7.0$ Hz, $J = 10$ Hz, C-18), 126.35 (dd, $J = 48.8$ Hz, $J = 1.9$ Hz, 2 C, C-14) 129.41 (d, $J = 11.2$ Hz, 4 C, C-16), 130.18 (s, 2 C, C-4), 130.44 (s, 2 C, C-10), 131.48 (s, 2 C, C-9), 131.68 (d, $J = 6.8$ Hz, 1 C, C-2) 134.04 (d, $J = 2.1$ Hz, 2 C, C-17), 135.38 (d, $J = 14.8$ Hz, 4 C, C-15), 137.34 (s, 2 C, C-3) 137.77 (s, 1 C, C-18), 140.44 (s, 1 C, C-5), 141.64 (s, 1 C, C-11) 169.17 (d, $J = 20.9$ Hz, 1 C, C-1).

$^{31}$P($^1$H)-NMR (161.88 MHz, CD$_2$Cl$_2$): $\delta$ (ppm) = 111.49 (d, $J = 176.3$ Hz, 1 P).

EA (C$_{39}$H$_{45}$N$_2$PRhBF$_4$): calcd. C: 61.43 %, H: 5.95 %, N: 3.67 %; found: C: 62.34 %, H: 6.09 %, N: 3.43 %.

HR-MS (ESI+): [M–BF$_4$]$^+$ = C$_{39}$H$_{45}$N$_2$PRh$^+$ calcd.: 675.2370 found: 675.2366.
Compound [2b-Rh(cod)]BF₄

**yield:** 115 mg yellow solid (136 µmol, 75 %, GP 3).

**¹H-NMR (399.89 MHz, CD₂Cl₂):** δ (ppm) = 0.21 (d, J = 6.6 Hz, 3 H, H-7), 0.92 (d, J = 6.8 Hz, 3 H, H-7), 1.27 (d, J = 6.9 Hz, 3 H, H-13), 1.61 (d, J = 6.8 Hz, 3 H, H-13), 2.07–2.28 (m, 6 H, H-19/H-20), 2.29–2.41 (m, 2 H, H-19/H-20), 2.68 (sept, J = 6.7 Hz, 2 H, H-6), 3.50 (sept, J = 6.8 Hz, 2 H, H-12), 3.71–3.78 (m, 2 H, H-21), 4.68 (m, 2 H, H-18), 7.06 (d, J = 7.8 Hz, 2 H, H-Ar), 7.28–7.38 (m, 4 H, H-Ar), 7.53–7.70 (m, 11 H, H-Ar/H-1).

**¹³C{¹H}-NMR (100.55 MHz, CD₂Cl₂):** δ (ppm) = 21.50 (s, 2 C, C-7), 23.13 (s, 2 C, C-7), 26.32 (s, 2 C, C-13), 27.94 (s, 2 C, C-13), 28.46 (d, J = 1.1 Hz, 2 C, C-20), 29.18 (s, 2 C, C-12), 30.08 (s, 2 C, C-6), 31.63 (d, J = 2.3 Hz, 2 C, C-19), 84.25 (d, J = 11.1 Hz, 2 C, C-21), 110.90 (dd, J = 10.0 Hz, J = 6.8 Hz, 2 C, C-18), 125.02 (s, 2 C, C-4/C-10), 125.58 (s, 2 C, C-4/C-10), 126.51 (dd, J = 48.4 Hz, J = 1.9 Hz, 2 C, C-14), 128.77 (s, 1 C, C-5/C-11), 129.93 (d, J = 11.2 Hz, 4 C, C-16), 130.53 (d, J = 6.6 Hz, 2 C, C-2), 131.26 (s, 2 C, C-5/C-11), 134.00 (d, J = 2.1 Hz, 2 C, C-17), 135.38 (d, J = 14.6 Hz, 4 C, C-15), 141.24 (s, 1 C, C-8), 142.33 (s, 2 C, C-3/C-9), 148.25 (s, 2 C, C-3/C-9), 167.24 (d, J = 20.7 Hz, 1 C, C-1).

**³¹P{¹H}-NMR (161.88 MHz, CD₂Cl₂):** δ (ppm) = 112.23 (d, J = 176.4 Hz, 1 P).

**HR-MS (ESI+):** [M−BF₄]⁺ = C₄₅H₅₇N₂PRh⁺ calcd.: 759.3309 found: 759.3299.
Compound [2c-Rh(cod)]BF$_4$

![Chemical Structure of [2c-Rh(cod)]BF$_4$]

**yield:** 150 mg yellow solid (212 µmol, 88 %, GP 3).

$^1$H-NMR (399.89 MHz, CD$_2$Cl$_2$): $\delta$ (ppm) = 2.11–2.19 (m, 2 H, H-16), 2.19–2.26 (m, 2 H, H-17), 2.26–2.38 (m, 2 H, H-17), 2.38–2.46 (m, 2 H, H-16), 3.71–3.78 (m, 2 H, H-18), 4.99–5.12 (m, 2 H, H-15), 6.72–6.80 (m, 2 H, H-3), 6.83–6.89 (m, 2 H, H-4), 7.11–7.18 (m, 2 H, H-8), 7.28–7.33 (m, 2 H, H-7), 7.58–7.64 (m, 4 H, H-12), 7.66–7.75 (m, 6 H, H-11/H-13), 7.79 (dd, $J = 2.7$ Hz, $J = 27.1$ Hz, 1 H, H-1).

$^{13}$C($^1$H)-NMR (100.55 MHz, CD$_2$Cl$_2$): $\delta$ (ppm) = 28.78 (s, 2 C, C-16), 31.73 (d, $J = 2.3$ Hz, 2 C, C-17), 81.44 (d, $J = 11.8$ Hz, 2 C, C-18), 111.03 (dd, $J = 10.2$ Hz, 2 C, C-15), 116.64 (d, $J = 22.9$ Hz, 2 C, C-8), 116.89 (d, $J = 23.0$ Hz, 2 C, C-4), 126.32 (d, $J = 8.6$ Hz, 2 C, C-7), 126.25 (dd, $J = 48.3$ Hz, $J = 2.0$ Hz, 2 C, C-10), 130.10 (d, $J = 11.0$ Hz, 4 C, C-12), 133.80 (d, $J = 9.1$ Hz, 2 C, C-3), 132.42 (dd, $J = 6.5$ Hz, $J = 3.4$ Hz, 1 C, C-2), 133.68 (d, $J = 14.0$ Hz, 4 C, C-11), 133.80 (d, $J = 2.2$ Hz, 2 C, C-13), 143.07 (d, $J = 3.0$ Hz, 2 C, C-6), 161.80 (d, $J = 246.5$ Hz, 1 C, C-9), 162.93 (d, $J = 250.1$ Hz, 1 C, C-5), 167.50 (d, $J = 19.2$ Hz, 1 C, C-1).

$^{31}$P($^1$H)-NMR (242.94 MHz, CD$_2$Cl$_2$): $\delta$ (ppm) = 113.41 (d, $J = 172.8$ Hz, 1).

**EA (C$_{33}$H$_{31}$F$_2$N$_2$PRhBF$_4$):** calcd. C: 55.49 %, H: 4.37 %, N: 3.91 %; found: C: 55.43 %, H: 4.51 %, N: 4.09 %.

**HR-MS (ESI+):** [M–BF$_4$]$^+ = C_{33}H_{31}F_2N_2PRh^+$ calcd.: 627.1242 found: 627.1235.
Compound [3a-Rh(cod)]BF$_4$

yield: 222 mg yellow solid (249 µmol, 74 %, GP 3).

$^1$H-NMR (600.13 MHz, CD$_2$Cl$_2$): $\delta$ (ppm) = 1.99 (s, 3 H, H-6/H-7), 2.06–2.53 (m, 8 H, H-25/H-26), 2.22 (s, 3 H, H-6/H-7), 2.31 (s, 3 H, H-12/H-13), 2.39 (s, 3 H, H-12/H-13), 2.46 (s, 3 H, H-12/H-13), 2.72 (s, 3 H, H-6/H-7), 2.86–2.93 (m, 1 H, H-27), 4.58–4.67 (m, 1 H, H-27), 4.72–4.82 (m, 1 H, H-24), 5.00–5.11 (m, 1 H, H-24), 6.53 (s, 1 H, H-Ar), 6.78 (d, $J = 9.0$ Hz, 1 H, H-Ar), 7.01 (s, 1 H, H-Ar), 7.03 (s, 1 H, H-Ar), 7.10–7.14 (m, 2 H, H-Ar), 7.16–7.27 (m, 3 H, H-Ar), 7.32 (t, $J = 7.4$ Hz, 1 H, H-Ar), 7.46 (t, $J = 7.6$ Hz, 1 H, H-Ar), 7.54–7.59 (m, 2 H, H-Ar), 7.82 (d, $J = 8.2$ Hz, 1 H, H-Ar), 7.91 (d, $J = 8.9$ Hz, 1 H, H-Ar), 8.07 (d, $J = 8.2$ Hz, 1 H, H-Ar), 8.27 (d, $J = 8.9$ Hz, 1 H, H-Ar).

$^{13}$C$^{[1]}$H-NMR (150.90 MHz, CD$_2$Cl$_2$): $\delta$ (ppm) = 18.77 (s, 1 C, C-6/C-7), 18.79 (s, 1 C, C-6/C-7), 19.17 (s, 1 C, C-12/C-13), 20.11 (s, 1 C, C-6/C-7), 20.00 (s, 1 C, C-12/C-13), 21.06 (s, 1 C, C-12/C-13), 27.50 (s, 1 C, C-25/C-26), 29.51 (d, $J = 1.3$ Hz, 1 C, C-25/C-26), 31.21 (d, $J = 2.0$ Hz, 1 C, C-25/C-26), 32.89 (d, $J = 1.9$ Hz, 1 C, C-25/C-26), 78.04 (d, $J = 9.9$ Hz, 1 C, C-27), 87.04 (d, $J = 11.1$ Hz, 1 C, C-27), 117.50 (dd, $J = 13.2$ Hz, $J = 4.2$ Hz, 1 C, C-24), 118.20 (dd, $J = 12.5$ Hz, $J = 5.0$ Hz, 1 C, C-24), 119.05 (s, 1 C, C-Ar), 119.90 (d, $J = 2.2$ Hz, 1 C, C-Ar), 121.10 (d, $J = 2.5$ Hz, 1 C, C-Ar), 123.34 (d, $J = 2.6$ Hz, 1 C, C-Ar), 126.41 (s, 1 C, C-Ar) 127.06 (s, 1 C, C-Ar), 127.17 (s, 1 C, C-Ar), 127.21 (s, 1 C, C-Ar), 127.40 (s, 1 C, C-Ar), 127.87 (s, 1 C, C-Ar), 128.59 (d, $J = 10.9$ Hz, 1 C, C-Ar), 128.63 (s, 1 C, C-Ar), 129.22 (s, 1 C, C-Ar), 129.29 (d, $J = 22.0$ Hz, 1 C, C-Ar), 129.97 (d, $J = 6.6$ Hz, 1 C, C-Ar), 130.24 (s, 3 C, C-Ar), 130.37 (s, 1 C, C-Ar), 130.66 (s, 1 C, C-Ar), 130.76 (s, 1 C, C-Ar), 131.59 (s, 1 C, C-Ar), 131.71 (s, 1 C, C-Ar), 131.94 (s, 1 C, C-Ar), 132.17 (s, 1 C, C-Ar), 132.24 (d, $J = 1.1$ Hz, 1 C, C-Ar), 132.50 (s, 1 C, C-Ar), 137.22 (s, 1 C, C-Ar), 137.29 (s, 1 C, C-Ar), 138.15 (s, 1 C, C-Ar), 141.06 (s, 1 C, C-Ar), 141.14 (s, 1 C, C-Ar), 146.05 (d, $J = 5.6$ Hz, 1 C, C-Ar), 148.10 (d, $J = 16.3$ Hz, 1 C, C-Ar), 164.43 (d, $J = 27.4$ Hz, 1 C, C-1).

$^{31}$P$^{[1]}$H-NMR (242.94 MHz, CD$_2$Cl$_2$): $\delta$ (ppm) = 143.62 (d, $J = 278.5$ Hz, 1 P).
EA (C₄₇H₄₇N₂O₂PRhBF₄): calcd. C: 63.24 %, H: 5.31 %, N: 3.14 %; found: C: 62.13 %, H: 5.23 %, N: 3.27 %.

HR-MS (ESI+): [M−BF₄]⁺ = C₄₇H₄₇N₂O₂PRh⁺ calcd.: 805.2425  found: 805.2419.

Compound [3b-Rh(cod)]BF₄

yield: 130 mg yellow solid (133 µmol, 90 %, GP 3).

¹H-NMR (600.13 MHz, CD₂Cl₂): δ (ppm) = 0.00 (d, J = 6.7 Hz, 3 H, H-7/H-13), 0.85 (d, J = 7.0 Hz, 3 H, H-7/H-13), 1.19 (d, J = 6.8 Hz, 3 H, H-7/H-13), 1.30 (d, J = 6.8 Hz, 3 H, H-7), 1.42 (d, J = 6.8 Hz, 3 H, H-7/H-13), 1.45 (d, J = 6.8 Hz, 3 H, H-13), 1.74 (d, J = 6.8 Hz, 3 H, H-7), 1.82 (d, J = 6.7 Hz, 3 H, H-13), 1.94–2.09 (m, 2 H, H-25/H-26), 2.10–2.26 (m, 2 H, H-25/H-26), 2.32–2.37 (m, 2 H, H-25/H-26), 2.38–2.46 (m, 2 H, H-25/H-26), 2.48–2.56 (m, 1 H, H-27), 3.08–3.22 (m, 1 H, H-6/H-12), 3.60 (sept, J = 6.8 Hz, 1 H, H-12), 3.86 (sept, J = 6.8 Hz, 1 H, H-12), 4.64–4.70 (m, 1 H, H-27), 4.89–4.96 (m, 1 H, H-24), 4.98–5.04 (m, 1 H, H-24), 6.19 (d, J = 9.0 Hz, 1 H, H-Ar), 6.94 (d, J = 3.3 Hz, J = 6.0 Hz, 1 H, H-Ar), 7.13 (d, J = 8.5 Hz, 1 H, H-Ar), 7.22 (dd, J = 1.5 Hz, J = 30.8 Hz, 1 H, H-1), 7.24–7.27 (m, 2 H, H-Ar), 7.29–7.39 (m, 4 H, H-Ar), 7.47 (d, J = 8.5 Hz, 1 H, H-Ar), 7.51–7.51 (m, 2 H, H-Ar), 7.58–7.62 (m, 1 H, H-Ar), 7.83 (d, J = 8.2 Hz, 1 H, H-Ar), 7.84 (d, J = 8.8 Hz, 1 H, H-Ar), 8.10 (d, J = 8.2 Hz, 1 H, H-Ar), 8.34 (d, J = 8.9 Hz, 1 H, H-Ar).

¹³C¹H-NMR (150.90 MHz, CD₂Cl₂): δ (ppm) = 21.71 (s, 1 C, C-7/C-13), 21.97 (s, 1 C, C-7), 23.28 (s, 1 C, C-7/C-13), 24.33 (s, 1 C, C-13), 25.05 (s, 1 C, C-7), 25.46 (s, 1 C, C-7/C-13), 25.74 (s, 1 C, C-13), 27.18 (s, 1 C, C-7/C-13), 28.29 (s, 1 C, C-6/C-12), 27.37 (s, 1 C, C-25/C-26), 28.47 (s, 1 C, C-6/C-12), 29.14 (d, J = 1.9 Hz, 1 C, C-25/C-26), 30.29 (s, 1 C, C-6), 30.48 (s, 1 C, C-12), 31.29 (d, J = 2.9 Hz, 1 C, C-25/C-26), 33.01 (d, J = 1.7 Hz, 1 C, C-25/C-26), 77.49 (d, J = 10.2, 1 C, C-24), 85.71 (d, J = 11.5 Hz, 1 C, C-24), 116.76 (dd, J = 12.6 Hz, J = 5.4 Hz, 1 C, C-27), 118.35 (s, 1 C, C-Ar), 118.43 (dd, J = 13.4 Hz, J = 4.8 Hz, 1 C, C-27), 120.31 (d, J = 2.6 Hz, 1 C, C-Ar), 120.80 (d, J = 2.4 Hz, 1 C, C-Ar), 123.84 (d, J = 3.4 Hz, 1 C, C-Ar), 124.53 (s, 1 C, C-Ar), 125.32
(s, 1 C, C-Ar), 125.67 (s, 1 C, C-Ar), 126.22 (s, 1 C, C-Ar), 126.56 (s, 1 C, C-Ar), 126.82 (s, 1 C, C-Ar),
127.29 (s, 1 C, C-Ar), 127.33 (s, 1 C, C-Ar), 127.47 (s, 1 C, C-Ar), 128.13 (s, 1 C, C-Ar), 128.62 (s, 1 C, C-Ar), 128.95 (s, 1 C, C-Ar), 129.03 (s, 1 C, C-Ar), 131.20 (s, 1 C, C-Ar), 131.45 (s, 1 C, C-Ar), 132.06 (s, 1 C, C-Ar),
132.32 (s, 1 C, C-Ar), 132.67 (d, J = 0.8 Hz, 1 C, C-Ar), 132.67 (d, J = 1.7 Hz, 1 C, C-Ar), 140.25 (s, 1 C, C-Ar), 140.88 (s, 1 C, C-Ar), 142.51 (s, 1 C, C-Ar), 145.73 (d, J = 5.4 Hz, 1 C, C-Ar), 148.41 (d, J = 15.3 Hz, 1 C, C-Ar), 148.42 (s, 1 C, C-Ar), 148.63 (d, J = 1.1 Hz, 1 C, C-Ar), 161.78 (d, J = 25.7 Hz, 1 C, C-1).

$^{31}$P$^1$H-NMR (242.94 MHz, CD$_2$Cl$_2$): $\delta$ (ppm) = 145.07 (d, J = 273.8 Hz, 1 P).

EA (C$_{53}$H$_{59}$N$_2$O$_2$PRhBF$_4$): calcd. C: 65.17 %, H: 6.09 %, N: 2.87 %; found: C: 65.40 %, H: 6.37 %, N: 2.89 %.

HR-MS (ESI+): [M−BF$_4$]$^+$ = C$_{53}$H$_{59}$N$_2$O$_2$PRh$^+$ calcd.: 889.3364 found: 889.3357.

**Compound [3c-Rh(cod)]BF$_4$**

![Diagram of Compound [3c-Rh(cod)]BF$_4$]

**yield:** 126 mg yellow solid (148 µmol, 81 %, GP 3).

$^1$H-NMR (399.89 MHz, CD$_2$Cl$_2$): $\delta$ (ppm) = 2.07–2.29 (m, 4 H, H-21/H-22), 2.34–2.60 (m, 4 H, H-21/H-22), 3.81–3.91 (m, 1 H, H-23), 4.40–4.49 (m, 1 H, H-23), 5.09–5.22 (m, 1 H, H-20), 5.29–5.39 (m, 1 H, H-20), 6.47 (t, J = 8.8 Hz, 1 H, H-Ar), 6.61 (t, J = 8.4 Hz, 2 H, H-Ar), 6.73 (t, J = 8.4 Hz, 1 H, H-Ar), 6.90–6.95 (m, 1 H, H-Ar), 7.03 (d, J = 9.0 Hz, 1 H, H-Ar), 7.16 (d, J = 8.3 Hz, 1 H, H-Ar), 7.17–7.21 (m, 3 H, H-Ar), 7.27 (d, J = 8.2 Hz, 1 H, H-Ar), 7.30–7.32 (m, 2 H, H-Ar), 7.35–7.40 (m, 2 H, H-Ar), 7.46 (t, J = 7.3 Hz, 1 H, H-Ar), 7.57 (d, J = 9.1 Hz, 1 H, H-Ar), 7.83 (d, J = 8.2 Hz, 1 H, H-Ar), 7.95 (d, J = 8.6 Hz, 1 H, H-Ar), 8.04 (d, J = 8.2 Hz, 1 H, H-Ar), 8.22 (d, J = 9.0 Hz, 1 H, H-Ar).

$^{13}$C$^1$H-NMR (100.55 MHz, CD$_2$Cl$_2$): $\delta$ (ppm) = 28.17 (s, 1 C, C-21/C-22), 28.48 (s, 1 C, C-21/C-22), 32.08 (d, J = 2.3 Hz, 1 C, C-21/C-22), 32.13 (d, J = 3.1 Hz, 1 C, C-21/C-22), 77.53 (d, J = 10.5 Hz, 1 C, C-23), 85.95 (d, J = 11.8 Hz, 1 C, C-23), 116.24 (dd, J = 5.7 Hz, J = 12.7 Hz,
1 C, C-20), 116.53 (d, J = 23.1 Hz, 2 C, C-4/C-8), 116.87 (d, J = 23.0 Hz, 2 C, C-4/C-8), 117.37 (dd, J = 5.6 Hz, J = 12.5 Hz, 1 C, C-20), 120.83 (d, J = 2.7 Hz, 1 C, C-Ar), 122.38 (s, 1 C, C-Ar), 122.99 (d, J = 2.5 Hz, 1 C, C-Ar), 126.05 (d, J = 8.6 Hz, 2 C, C-Ar), 126.38 (s, 1 C, C-Ar), 126.82 (s, 1 C, C-Ar), 126.87 (s, 1 C, C-Ar), 127.21 (s, 1 C, C-Ar), 127.37 (s, 1 C, C-Ar), 127.64 (s, 1 C, C-Ar), 128.57 (s, 1 C, C-Ar), 129.09 (s, 1 C, C-Ar), 129.16 (d, J = 9.2 Hz, 1 C, C-Ar), 128.52 (s, 1 C, C-Ar), 129.60 (d, J = 8.8 Hz, 2 C, C-Ar), 130.94 (s, 1 C, C-Ar), 131.27 (dd, J = 2.9 Hz, J = 6.1 Hz, 1 C, C-Ar), 131.92 (s, 1 C, C-Ar), 132.04 (s, 1 C, C-Ar), 132.73 (s, 1 C, C-Ar), 142.86 (d, J = 3.0 Hz, 1 C, C-Ar), 146.19 (d, J = 5.9 Hz, 1 C, C-Ar), 148.22 (d, J = 14.9 Hz, 1 C, C-Ar), 161.99 (d, J = 247.1 Hz, 1 C, C-9), 162.67 (d, J = 249.8 Hz, 1 C, C-5), 164.15 (d, J = 25.7 Hz, 1 C, C-1).

$^{31}$P{H}-NMR (161.88 MHz, CD$_2$Cl$_2$): δ (ppm) = 139.10 (d, J = 279.38 Hz, 1 P).[19]

EA (C$_{41}$H$_{33}$F$_2$N$_2$O$_2$PRhBF$_4$ + 0.5 C$_7$H$_8$): calcd. C: 60.36 %, H: 3.64 %, N: 3.16 %; found: C: 59.51 %, H: 3.99 %, N: 3.43 %. The presence of half an equivalent of toluene was accounted for.

HR-MS (ESI+): [M−BF$_4^{-}$]$^+$ = C$_{41}$H$_{33}$F$_2$N$_2$O$_2$PRh$^+$ calcd.: 757.1297 found: 757.1294.

**Compound [2a-Cp*RhCl]BF$_4$**

yield: 155 mg red-brown solid (188 μmol, 87 %, GP 2).

$^1$H-NMR (600.13 MHz, CD$_2$Cl$_2$): δ (ppm) = 1.26 (d, J = 4.0 Hz, H-19), 1.71 (s, 3 H, CH$_3$), 1.82 (s, 3 H, CH$_3$), 2.23 (s, 3 H, CH$_3$), 2.31 (s, 3 H, CH$_3$), 2.34 (s, 3 H, CH$_3$), 2.50 (s, 3 H, CH$_3$), 6.71 (s, 1 H, H-4/H-10), 6.85 (s, 1 H, H-4/H-10), 7.01 (s, 1 H, H-4/H-10), 7.04 (s, 1 H, H-4/H-10), 7.29−7.34 (m, 2 H, H-Ar), 7.37−7.43 (m, 3 H, H-Ar), 7.46−7.53 (m, 2 H, H-Ar), 7.56−7.61 (m, 2 H, H-Ar), 7.64−7.72 (m, 2 H, H-Ar).

$^{13}$C{H}-NMR (150.90 MHz, CD$_2$Cl$_2$): δ (ppm) = 8.89 (d, J = 1.3 Hz, 5 C, C-19), 20.24 (s, 1 C, CH$_3$), 20.61 (s, 1 C, CH$_3$), 20.83 (s, 1 C, CH$_3$), 20.90 (s, 1 C, CH$_3$), 20.97 (s, 1 C, CH$_3$), 21.60 (s, 1 C, CH$_3$), 102.83 (dd, J = 3.1 Hz, J = 6.5 Hz, 5 C, C-18), 121.90 (d, J = 65.0 Hz, 1 C, C-Ar) 124.22 (d, J = 12.0 Hz, 2 C, C-Ar), 129.34 (d, J = 11.0 Hz, 2 C, C-Ar), 129.70 (s, 1 C, C-Ar), 130.05 (s, 2 C,
C-Ar), 130.79 (s, 1 C, C-Ar), 131.00 (s, 1 C, C-Ar), 131.20 (s, 1 C, C-Ar), 132.59 (s, 1 C, C-Ar),
133.91 (d, \( J_{\text{alt}} = 2.6 \) Hz, 1 C, C-Ar), 134.10 (d, \( J_{\text{alt}} = 2.4 \) Hz, 1 C, C-Ar), 134.59 (s, 1 C, C-Ar), 134.81
(d, \( J_{\text{alt}} = 12.2 \) Hz, 2 C, C-Ar), 135.48 (s, 1 C, C-Ar), 136.35 (d, \( J_{\text{alt}} = 12.5 \) Hz, 2 C, C-Ar), 138.00 (s, 1 C,
C-Ar), 140.67 (s, 1 C, C-Ar), 141.25 (s, 1 C, C-Ar), 141.72 (s, 1 C, C-Ar), 166.51 (d, \( J_{\text{alt}} = 19.1 \) Hz, 1 C,
C-1).

\[ ^{31}P\{^1H\}-NMR \ (242.93 \text{ MHz}, CD_2Cl_2) : \delta \ (ppm) = 108.92 \ (d, \ J = 152.9 \text{ Hz}, 1 \text{ P}). \]

EA (C_{41}H_{48}ClN_2PRhBF_4 + 0.5 CH_2Cl_2): calcd. C: 57.46 %, H: 5.69 %, N: 3.23 %; found: C:
56.79 %, H: 5.83 %, N: 3.21 %. The presence of half an equivalent of dichloromethane was accounted for.

HR-MS (ESI+): \([M–BF_4]\) = C_{41}H_{48}ClN_2PRh \ calibrated: 737.2293 found: 737.2285.

**Compound \([2a-Ir(cod)]BF_4\)**

![Structure of \([2a-Ir(cod)]BF_4\)](image)

**yield:** 163 mg bright red solid (166 \( \mu \text{mol}, 77 \%), \text{GP} \ 2).

\(^1H\)-NMR (399.89 MHz, CD_2Cl_2): \( \delta \ (ppm) = 1.50 \ (s, 6 \text{ H, H-7}), 2.26 \ (s, 3 \text{ H, H-6}), 2.38 \ (s, 3 \text{ H,}
H-12), 2.44 \ (s, 6 \text{ H, H-13}), 3.48–3.59 \ (m, 2 \text{ H, H-21}), 4.46–4.65 \ (m, 2 \text{ H, H-18}), 6.77 \ (s, 2 \text{ H, H-4),}
7.09 \ (s, 2 \text{ H, H-10}), 7.57–7.66 \ (m, 5 \text{ H, H-1/H-16}), 7.73–7.79 \ (m, 2 \text{ H, H-17}), 7.79–8.78 \ (m, 4 \text{ H,}
H-15).

\(^{13}C\{^1H\}-NMR \ (100.55 \text{ MHz, CD}_2\text{Cl}_2) : \delta \ (ppm) = 18.85 \ (s, 2 \text{ C, C-7/C-13}), 18.93 \ (s, 2 \text{ C, C-7/C-13}), 20.92 \ (s, 1 \text{ C, C-6/C-12}), 20.96 \ (s, 1 \text{ C, C-6/C12}), 29.55 \ (d, \ J = 2.3 \text{ Hz, 2 C, C-20}), 32.43 \ (d, \ J = 2.7 \text{ Hz, 2 C, C-19}), 68.93 \ (s, 2 \text{ C, C-21}), 102.30 \ (d, \ J = 12.15, 2 \text{ C, C-18}), 125.82 \ (d, \ J = 58.4 \text{ Hz, 2 C, C-14}), 129.78 \ (d, \ J = 11.6 \text{ Hz, 4 C, C-16}), 130.12 \ (s, 2 \text{ C, C-10}), 130.50 \ (s, 2 \text{ C, C-4}), 131.33 \ (d, \ J = 6.0 \text{ Hz, 1 C, C-2}), 132.01 \ (s, 2 \text{ C, C-9}), 134.35 \ (d, \ J = 2.2 \text{ Hz, 2 C, C-17}), 135.65 \ (d, \ J = 14.2 \text{ Hz, 4 C, C-15}), 137.31 \ (s, 2 \text{ C, C-3}), 138.44 \ (s, 1 \text{ C, C-8}), 140.78 \ (s, 1 \text{ C, C-11}), 140.94 \ (s, 1 \text{ C, C-5}), 172.59 \ (d, \ J = 18.1 \text{ Hz, 1 C, C-1}).

\(^{31}P\{^1H\}-NMR \ (161.88 \text{ MHz, CD}_2\text{Cl}_2) : \delta \ (ppm) = 97.35 \ (s, 1 \text{ P}). \]

EA (C_{39}H_{45}N_2PIrBF_4 + CH_2Cl_2): calcd. C: 51.69 %, H: 5.40 %, N: 2.94 %; found: C: 51.33 %,
H: 5.09 %, N: 3.15 %. The presence of one molecule of dichloromethane in the crystal structure was accounted for.

**HR-MS (ESI+):** \([M–BF_4]^+\) = C_{39}H_{45}N_2Pir^+  

Calcd.: 765.2946  

Found: 765.2940.

**Compound [2b-Ir(cod)]BF_4**

![Chemical structure](image)

**yield:** 136 mg bright red solid (73.0 µmol, 80 %, GP 2).

**1H-NMR (600.13 MHz, CD_2Cl_2):** \(\delta\) (ppm) = 0.19 (d, \(J = 6.6 \text{ Hz}, 6 \text{ H, H-7}\)), 0.91 (d, \(J = 6.8 \text{ Hz}, 6 \text{ H, H-7}\)), 1.25 (d, \(J = 6.9 \text{ Hz}, 6 \text{ H, H-13}\)), 1.56 (d, \(J = 6.8 \text{ Hz}, 6 \text{ H, H-13}\)), 1.92–2.15 (m, 6 H, H-19/H-20), 2.16–2.26 (m, 2 H, H-19/H-20), 2.63 (sept, \(J = 6.7 \text{ Hz}, 2 \text{ H, H-6}\)), 3.35–3.46 (m, 4 H, H-21/H-12), 4.49–4.56 (m, 2 H, H-18), 7.05–7.11 (m, 2 H, H-Ar), 7.33–7.39 (m, 4 H, H-Ar), 7.53–7.59 (m, 4 H, H-16), 7.59–7.65 (m, 4 H, H-15), 7.65–7.69 (m, 2 H, H-17), 7.78 (d, \(J = 25.3 \text{ Hz}, 1 \text{ H, H-1}\)).

**13C{\text{1H}}-NMR (100.55 MHz, CD_2Cl_2):** \(\delta\) (ppm) = 21.43 (s, 2 C, C-7), 23.24 (s, 2 C, C-13), 26.44 (s, 2 C, C-13), 28.01 (s, 2 C, C-7), 29.02 (s, 2 C, C-12), 29.09 (d, \(J = 1.9 \text{ Hz}, 2 \text{ C, C-17}\)), 30.07 (s, 2 C, C-6) 32.35 (d, \(J = 2.7 \text{ Hz}, 2 \text{ C, C-16}\)), 69.87 (s, 2 C, C-21), 101.77 (d, \(J = 12.1 \text{ Hz}, 2 \text{ C, C-18}\)), 124.97 (s, 2 C, C-4/C-10), 125.62 (s, 2 C, C-4/C-10), 125.86 (d, \(J = 58.3 \text{ Hz}, 2 \text{ C, C-14}\)), 129.36 (s, 1 C, C-5/C-11), 129.89 (d, \(J = 11.6 \text{ Hz}, 4 \text{ C, C-16}\)), 130.03 (d, \(J = 5.6 \text{ Hz}, 1 \text{ C, C-2}\)), 131.45 (s, 1 C, C5/C-11), 134.26 (d, \(J = 2.2 \text{ Hz}, 2 \text{ C, C-17}\)), 140.34 (s, 1 C, C-8), 142.78 (s, 2 C, C-3/C-9), 148.09 (s, 2 C, C-3/C-9), 135.61 (d, \(J = 14.0 \text{ Hz}, 4 \text{ C, C-15}\)), 170.56 (d, \(J = 18.2 \text{ Hz}, 1 \text{ C, C-1}\)).

**31P{\text{1H}}-NMR (242.94 MHz, CD_2Cl_2):** \(\delta\) (ppm) = 100.93 (s, 1 P).

**EA (C_{45}H_{47}N_2PirBF_4):** Calcd. C: 57.75 %, H: 6.14 %, N: 2.99 %; found: C: 57.62 %, H: 6.02 %, N: 2.92 %.

**HR-MS (ESI+):** \([M–BF_4]^+\) = C_{45}H_{47}N_2Pir^+  

Calcd.: 849.3886  

Found: 849.3883.
Compound [2c-Ir(cod)]BF₄

**yield:** 170 mg red solid (212 μmol, 88 %, GP 2).

**¹H-NMR (600.13 MHz, CD₂Cl₂):** \( \delta \) (ppm) = 1.97–2.05 (m, 2 H, H-16), 2.05–2.11 (m, 2 H, H-17), 2.14–2.21 (m, 2 H, H-17), 2.21–2.30 (m, 2 H, H-16), 3.41–3.49 (m, 2 H, H-18), 4.81–4.90 (m, 2 H, H-15), 6.76–6.81 (m, 2 H, H-3), 6.84–6.91 (m, 2 H, H-4), 7.16–7.21 (m, 2 H, H-8), 7.31–7.36 (m, 2 H, H-7), 7.58–7.63 (m, 4 H, H-12), 7.67–7.73 (m, 6 H, H-11/H-13), 8.03 (d, \( J = 23.9 \) Hz, 1 H, H-1).

**¹³C{¹H}-NMR (150.90 MHz, CD₂Cl₂):** \( \delta \) (ppm) = 29.50 (d, \( J = 2.0 \) Hz, 2 C, C-16), 32.47 (d, \( J = 2.9 \) Hz, 2 C, C-17), 67.02 (s, 2 C, C-18), 101.75 (d, \( J = 12.3 \) Hz, 2 C, C-15), 116.60 (d, \( J = 22.8 \) Hz, 2 C, C-8), 116.98 (d, \( J = 23.1 \) Hz, 2 C, C-4), 126.03 (d, \( J = 8.8 \) Hz, 2 C, C-7), 130.06 (d, \( J = 11.3 \) Hz, 4 C, C-12), 130.69 (d, \( J = 8.8 \) Hz, 2 C, C-3), 132.03 (d, \( J = 5.1 \) Hz, \( J = 3.2 \) Hz, 1 C, C-2), 133.90 (d, \( J = 13.8 \) Hz, 4 C, C-11), 134.09 (d, \( J = 2.2 \) Hz, 2 C, C-13), 142.10 (d, \( J = 3.3 \) Hz, 1 C, C-6), 162.20 (d, \( J = 247.3 \) Hz, 1 C, C-9), 163.13 (d, \( J = 250.6 \) Hz, 1 C, C-5), 170.67 (d, \( J = 17.1 \) Hz, 1 C, C-1).

**³¹P{¹H}-NMR (242.94 MHz, CD₂Cl₂):** \( \delta \) (ppm) = 99.91 (s, 1 P).

**EA (C₃₃H₃₁F₂N₂PİrBF₄):** calcd. C: 49.32 %, H: 3.89 %, N: 3.49 %; found: C: 50.37 %, H: 4.14 %, N: 3.68 %.

**HR-MS (ESI+):** \([M–BF₄]^+ = C₃₃H₃₁F₂N₂Pİr^+\) calcd.: 717.1817 found: 717.1807.

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Compound [3a-Ir(cod)]BF$_4$

yield: 160 mg brown-red solid (163 µmol, 65 %, GP 2).

$^1$H-NMR (399.89 MHz, CD$_2$Cl$_2$): δ (ppm) = 1.94–2.34 (m, 8 H, H-26/H-27), 2.05 (s, 3 H, H-6/H-7), 2.21 (s, 3 H, H-6/H-7), 2.35 (s, 3 H, H-12/H-13), 2.39 (s, 3 H, H-12/H-13), 2.45 (s, 3 H, H-12/H-13), 2.53–2.64 (m, 1 H, H-27), 2.70 (s, 3 H, H-6/H-7), 4.10–4.27 (m, 1 H, H-27), 4.65–4.79 (m, 1 H, H-24), 5.04–5.19 (m, 1 H, H-24), 6.55 (s, 1 H, H-Ar), 6.89 (d, $J = 9.0$ Hz, 1 H, H-Ar), 7.02–7.14 (m, 4 H, H-Ar), 7.18 (d, $J = 8.6$ Hz, 1 H, H-Ar), 7.21–7.27 (m, 1 H, H-Ar), 7.32 (d, $J = 29.5$ Hz, 1 H, H-1), 7.29–7.35 (m, 1 H, H-Ar), 7.42–7.49 (m, 1 H, H-Ar), 7.53–7.65 (m, 2 H, H-Ar), 7.84 (t, $J = 8.7$ Hz, 2 H, H-Ar), 8.07 (d, $J = 8.2$ Hz, 1 H, H-Ar), 8.24 (d, $J = 8.9$ Hz, 1 H, H-Ar).

$^{13}$C{$^1$H}-NMR (100.55 MHz, CD$_2$Cl$_2$): δ (ppm) = 18.51 (s, 1 C, C-12/C-13), 18.78 (s, 1 C, C-6/C-7), 18.94 (s, 1 C, C-12/C-13), 20.01 (s, 1 C, C-6/C-7), 20.96 (s, 1 C, C-6/C-7), 20.97 (s, 1 C, C-12/C-13), 28.07 (s, 1 C, C-25/C-26), 30.45 (s, 1 C, C-25/C-26), 32.11 (s, 1 C, C-25/C-26), 33.59 (s, 1 C, C-25/C-26), 64.30 (s, 1 C, C-27), 72.60 (s, 1 C, C-27), 111.03 (d, $J = 16.0$ Hz, 1 C, C-24), 112.19 (d, $J = 15.3$ Hz, 1 C, C-24), 119.14 (d, $J = 1.8$ Hz, 1 C, C-Ar), 119.81 (d, $J = 2.6$ Hz, 1 C, C-Ar), 121.17 (d, $J = 2.8$ Hz, 1 C, C-Ar), 123.04 (d, $J = 3.2$ Hz, 1 C, C-Ar), 126.40 (s, 1 C, C-Ar), 127.01 (s, 1 C, C-Ar), 127.20 (s, 2 C, C-Ar), 127.41 (s, 1 C, C-Ar), 127.81 (s, 1 C, C-Ar), 128.61 (s, 1 C, C-Ar), 129.20 (s, 1 C, C-Ar), 129.61 (d, $J = 5.6$ Hz, 1 C, C-Ar), 130.14 (s, 1 C, C-Ar), 130.18 (s, 1 C, C-Ar), 130.23 (s, 1 C, C-Ar), 130.65 (s, 1 C, C-Ar), 130.89 (s, 1 C, C-Ar), 131.04 (s, 1 C, C-Ar), 131.61 (s, 1 C, C-Ar), 131.91 (d, $J = 1.1$ Hz, 1 C, C-Ar), 132.09 (s, 1 C, C-Ar), 132.27 (s, 1 C, C-Ar), 132.45 (d, $J = 1.2$ Hz, 1 C, C-Ar), 132.67 (d, $J = 1.7$ Hz, 1 C, C-Ar), 137.07 (s, 2 C, C-Ar), 138.80 (s, 1 C, C-Ar), 140.67 (s, 1 C, C-Ar), 141.18 (s, 1 C, C-Ar), 146.01 (d, $J = 6.1$ Hz, 1 C, C-Ar), 147.85 (d, $J = 15.5$ Hz, 1 C, C-Ar), 167.98 (d, $J = 24.0$ Hz, 1 C, C-1).

$^{31}$P{$^1$H}-NMR (161.88 MHz, CD$_2$Cl$_2$): δ (ppm) = 125.08 (s, 1 P).
EA (C$_{47}$H$_{47}$N$_2$O$_2$P$\text{Ir}$BF$_4$): calcd. C: 57.49 %, H: 4.85 %, N: 2.85 %; found: C: 57.27 %, H: 4.84 %, N: 2.99 %.

HR-MS (ESI+): [M–BF$_4$]$^+$ = C$_{47}$H$_{47}$N$_2$O$_2$P$\text{Ir}$$^+$ calcd.: 895.2999 found: 895.2998.

Compound [3b-Ir(cod)]BF$_4$

yield: 127 mg dark red solid (119 $\mu$mol, 81 %, GP 2).

$^1$H-NMR (600.13 MHz, CD$_2$Cl$_2$): $\delta$ (ppm) = 0.05 (d, $J = 6.7$ Hz, 3 H, H-13), 0.87 (d, $J = 7.0$ H, 3 H, H-13), 1.20 (d, $J = 6.8$ H, 3 H, H-7), 1.30 (d, $J = 6.8$ H, 3 H, H-7), 1.40–1.44 (m, 6 H, H-7/H-13), 1.68 (d, $J = 6.8$ H, 3 H, H-7), 1.81 (d, $J = 6.7$ H, 3 H, H-13), 1.91–2.27 (m, 9 H, H-25/H-26/H-27), 3.11 (sept, $J = 6.8$ Hz, 1 H, H-6), 3.17 (sept, $J = 6.9$ Hz, 1 H, H-12), 3.52 (sept, $J = 6.8$ Hz, 1 H, H-12), 3.76 (sept, $J = 6.4$ Hz, 1 H, H-6), 4.19–4.25 (m, 1 H, H-27), 4.91–5.00 (m, 2 H, H-24), 6.28 (d, $J = 9.1$ Hz, 1 H, H-Ar), 6.91 (dd, $J = 2.1$ Hz, $J = 7.1$ Hz, 1 H, H-Ar), 7.12 (d, $J = 8.7$ Hz, 1 H, H-Ar), 7.21–7.30 (m 3 H, H-Ar), 7.32–7.39 (m, 4 H, H-Ar), 7.44–7.54 (m, 4 H, H-Ar), 7.57–7.62 (m 1 H, H-Ar), 7.76 (d, $J = 8.9$ Hz, 1 H, H-Ar), 7.82 (d, $J = 7.8$ Hz, 1 H, H-Ar), 8.09 (d, $J = 8.1$ Hz, 1 H, H-Ar), 8.29 (d, $J = 8.9$ Hz, 1 H, H-Ar).

$^{13}$C$[^1$H$]$-NMR (150.90 MHz, CD$_2$Cl$_2$): $\delta$ (ppm) = 21.91 (s, 1 C, C-13), 22.02 (s, 1 C, C-7), 23.40 (s, 1 C, C-7/C-13), 24.34 (s, 1 C, C-13), 25.17 (s, 1 C, C-7), 25.52 (s, 1 C, C-13), 25.87 (s, 1 C, C-7/C-13), 27.26 (s, 1 C, C-7), 28.19 (s, 1 C, C-6), 28.32 (d, $J = 2.3$ Hz, 1 C, C-25/C-26), 28.57 (s, 1 C, C-12), 29.87 (d, $J = 3.0$ Hz, 1 C, C-25/C-26), 30.21 (s, 1 C, C-12), 30.32 (s, 1 C, C-12), 34.10 (d, $J = 3.9$ Hz, 1 C, C-25/C-26), 33.44 (d, $J = 3.8$ Hz, 1 C, C-25/C-26), 63.68 (s, 1 C, C-27), 71.54 (s, 1 C, C-27), 110.14 (d, $J = 15.4$ Hz, 1 C, C-24), 117.73 (d, $J = 16.1$ Hz, 1 C, C-24), 118.44 (s, 1 C, C-Ar), 120.25 (d, $J = 2.4$ Hz, 1 C, C-Ar), 120.91 (d, $J = 2.4$ Hz, 1 C, C-Ar), 123.59 (d, $J = 3.4$ Hz, 1 C, C-Ar), 124.55 (s, 1 C, C-Ar), 125.36 (s, 1 C, C-Ar), 125.68 (s, 1 C, C-Ar), 126.27 (s, 1 C, C-Ar), 126.59 (s, 1 C, C-Ar), 126.86 (s, 1 C, C-Ar), 127.28 (s, 1 C, C-Ar), 127.36 (s, 1 C, C-Ar), 127.50 (s, 1 C, C-Ar), 128.12 (s, 1 C, C-Ar), 128.63 (s, 1 C, C-Ar), 128.69 (d, $J = 4.9$ Hz, 1 C, C-Ar), 129.24
(s, 1 C, C-Ar), 129.66 (s, 1 C, C-Ar), 131.28 (s, 1 C, C-Ar), 131.45 (s, 1 C, C-Ar), 132.00 (s, 1 C, C-Ar), 132.04 (s, 1 C, C-Ar), 132.21 (s, 1 C, C-Ar), 132.41 (d, J = 1.0 Hz, 1 C, C-Ar), 132.61 (d, J = 1.8 Hz, 1 C, C-Ar), 139.88 (s, 1 C, C-Ar), 141.45 (s, 1 C, C-Ar), 143.14 (s, 1 C, C-Ar), 145.76 (d, J = 5.8 Hz, 1 C, C-Ar), 148.09 (d, J = 15.5 Hz, 1 C, C-Ar), 148.35 (s, 1 C, C-Ar), 148.46 (s, 1 C, C-Ar), 164.89 (d, J = 22.6 Hz, 1 C, C-1).

$^{31}$P$^{1}$H-NMR (242.93 MHz, CD$_2$Cl$_2$): $\delta$ (ppm) = 127.52 (s, 1 P).

EA (C$_{53}$H$_{59}$N$_2$O$_2$P$^{1}$IrBF$_4$): calcd. C: 59.71 %, H: 5.58 %, N: 2.63 %; found: C: 59.78 %, H: 5.81 %, N: 2.74 %.

HR-MS (ESI+): [M–BF$_4$]$^+$ = C$_{53}$H$_{59}$N$_2$O$_2$P$^{1}$Ir$^+$ calcd.: 979.3938 found: 979.3923.

**Compound [3c-Ir(cod)]BF$_4$**

**yield:** 140 mg dark red solid (150 µmol, 82 %, GP 2).

$^1$H-NMR (600.13 MHz, CDCl$_2$): $\delta$ (ppm) = 1.47–1.64 (m, 2 H, H-21/H-22), 1.85–2.23 (m, 6 H, H-21/H-22/H-23), 3.42–3.60 (m, 1 H, H-23), 3.83–4.01 (m, 1 H, H-23), 5.01–5.15 (m, 1 H, H-20), 5.32–5.36 (m, 1 H, H-20) 6.45–6.58 (m, 2 H, H-Ar), 6.94–6.98 (m, 1 H, H-Ar), 7.06–7.10 (m, 2 H, H-Ar), 7.13–7.17 (m, 4 H, H-Ar), 7.17–7.26 (m, 4 H, H-Ar), 7.38–7.41 (m, 1 H, H-Ar), 7.46–7.49 (m, 1 H, H-Ar), 7.50 (d, J = 9.0 Hz, 1 H, H-Ar), 7.68 (d, J = 9.8 Hz, 1 H, H-1), 7.75 (d, J = 8.0 Hz, 1 H, H-Ar) 7.80 (d, J = 8.9 Hz, 1 H, H-Ar) 7.96 (d, J = 8.2 Hz, 1 H, H-Ar), 8.12 (d, J = 10.1 Hz, 1 H, H-Ar).

$^{13}$C$^{1}$H-NMR (150.90 MHz, CD$_2$Cl$_2$): $\delta$ (ppm) = 29.17 (s, 2 C, C-21/C-22), 32.75 (s, 1 C, C-21/C-22), 33.30 (s, 1 C, C-21/C-22), 64.16 (s, 1 C, C-23), 71.51 (s, 1 C, C-23), 109.31 (d, J = 13.3 Hz, 1 C, C-20), 110.92 (d, J = 13.9 Hz, 1 C, C-20), 116.64 (d, J = 23.2 Hz, 2 C, C-4/C-8), 116.88 (d, J = 23.1 Hz, 2 C, C-4/C-8), 120.45 (s, 2 C, C-Ar), 120.79 (d, J = 3.0 Hz, 2 C, C-Ar), 125.60 (s, 1 C, C-Ar), 126.47 (s, 1 C, C-Ar), 126.73 (d, J = 8.6 Hz, 2 C, C-3/C-7), 126.89 (s, 2 C, C-Ar), 127.29
(s, 1 C, C-Ar), 127.42 (s, 1 C, C-Ar), 127.69 (s, 1 C, C-Ar), 128.53 (s, 1 C, C-Ar), 128.61 (s, 1 C, C-Ar), 129.09 (s, 1 C, C-Ar), 129.34 (s, 1 C, C-Ar), 129.51 (d, J = 9.1 Hz, 2 C, C-3/C-7), 131.08 (s, 1 C, C-Ar), 131.64 (s, 1 C, C-Ar), 131.89 (s, 1 C, C-Ar), 132.02 (s, 1 C, C-Ar), 132.46 (s, 1 C, C-Ar), 145.96 (d, J = 8.8 Hz, 1 C, C-Ar), 147.91 (d, J = 14.5 Hz, 1 C, C-Ar), 162.40 (d, J = 247.9 Hz, 1 C, C-9), 162.78 (d, J = 250.1 Hz, 1 C, C-5), 167.34 (d, J = 23.7 Hz, 1 C, C-1).

$^{31}$P$^1$H-NMR (242.95 MHz, CD$_2$Cl$_2$): $\delta$ (ppm) = 122.49 (s, 1 P).

EA (C$_{41}$H$_{33}$F$_2$N$_2$O$_2$PIrBF$_4$ + 0.5 C$_7$H$_8$): calcd. C: 54.55 %, H: 3.81 %, N: 2.86 %; found: C: 54.78 %, H: 3.91 %, N: 2.88 %. The presence of half an equivalent of toluene was accounted for.

HR-MS (ESI+): [M–BF$_4$]$^+$ = C$_{41}$H$_{33}$F$_2$N$_2$O$_2$P$^+$ calcd.: 847.1871 found: 847.1859.

Compound [2a-Cp*Irl]BF$_4$

yield: 165 mg orange solid (164 mmol, 76 %, GP 2).

$^1$H-NMR (600.13 MHz, CD$_2$Cl$_2$): $\delta$ (ppm) = 1.41 (d, J = 2.3 Hz, 18 H, H-19), 1.50 (s, 3 H, H-6/H-7), 2.05 (s, 3 H, H-6/H-7), 2.21 (s, 3 H, H-6/H-7), 2.23 (s, 3 H, H-12/H-13), 2.34 (s, 3 H, H-12/H-13), 2.42 (s, 3 H, H-12/H-13), 6.77 (s, 1 H, H-4/H-10), 6.80 (s, 1 H, H-4/H-10), 6.87 (s, 1 H, H-4/H-10), 7.09 (d, J = 21.2 Hz, 1 H, H-1), 7.11–7.18 (m, 2 H, H-Ar), 7.26–7.35 (m, 4 H, H-Ar), 7.42–7.50 (m, 2 H, H-Ar), 7.51–7.56 (m, 1 H, H-Ar), 7.56–7.61 (m, 1 H, H-Ar).

$^{13}$C$^1$H-NMR (150.90 MHz, CD$_2$Cl$_2$): $\delta$ (ppm) = 9.51 (d, J = 1.0 Hz, 5 C, C-19), 19.94 (s, 1 C, C-6/C-7), 20.73 (s, 1 C, C-6/C-7), 20.83 (s, 1 C, CH$_3$), 20.91 (s, 1 C, CH$_3$), 22.74 (s, 1 C, CH$_3$), 25.67 (s, 1 C, C-12/C-13), 97.25 (d, J = 3.8 Hz, 5 C, C-18), 127.05 (d, J = 78.4 Hz, 1 C, C-14), 128.33 (d, J = 12.8 Hz, 2 C, C-Ar), 129.34 (d, J = 10.9 Hz, 2 C, C-Ar), 129.97 (s, 1 C, C-Ar), 130.85 (s, 1 C, C-Ar), 131.25 (s, 1 C, C-Ar), 131.35 (s, 1 C, C-Ar), 132.85 (s, 1 C, C-Ar), 133.06 (d, J = 6.4 Hz, 1 C, C-Ar), 133.82 (d, J = 51.2 Hz, 1 C, C-14), 134.22 (s, 1 C, C-Ar), 134.43 (d, J = 2.7 Hz, 1 C, C-Ar), 134.36 (d, J = 2.7 Hz, 1 C, C-Ar), 135.39 (br s, 2 C, C-Ar), 135.53 (d,
$J = 12.9 \text{ Hz}, 2 \text{ C, C-Ar}), 135.74 \text{ (s, 1 C, C-Ar), 138.59 \text{ (s, 1 C, C-Ar), 140.92–140.97 \text{ (m, 2 C, C-Ar),}}$

$141.81 \text{ (d, } J = 0.6 \text{ Hz, C-Ar), 168.37 \text{ (d, } J = 16.6 \text{ Hz, 1 C, C-1).}}$

$^{31}\text{P}[^1\text{H}-\text{NMR} (242.93 \text{ MHz, CD}_2\text{Cl}_2): \delta \text{ (ppm) = 80.64 \text{ (s, 1 P).}}$

$\text{EA (C}_{41}\text{H}_{48}\text{N}_2\text{PIrBF}_4): \text{ calcd. C: 49.27 \%, H: 5.32 \%, N: 2.74 \%; found: C: 49.76 \%, H: 4.96 \%, N: 2.72 \%.}}$

$\text{HR-MS (ESI+: [M–BF}_4^+ \text{) = C}_{41}\text{H}_{48}\text{N}_2\text{PIr}^+ \text{ calcd.: 919.2229 found: 919.2227.}}$

$\text{Compound [5-Pd(2-Me-allyl)]OTf}$

$\text{yield: 287 mg yellow solid (536 \mu\text{mol, 41 \%, GP 2).}}$

$^1\text{H-NMR (600.13 MHz, CDCl}_3): \delta \text{ (ppm) = 1.52 \text{ (d, } J = 3.2 \text{ Hz, 3 H, H-9), 1.55 \text{ (d, } J = 3.2 \text{ Hz,}}$

$3 \text{ H, H-9), 1.87 \text{ (s, 3 H, H-6/H-17), 2.14 \text{ (s, 6 H, H-7), 2.27 \text{ (s, 3 H, H-6/H-17), 3.20 \text{ (br s, 2 H,}}$

$H-14/H-16), 3.51 \text{ (br s, 1 H, H-14/H-16), 3.63 \text{ (br s, 1 H, H-14/H-16), 6.87 \text{ (s, 1 H, H-4), 7.53–7.61}}$

$(m, 6 \text{ H, H-Ar), 7.62–7.70 \text{ (m, 4 H, H-Ar), 8.30 \text{ (d, } J = 19.4 \text{ Hz), 1 H, H-Ar).}}$

$^{13}\text{C-NMR (150.90 MHz, CDCl}_3): \delta \text{ (ppm) = 18.93 \text{ (s, 2 C, C-7), 20.84 \text{ (s, 1 C, C-6/C-17), 23.69}}$

$(\text{br s, 2 C, C-9), 23.98 \text{ (s, 1 C, C-6/C-17), 50.60 \text{ (d, } J = 23.4 \text{ Hz, 1 C, C-8), 54.55 \text{ (s, 1 C, C-16), 80.22}}$

$(\text{d, } J = 30.1 \text{ Hz, 1 C, C-14), 120.95 \text{ (q, } J = 321.0 \text{ Hz, 1 C, C-18), 126.80 \text{ (d, } J = 41.8 \text{ Hz, 2 C, C-10),}}$

$127.13 \text{ (s, 2 C, C-3) 129.52 \text{ (s, 2 C, C-4), 129.62 \text{ (d, } J = 10.5 \text{ Hz, 4 C, C-12), 132.24 \text{ (d, } J = 2.1 \text{ Hz,}}$

$2 \text{ C, C-13), 134.03 \text{ (d, } J = 12.3 \text{ Hz, 4 C, C-11), 136.42 \text{ (s, 1 C, C-5), 136.98 \text{ (d, } J = 5.4 \text{ Hz, 1 C,}}$

$C-15), 148.56 \text{ (s, 1 C, C-2), 185.71 \text{ (s, 1 C, C-1).}}$

$^{31}\text{P-NMR (242.94 MHz, CDCl}_3): \delta \text{ (ppm) = 58.79 \text{ (br s, 1 P).}}$

$\text{HR-MS (ESI+: [M–OTf] = C}_{29}\text{H}_{33}\text{NPPd}^+ \text{ calcd.: 534.1536 found: 534.1539.}$

30
Compound [5-Rh(cod)]BF₄

yield: 232 mg orange solid (398 µmol, 52 %, GP 3).

¹H-NMR (600.13 MHz, CDCl₃): δ (ppm) = 1.52 (d, J = 12.1 Hz, 6 H, H-9), 1.98–2.05 (m, 2 H, H-15/H-16), 2.08–2.14 (m, 2 H, H-15/H-16), 2.18–2.34 (m, 4 H, H-15/H-16), 2.20 (s, 6 H, H-7), 2.22 (s, 3 H, H-6), 4.16 (br s, 2 H, H-17), 4.28 (br s, 2 H, H-14), 6.68 (s, 2 H, H-4), 7.56–7.61 (m, 6 H, H-Ar), 7.62-7.65 (m, 4 H, H-Ar), 8.12-8.17 (dd, J = 27.2 Hz, J = 3.0 Hz, 1 H, H-1).

¹³C-NMR (150.90 MHz, CDCl₃): δ (ppm) = 19.14 (s, 2 C, C-7), 20.88 (s, 1 C, C-6), 24.24 (s, 2 C, C-9), 28.62 (d, J = 1.0 Hz, 2 C, C-16), 31.59 (d, J = 2.5 Hz, 2 C, C-15), 50.89 (d, J = 23.5 Hz, 1 C, C-8), 80.72 (d, J = 17.0 Hz, 2 C, C-17), 106.60 (dd, J = 2.6 Hz, J = 9.8 Hz, 2 C, C-14), 125.12 (d, J = 40.1 Hz, 2 C, C-10), 128.62 (s, 2 C, C-3), 129.46 (d, J = 9.9 Hz, 4 C, C-12), 129.85 (s, 2 C, C-4), 132.09 (d, J = 2.3 Hz, 2 C, C-13), 134.03 (d, J = 10.5 Hz, 4 C, C-11), 137.32 (s, 1 C, C-5), 143.98 (s, 1 C, C-2), 190.28 (d, J = 12.3 Hz, 1 C, C-1).

³¹P-NMR (242.94 MHz, CDCl₃): δ (ppm) = 66.66 (d, J = 154.9 Hz, 1 P).

EA (C₃₄H₄₀F₃NO₃PSRh): calcd. C: 59.04 %, H: 6.01 %, N: 2.09 %; found: C: 59.52 %, H: 5.98 %, N: 2.04 %.

HR-MS (ESI⁺): [M–OTf] = C₃₃H₄₀NPRh⁺ calcd: 584.1948 found: 594.1947.
Compound [5-Ir(cod)]OTf

![Chemical structure](image)

**yield:** 180 mg red crystalline solid (269.1 µmol, 67 %, GP 2).

$^1$H-NMR (600.13 MHz, CDCl$_3$): $\delta$ (ppm) = 1.55 (d, $J = 12.0$ Hz, 6 H, H-9), 1.69 (br s, 4 H, H-15/H-16), 2.08 (d, $J = 12.1$ Hz, 4 H, H-15/H-16), 2.20 (s, 6 H, H-7), 2.27 (s, 3 H, H-6), 3.96 (br s, 4 H, H-14/H-17), 6.90 (s, 2 H, H-4), 7.57–7.62 (m, 6 H, H-Ar), 7.63–7.68 (m, 4 H, H-Ar), 8.66 (d, $J = 2.4$ Hz, 1 H, H-1).

$^{13}$C-NMR (150.90 MHz, CDCl$_3$): $\delta$ (ppm) = 19.03 (s, 2 C, C-7), 20.91 (s, 1 C, C-6), 24.16 (s, 2 C, C-9), 29.47 (br s, 2 C, C-15/C-16), 32.30 (br s, 2 C, C-15/C-16), 51.72 (d, $J = 29.3$ Hz, 1 C, C-8), 66.88 (br s, 2 C, C-14/C-17), 95.45 (br s, 2 C, C-14/C-17), 120.86 (q, $J = 320.7$ Hz, 1 C, C-18), 124.43 (d, $J = 48.8$ Hz, 2 C, C-10), 129.19 (s, 2 C, C-3), 129.55 (d, $J = 10.3$ Hz, 4 C, C-12), 129.78 (s, 2 C, C-4), 132.34 (d, $J = 2.4$ Hz, 2 C, C-13), 134.25 (d, $J = 10.4$ Hz, 4 C, C-11), 138.27 (s, 1 C, C-5), 143.47 (s, 1 C, C-2), 195.45 (d, $J = 10.1$ Hz, 1 C, C-1).

$^{31}$P-NMR (242.94 MHz, CDCl$_3$): $\delta$ (ppm) = 55.30 ppm (s, 1 P).

EA (C$_{34}$H$_{40}$F$_3$NO$_3$PSIr): calcd. C: 49.62 %, H: 4.90 %, N: 1.70 %; found: C: 48.99 %, H: 4.93 %, N: 1.79 %.

HR-MS (ESI$^+$): [M–OTf]$^+$ = C$_{33}$H$_{40}$IrNP$^+$ calcd.: 674.2522 found: 674.2513.
Compound [5-Cp*Ir]OTf

yield: 51.0 mg orange solid (72.8 μmol, 80 %, GP 2).

$^1$H-NMR (600.13 MHz, CDCl$_3$): $\delta$ (ppm) = 1.34 (d, $J = 2.3$ Hz, 15 H, H-15), 1.73 (d, $J = 11.0$ Hz, 3 H, H-9), 1.92 (d, $J = 11.6$ Hz, 3 H, H-9), 2.32 (s, 3 H, H-6), 2.37 (s, 3 H, H-7), 2.45 (s, 3 H, H-7), 6.93 (s, 1 H, H-4), 7.04 (s, 1 H, H-4), 7.52–7.57 (m, 2 H, H-Ar), 7.57–7.62 (m, 3 H, H-Ar), 7.63–7.71 (m, 5 H, H-Ar), 7.76 (d, $J = 23.0$ Hz, 1 H, H-1).

$^{13}$C-NMR (150.90 MHz, CDCl$_3$): $\delta$ (ppm) = 9.37 (s, 5 C, C-15), 20.71 (s, 1 C, C-6), 20.89 (s, 1 C, C-7), 24.20 (d, $J = 0.9$ Hz, 1 C, C-9), 25.27 (s, 1 C, C-7), 25.69 (d, $J = 3.9$ Hz, 1 C, C-9), 52.98 (d, $J = 31.1$ Hz, 1 C, C-8), 96.63 (d, $J = 2.4$ Hz, 5 C, C-14), 121.02 (q, $J = 320.8$ Hz, 1 C, C-16), 124.47 (d, $J = 64.7$ Hz, 1 C, C-10), 128.80 (d, $J = 11.4$ Hz, 2 C, C-Ar), 129.10 (br s, 4 C, C-Ar), 129.47 (s, 1 C, C-3), 129.96 (s, 1 C, C-4), 130.53 (d, $J = 49.5$ Hz, 1 C, C-10), 131.03 (s, 1 C, C-4), 131.25 (s, 1 C, C-3), 132.63 (d, $J = 2.6$ Hz, 1 C, C-13), 132.90 (d, $J = 2.6$ Hz, 1 C, C-13), 133.69 (d, $J = 9.5$ Hz, 2 C, C-Ar), 138.59 (s, 1 C, C-5), 146.63 (s, 1 C, C-2), 190.74 (d, $J = 10.9$ Hz, 1 C, C-1).

$^{31}$P-NMR (242.94 MHz, CDCl$_3$): $\delta$ (ppm) = 39.20 (s, 1 P).

EA (C$_{36}$H$_{45}$F$_3$NO$_3$PSIIr): calcd. C: 44.26 %, H: 4.44 %, N: 1.43 %; found: C: 43.23 %, H: 5.04 %, N: 1.03 %.

HR-MS (ESI$^+$): [M–OTf]$^+$ = C$_{35}$H$_{45}$NPiIr calcd.: 828.1802 found: 828.1788.
Compound [7-Rh(cod)]BF$_4$

![Chemical Structure](image)

**yield:** red crystalline solid (464.4 mg, 659 μmol, 92 %, GP 3).

$^1$H-NMR (600.13 MHz, CDCl$_3$): δ (ppm) = 2.03–2.10 (m, 2 H, H-19/H-20), 2.11 (s, 6 H, H-7), 2.12–2.18 (m, 2 H, H-19/H-20), 2.31–2.40 (m, 2 H, H-19/H-20), 2.43–2.52 (m, 2 H, H-19/H-20), 2.56 (s, 3 H, H-6), 3.73–3.78 (m, 2 H, H-21), 4.48–4.54 (m, 2 H, H-18), 6.87 (s, 2 H, H-4), 7.32 (dd, $J = 8.6$ Hz, $J = 7.7$ Hz, 1 H, H-10), 7.41 (dd, $J = 11.1$ Hz, $J = 7.8$ Hz, 4 H, H-15), 7.53 (td, $J = 7.6$ Hz, $J = 2.3$ Hz, 4 H, H-16), 7.58 (td, $J = 7.3$ Hz, $J = 1.5$ Hz, 2 H, H-17), 7.68–7.72 (m, 1 H, H-11), 7.87–7.90 (m, 1 H, H-12), 7.91–7.94 (m, 1 H, H-13), 7.95 (d, $J = 2.8$ Hz, 1 H, H-1).

$^{13}$C-NMR (150.90 MHz, CDCl$_3$): δ (ppm) = 19.30 (s, 2 C, C-7), 20.94 (s, 1 C, C-6), 28.64 (d, $J = 1.5$ Hz, 2 C, C-19/C-20), 32.01 (d, $J = 2.8$ Hz, 2 C, C-19/C-20), 79.86 (d, $J = 12.4$ Hz, 2 C, C-21), 109.96 (dd, $J = 10.4$ Hz, $J = 6.7$ Hz, 2 C, C-18), 124.38 (d, $J = 40.0$ Hz, 1 C, C-13), 126.93 (d, $J = 47.5$ Hz, 2 C, C-9), 129.16 (s, 2 C, C-3), 129.57 (d, $J = 10.5$ Hz, 4 C, C-16), 129.86 (s, 2 C, C-4), 132.25 (d, $J = 2.8$ Hz, 2 C, C-17), 133.51 (d, $J = 2.4$ Hz, 1 C, C-12), 133.75 (d, $J = 11.2$ Hz, 4 C, C-15), 134.26 (s, 1 C, C-10), 134.85 (d, $J = 6.6$ Hz, 1 C, C-11), 136.41 (d, $J = 17.5$ Hz, 1 C, C-8), 137.44 (s, 1 C, C-5), 139.77 (d, $J = 8.9$ Hz, 1 C, C-13), 147.75 (s, 1 C, C-2), 171.72 (d, $J = 8.1$ Hz, 1 C, C-1).

$^{31}$P-NMR (242.94 MHz, CDCl$_3$): δ (ppm) = 30.92 (d, $J = 152.91$ Hz).

EA (C$_{36}$H$_{38}$RhNPBF$_4$): calcd. C: 61.30 %, H: 5.43 %, N: 1.99 %; found: C: 56.91 %, H: 5.30 %, N: 1.88 %.

HR-MS (FAB+): [M–BF$_4$]$^+$ = C$_{36}$H$_{38}$RhNP$^+$ calcd.: 618.1791 found: 618.1818.
Compound [7-Ir(cod)]OTf

yield: black crystalline solid (925.7 mg, 1.08 mmol, 85 %, GP 2).

$^1$H-NMR (600.13 MHz, CDCl$_3$): $\delta$ (ppm) = 1.87—1.98 (m, 4 H, H-19/H-20), 2.14 (s, 6 H, H-7), 2.21 (m, 2 H, H-19/H-20), 2.28 (m, 2 H, H-19/H-20), 2.30 (s, 3 H, H-6), 3.42—3.47 (m, 2 H, H-19/H-20), 4.22—4.29 (m, 2 H, H-18), 6.91 (s, 2 H, H-4), 7.38—7.44 (m, 5 H, H-15, H-10), 7.51—7.55 (m, 4 H, H-16), 7.56—7.61 (tdd, $J = 7.5$ Hz, $J = 1.7$ Hz, $J = 1.2$ Hz, 2 H, 2 H-17), 7.77 (tdd, $J = 7.6$ Hz, $J = 1.2$ Hz, $J = 1.2$ Hz, 1 H, H-11), 7.90 (tdd, $J = 7.6$ Hz, $J = 1.3$ Hz, $J = 1.3$ Hz, 1 H, H-12), 8.02 (ddd, $J = 7.7$ Hz, $J = 4.3$ Hz, $J = 1.2$ Hz, 1 H, H-13), 8.12 (s, 1 H, H-1).

$^{13}$C-NMR (150.90 MHz, CDCl$_3$): $\delta$ (ppm) = 19.28 (s, 2 C, C-7), 20.90 (s, 1 C, C-6), 29.45 (d, $J = 2.2$ Hz, 2 C, C-19/C-20), 32.32 (d, $J = 3.8$ Hz, 2 C, C-19/C-20), 65.76 (s, 2 C, C-21), 98.66 (d, $J = 12.0$ Hz, 2 C, C-18), 120.95 (q, $J = 320.8$ Hz, 1 C, C-22), 125.03 (d, $J = 47.7$ Hz, 1 C, C-9), 126.47 (d, $J = 55.6$ Hz, 2 C, C-14), 129.49 (d, $J = 10.8$ Hz, 4 C, C-16), 129.74 (s, 2 C, C-4), 129.76 (s, 2 C, C-3), 132.49 (d, $J = 2.8$ Hz, 1 C, C-17), 133.68 (d, $J = 2.5$ Hz, 1 C, C-10), 134.04 (d, $J = 11.0$ Hz, 4 C, C-15), 134.41 (d, $J = 2.0$ Hz, 1 C, C-12), 135.46 (d, $J = 7.1$ Hz, 1 C, C-11), 136.69 (d, $J = 5.7$ Hz, 1 C, C-8), 138.07 (s, 1 C, C-2), 140.59 (d, $J = 9.1$ Hz, 1 C, C-9), 147.25 (d, $J = 5.6$ Hz, 1 C, C-6), 172.50 (d, $J = 7.2$ Hz, 1 C, C-7).

$^{31}$P-NMR (242.94 MHz, CDCl$_3$): $\delta$ (ppm) = 16.74 (s).

EA (C$_{37}$H$_{38}$F$_3$NO$_3$PSIr): calcld. C: 51.86 %, H 4.47 %, N 1.63 %; found: C: 49.69 %, H: 4.53 %, N: 1.59 %.

HR-MS (FAB+): [M–OTf]$^+$ = C$_{36}$H$_{38}$IrNP$^+$ calcd.: 708.2366 found: 708.2393.
Compound [7-Pd(2-Me-allyl)]OTf

yield: yellow solid (445.0 mg, 620 μmol, 49 %, GP 2).

$^1$H-NMR (600.13 MHz, CDCl$_3$): $\delta$ (ppm) = 1.86 (s, 3 H, H-7), 1.94 (s, 3 H, H-21), 2.04 (s, 3 H, H-7), 2.29 (s, 3 H, H-6), 2.82–2.89 (m, 1 H, H-20), 3.25–3.26 (m, 1 H, H-20), 3.35 (dd, $J = 5.8$ Hz, $J = 3.1$ Hz, 1 H, H-18), 3.51 (d, $J = 9.6$ Hz, 1 H, H-19), 6.86 (s, 1 H, H-4), 6.90 (s, 1 H, H-4), 7.21 (dd, $J = 10.6$ Hz, $J = 7.7$ Hz, 1 H, H-10), 7.23–7.28 (m, 2 H, H-15), 7.37–7.42 (m, 2 H, H-15), 7.50–7.61 (m, 6 H, H-17, H-16), 7.70 (t, $J = 7.6$ Hz, 1 H, H-11), 7.85 (t, $J = 7.6$ Hz, 1 H, H-12), 7.93 (dd, $J = 6.9$ Hz, $J = 4.8$ Hz, 1 H, H-13), 8.18 (d, $J = 2.3$ Hz, 1 H, H-1).

$^{13}$C-NMR (150.90 MHz, CDCl$_3$): $\delta$ (ppm) = 18.20 (s, 1 C, C-7), 18.42 (s, 1 C, C-7), 20.93 (s, 1 C, C-6), 24.03 (s, 1 C, C-21), 56.06 (d, $J = 3.8$ Hz, 1 C, C-20), 83.13 (d, $J = 30.3$ Hz, 1 C, C-18), 120.90 (q, $J = 320.8$ Hz, 1 C, C-22), 124.26 (d, $J = 37.3$ Hz, 1 C, C-9), 126.90 (s, 1 C, C-3), 127.00 (s, 1 C, C-3), 128.36 (s, 1 C, C-14), 129.17 (s, 1 C, C-14), 129.35 (s, 1 C, C-4), 129.67 (s, 1 C, C-4), 129.88 (d, $J = 11.0$ Hz, 2 C, C-16), 129.95 (d, $J = 11.0$ Hz, 2 C, C-16), 132.26 (d, $J = 2.8$ Hz, 1 C, C-17), 133.28 (d, $J = 2.8$ Hz, 1 C, C-17), 133.27 (d, $J = 14.0$ Hz, 2 C, C-15), 133.41 (d, $J = 2.5$ Hz, 1 C, C-12), 133.57 (d, $J = 13.9$ Hz, 2 C, C-15), 134.94 (d, $J = 6.7$ Hz, 1 C, C-11), 135.45 (s, 1 C, C-10), 136.22 (d, $J = 15.7$ Hz, 1 C, C-8), 136.75 (s, 1 C, C-5), 138.82 (d, $J = 5.7$ Hz, 1 C, C-19), 139.36 (d, $J = 9.0$ Hz, 1 C, C-13), 152.85 (s, 1 C, C-2), 169.91 (d, $J = 5.3$ Hz, 1 C, C-1).

$^{31}$P-NMR (242.94 MHz, CDCl$_3$): $\delta$ (ppm) = 23.97 (s).

EA (C$_{33}$H$_{33}$F$_3$NO$_3$PPd): calcd. C: 55.20 %, H: 4.63 %, N: 1.95 %; found: C: 55.80 %, H: 5.20 %, N: 1.89 %.

HR-MS (FAB+): [M–OTf]$^+$ = C$_{32}$H$_{35}$PdNP$^+$ calcd.: 568.1385 found: 568.1400.
3 VT-NMR Studies

Compound $[2a\text{-PdCl}_2](\text{BF}_4)_2$ is dimeric in the solid state, with two chlorides bridging the cationic palladium centers. Its $^{31}\text{P}$-NMR spectrum in $\text{CD}_2\text{Cl}_2$ at room temperature features a single, broad resonance, whereas in $\text{CDCl}_3$ solution, three broad signals were found. To clarify these findings, a variable-temperature NMR study of this compound in dichloromethane was conducted, revealing that at low temperatures three species can be distinguished in solution (Figure 1).

![NMR spectra](image)

**Figure 1:** $^{31}\text{P}$-NMR spectra of $2a$, $[2a\text{-PdCl}_2]$ and variable-temperature $^{31}\text{P}$-NMR study of the dimeric complex $[2a\text{-PdCl}_2](\text{BF}_4)_2$. Solvents used: (a) THF-$d_8$, (b)–(d) dichloromethane-$d_2$.

This is in line with a solvent-dependent equilibrium between dimeric and monomeric solvated T-shaped stereoisomers, although an additional stabilizing coordination of the BF$_4$ anion is also possible [20].
4 X-Ray Crystal Structure Determinations

Crystal data and details of the structure determinations are compiled in Tables 1–4. Full shells of intensity data were collected at low temperature with Agilent Technologies Supernova E (Mo- or Cu-$K_{\alpha}$ radiation, microfocus X-ray tube, multilayer mirror optics) or Bruker AXS Smart 1000 (Mo-$K_{\alpha}$ radiation, sealed X-ray tube, graphite monochromator) CCD diffractometers. Data were corrected for air and detector absorption, Lorentz and polarization effects [21–23]; absorption by the crystal was treated with a semiempirical multiscan method (data collected with the Bruker instrument) [24–26] or numerically (data collected with the Agilent instrument, Gaussian grid) [21, 22, 27]. For datasets collected with the microfocus tube(s) an illumination correction was performed [28, 29]. The structures were solved by intrinsic phasing (for 2b-Ir(cod)BF$_4$·0.5 CH$_2$Cl$_2$·C$_7$H$_8$) [30–32], by direct methods with dual-space recycling (for 2a-Ir(cod)BF$_4$·CH$_2$Cl$_2$) [33, 34], by the heavy atom method combined with structure expansion by direct methods applied to difference structure factors (for 7-Rh(cod)BF$_4$·CH$_2$Cl$_2$) [35, 36], or by the charge flip procedure (all other structures) [37, 38]. Refinement was carried out by full-matrix least squares methods based on $F^2$ against all unique reflections [39–41]. All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms were generally input at calculated positions and refined with a riding model. When justified by the quality of the data, the positions of some hydrogen atoms were taken from difference Fourier synthesis and refined. When found necessary, disordered groups and/or solvent molecules were subjected to suitable geometry and adp restraints. The two independent complex cations in the structures of 2b-M(cod)BF$_4$·0.5 CH$_2$Cl$_2$·0.5 C$_7$H$_8$ (M = Rh, Ir) are related by a pseudosymmetry translation. The symmetry is however broken by the toluene solvent molecule.

Due to severe disorder and/or fractional occupancy, electron density attributed to solvent of crystallization was removed from the structures of 2a-Cp*Irl]BF$_4$·1.5 CH$_2$Cl$_2$ and 7-Rh(cod)BF$_4$·1.x CH$_2$Cl$_2$ with the BYPASS procedure [42, 43], as implemented in PLATON (SQUEEZE) [44, 45]. Partial structure factors from the solvent masks were included in the refinement as separate contributions to $F_{\text{obs}}$.

CCDC 1451416–1451427 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.
Table 1: Details of the crystal structure determinations of [2a-PdCl₂], [2a-PdCl₂(BF₄)₂] and [2a-Rh(cod)]BF₄.

| Compound                              | [2a-PdCl₂] · 3 CH₂Cl₂ | [2a-PdCl₂(BF₄)₂] · CH₂Cl₂ · 0.5 C₇H₈ | [2a-Rh(cod)]BF₄ · 1.x CH₂Cl₂ |
|---------------------------------------|-----------------------|--------------------------------------|------------------------------|
| Empirical formula                     | C₂₃H₂₇Cl₉N₃PPd       | C₆₆₅H₆₃B₂Cl₁₄F₂N₃P₂Pd              | C₈₆₃H₂₇Cl₉N₃PrH             |
| Formula weight Mᵣ (g/mol)             | 896.64                | 1517.44                             | 847.38                      |
| Crystal system                        | monoclinic            | triclinic                            | triclinic                   |
| Space group                           | P 2₁/c (IT Nr. 14)    | P 1 (IT Nr. 2)                      | P 1 (IT Nr. 2)              |
| a (Å)                                 | 11.63996(6)           | 11.291(6)                           | 12.435(5)                   |
| b (Å)                                 | 22.90211(13)          | 13.841(7)                           | 15.735(7)                   |
| c (Å)                                 | 14.66629(6)           | 21.603(10)                          | 19.553(8)                   |
| α (°)                                 | 82.724(8)             | 82.724(8)                           | 89.234(11)                  |
| β (°)                                 | 92.3283(4)            | 80.839(13)                          | 89.261(14)                  |
| γ (°)                                 | 87.563(12)            | 87.563(12)                          | 89.370(9)                   |
| V (Å³)                                | 3906.51(3)            | 3305(3)                             | 3825(3)                     |
| Z                                      | 4                     | 2                                   | 4                           |
| F₀₀₀                                   | 1816                  | 1542                                | 1744                        |
| dₑ (Mg m⁻³)                           | 1.525                 | 1.525                               | 1.471                       |
| X-radiation, λ (Å)                    | Cu-Kα, 1.54184        | Mo-Kα, 0.71073                      | Mo-Kα, 0.71073              |
| μ (mm⁻¹)                              | 9.464                 | 0.821                               | 0.679                       |
| Transmission factors: max, min        | 0.828, 0.244          | 0.8828, 0.8021                      | 0.9039, 0.8467              |
| Data collect. temp. (K)               | 120(1)                | 100(1)                              | 100(1)                      |
| θ range for data collection (°)       | 3.6 to 71.0           | 1.9 to 32.4                         | 1.6 to 31.5                 |
| Index ranges h, k, l                  | −14 ... 14, −27 ... 25, −17 ... 17 | −16 ... 16, −20 ... 20, −29 ... 31 | −18 ... 18, −22 ... 23, −28 ... 28 |
| Reflections measured                  | 246179                | 65911                               | 98486                       |
| Independent refl. [R(int)]            | 7511 [0.0630]         | 21848 [0.0414]                      | 25065 [0.0484]              |
| Observed refl. [I ≥ 2σ(I)]            | 7242                  | 17078                               | 19118                       |
| data / restraints / parameter         | 7511 / 0 / 424        | 21848 / 222 / 876                   | 25065 / 168 / 983           |
| GoF on F²                              | 1.058                 | 1.024                               | 1.021                       |
| R [F > 4σ(F)] R(F), wR(F²)             | 0.0351, 0.0850        | 0.0465, 0.1082                      | 0.0399, 0.0891              |
| R (all data) R(F), wR(F²)              | 0.0364, 0.0859        | 0.0683, 0.1188                      | 0.0617, 0.0990              |
| Diff. density: rms, max (e Å⁻³)       | 0.080, 1.760, −1.075  | 0.128, 2.254, −1.702                | 0.104, 1.590, −1.039        |
| Diffractometer                        | Agilent Supernova-E   | Bruker AXS Smart 1000               | Bruker AXS Smart 1000       |
Table 2: Details of the crystal structure determinations of [2b-Rh(cod)]BF₄, [2a-Ir(cod)]BF₄ and [2b-Ir(cod)]BF₄.

| Compound                      | [2b-Rh(cod)]BF₄ - 0.5 CH₂Cl₂ - C₇H₈ | [2a-Ir(cod)]BF₄ - CH₂Cl₂ | [2b-Ir(cod)]BF₄ - 0.5 CH₂Cl₂ - C₇H₈ |
|-------------------------------|--------------------------------------|--------------------------|-------------------------------------|
| Empirical formula             | C₄₀H₆₂BCIF₂N₂PRh                     | C₄₀H₆₂BCIF₂N₂PRh        | C₄₀H₆₂BCIF₂N₂PRh                   |
| Formula weight M₀ (g/mol)     | 935.14                               | 936.67                   | 1024.43                             |
| Crystal system                | triclinic                            | triclinic                | triclinic                           |
| Space group                   | P 1 (IT Nr. 2)                       | P 1 (IT Nr. 2)           | P 1 (IT Nr. 2)                      |
| a (Å)                         | 10.903(4)                            | 12.47669(19)             | 10.95376(6)                         |
| b (Å)                         | 17.768(7)                            | 15.7562(2)               | 17.76136(11)                        |
| c (Å)                         | 24.913(9)                            | 19.5779(3)               | 24.96835(15)                        |
| α (°)                         | 107.751(13)                          | 89.2424(12)              | 107.7617(5)                         |
| β (°)                         | 96.045(9)                            | 89.4178(12)              | 95.9466(5)                          |
| γ (°)                         | 96.260(13)                           | 89.6008(12)              | 96.1981(5)                          |
| V (Å³)                        | 4520(3)                              | 3844.17(10)              | 4540.08(5)                          |
| Z                             | 4                                    | 4                        | 4                                   |
| F₀₀₀                          | 1952                                 | 1872                     | 2080                                |
| d₀ (Mg·m⁻³)                   | 1.374                                | 1.618                    | 1.499                               |
| X-radiation, λ (Å)            | Mo-Kα, 0.71073                       | Mo-Kα, 0.71073           | Mo-Kα, 0.71073                      |
| μ (mm⁻¹)                      | 0.525                                | 3.705                    | 3.087                               |
| Transmission factors: max, min| 0.7464, 0.6974                        | 0.918, 0.569             | 0.825, 0.591                        |
| Data collect. temp. (K)       | 100(1)                               | 120(1)                   | 120(1)                              |
| θ range for data collection (°)| 0.9 to 32.5                          | 3.3 to 26.4              | 3.2 to 32.9                         |
| Index ranges h, k, l          | −15 ... 15, −26 ... 26, −37 ... 37    | −15 ... 15, −19 ... 19, −24 ... 24 | −16 ... 16, −26 ... 26, −37 ... 38  |
| Reflections measured          | 117410                               | 80938                    | 658461                              |
| Independent refl. [Rint]      | 30412 [0.0376]                       | 15685 [0.0611]           | 32099 [0.0740]                      |
| Observed refl. [I ≥ 2σ(I)]   | 22684                                | 13294                    | 29136                               |
| data / restraints / parameter | 30412 / 100 / 1096                   | 15685 / 302 / 959        | 32099 / 100 / 1096                  |
| Goof on F²                    | 1.029                                | 1.196                    | 1.225                               |
| R [F > 4σ(F)] R(F), wR(F²)    | 0.0427, 0.1030                       | 0.0511, 0.1092           | 0.0460, 0.0716                      |
| R (all data) R(F), wR(F²)     | 0.0634, 0.1155                       | 0.0620, 0.1152           | 0.0549, 0.0739                      |
| Diff. density: rms, max, min (e·Å⁻³)| 0.116, 2.207, −1.111 | 0.158, 2.317, −2.827 | 0.116, 1.631, −1.997               |
| Diffractometer                | Bruker AXS Smart 1000                | Agilent SuperNova-E      | Agilent SuperNova-E                 |
Details of the crystal structure determinations of \(\text{[2a-Cp}^*\text{IrI]}\text{BF}_4\cdot 1.5\text{CH}_2\text{Cl}_2\), \(\text{[5-Pd(2-Me-allyl)]OTf}\) and \(\text{[5-Rh(cod)]BF}_4\).

**Table 3:** Details of the crystal structure determinations of \(\text{[2a-Cp}^*\text{IrI]}\text{BF}_4\cdot 1.5\text{CH}_2\text{Cl}_2\), \(\text{[5-Pd(2-Me-allyl)]OTf}\) and \(\text{[5-Rh(cod)]BF}_4\).

| Compound                  | \(\text{[2a-Cp}^*\text{IrI]}\text{BF}_4\cdot 1.5\text{CH}_2\text{Cl}_2\) | \(\text{[5-Pd(2-Me-allyl)]OTf}\) | \(\text{[5-Rh(cod)]BF}_4\) |
|---------------------------|-------------------------------------------------|---------------------------------|--------------------------|
| Empirical formula         | \(\text{C}_{42.5}\text{H}_{52.5}\text{BCl}_3\text{F}_4\text{IrN}_2\text{P}\) | \(\text{C}_{30}\text{H}_{35}\text{F}_3\text{NO}_3\text{PdS}\) | \(\text{C}_{31}\text{H}_{38}\text{BF}_4\text{NPRh}\) |
| Formula weight \(M_r\) (g/mol) | 1134.09                                      | 684.02                          | 671.35                   |
| Crystal system            | triclinic                                      | orthorhombic                    | monoclinic               |
| Space group               | \(P\) \(\bar{1}\) (IT Nr. 2)                   | \(P\) \(b\) \(c\) \(a\)       | \(P\) 2/\(i\) (IT Nr. 14) |
| \(a\) (Å)                 | 11.539(4)                                     | 17.413(9)                       | 12.941(5)                |
| \(b\) (Å)                 | 11.740(4)                                     | 17.673(8)                       | 12.948(6)                |
| \(c\) (Å)                 | 16.334(6)                                     | 19.974(10)                      | 19.111(8)                |
| \(α\) (°)                 | 101.867(10)                                   |                                 |                          |
| \(β\) (°)                 | 93.026(7)                                     |                                 |                          |
| \(γ\) (°)                 | 94.659(6)                                     |                                 |                          |
| \(V\) (Å\(^3\))           | 2152.9(14)                                    | 6147(5)                         | 3068(2)                  |
| \(Z\)                     | 2                                              | 8                               | 4                        |
| \(F_{000}\)               | 1097                                           | 2800                            | 1384                     |
| \(d_0\) (Mg m\(^{-1}\))  | 1.749                                          | 1.478                           | 1.453                    |
| X-radiation, \(λ\) (Å)    | \(\text{Mo-}K\alpha, 0.71073\)                | \(\text{Mo-}K\alpha, 0.71073\) | \(\text{Mo-}K\alpha, 0.71073\) |
| \(μ\) (mm\(^{-1}\))      | 4.092                                          | 0.773                           | 0.657                    |
| Transmission factors: max, min | 0.3391, 0.2665                               | 0.7464, 0.6717                  | 0.8623, 0.8050           |
| Data collect. temp. (K)   | 100(1)                                         | 100(1)                          | 100(1)                   |
| \(θ\) range for data collection (°) | 2.0 to 32.5                                  | 1.9 to 26.4                     | 1.9 to 32.5              |
| Index ranges \(h, k, l\)  | \(-17 \ldots 17, -17 \ldots 17, -24 \ldots 24\) | \(-21 \ldots 21, -22 \ldots 22, -24 \ldots 24\) | \(-19 \ldots 19, -19 \ldots 19, -28 \ldots 28\) |
| Reflections measured      | 55403                                          | 107373                          | 78525                    |
| Independent refl. [\(R_{int}\)] | 14467 [0.0243]                          | 6277 [0.0321]                   | 10718 [0.0300]           |
| Observed refl. [\(I \geq 2σ(I)\)] | 13900                          | 5102                            | 9691                     |
| data / restraints / parameter | 14467 / 0 / 498                             | 6277 / 12 / 382                 | 10718 / 21 / 390         |
| Goof on \(F^2\)           | 1.052                                          | 1.196                           | 1.047                    |
| \(R\) [\(F > 4σ(F)\)] \(R(F)\), \(wR(F^2)\) | 0.0186, 0.0463        | 0.0395, 0.0765                    | 0.0245, 0.0596           |
| \(R\) (all data) \(R(F)\), \(wR(F^2)\) | 0.0200, 0.0470        | 0.0569, 0.0929                    | 0.0288, 0.0629           |
| Diff. density: max, min (e Å\(^{-3}\)) | 0.096, 1.340, −1.700 | 0.109, 1.702, −0.553 | 0.073, 1.024, −0.754 |
| Diffraeometer              | \(\text{Bruker AXS Smart 1000}\)            | \(\text{Bruker AXS Smart 1000}\) | \(\text{Bruker AXS Smart 1000}\) |
Table 4: Details of the crystal structure determinations of [5-Ir(cod)]OTf, [5-Cp′Ir]OTf and [7-Rh(cod)]BF₄.

| Compound                        | [5-Ir(cod)]OTf | [5-Cp′Ir]OTf · CHCl₃ | [7-Rh(cod)]BF₄ · CH₂Cl₂ |
|---------------------------------|---------------|----------------------|------------------------|
| Empirical formula               | C₁₄H₁₄F₃IrNO₃PS | C₁₄H₁₄Cl₃IrNO₃PS | C₁₇H₁₆BCl₃F₄P NPRh |
| Crystal system                  | monoclinic    | monoclinic           | triclinic              |
| Space group                     | P 2₁/n (IT Nr. 14) | P 2₁/n (IT Nr. 14) | P 1 (IT Nr. 1) |
| a (Å)                           | 13.001(6)     | 18.967(8)            | 13.378(5)             |
| b (Å)                           | 18.967(8)     | 9.113(4)             | 25.210(11)            |
| c (Å)                           | 13.378(5)     | 14.13707(16)         | 20.6977(3)            |
| α (°)                           | 105.6171(11)  | 94.921(9)            | 104.3606(11)          |
| β (°)                           | 94.921(9)     | 101.562(11)          | 104.3606(11)          |
| γ (°)                           | 104.3606(11)  | 96.4680(11)          | 104.3606(11)          |
| V (Å³)                          | 3287(2)       | 3902(3)              | 2621.65(6)            |
| Z                               | 4             | 4                    | 3                     |
| F₁₀₀                            | 1640          | 2144                 | 1212                  |
| d₀ (Mg m⁻³)                     | 1.663         | 1.866                | 1.502                 |
| X-radiation, λ (Å)              | Mo-Κα, 0.71073| Mo-Κα, 0.71073       | Mo-Κα, 0.71073        |
| μ (mm⁻¹)                        | 4.227         | 4.565                | 0.737                 |
| Transmission factors: max, min  | 0.4949, 0.3820 | 0.7464, 0.5181       | 0.977, 0.926          |
| Data collect. temp. (K)         | 100(1)        | 100(1)               | 120(1)                |
| θ range for data collection (°) | 2.1 to 32.5   | 2.4 to 32.5          | 3.2 to 32.9           |
| Index ranges h, k, l            | −19 ... 18, −28 ... 28, −19 ... 19 | −25 ... 25, −13 ... 13, −38 ... 37 | −14 ... 14, −21 ... 21, −30 ... 30 |
| Reflections measured            | 83623         | 97716                | 87324                 |
| Independent refl. [Rint]        | 11337 [0.0345] | 13477 [0.0438]       | 34788 [0.0516]        |
| Observed refl. [I ≥ 2σ(I)]     | 10520         | 11946                | 30637                 |
| data / restraints / parameter   | 11337 / 0 / 417 | 13477 / 0 / 473      | 34788 / 169 / 1251    |
| Good-fit on F²                   | 1.947         | 1.026                | 1.926                 |
| R [F > 4σ(F)] R(F), wR(F²)      | 0.0181, 0.0397 | 0.0252, 0.0590       | 0.0446, 0.0896        |
| R (all data) R(F), wR(F²)       | 0.0223, 0.0412 | 0.0321, 0.0620       | 0.0542, 0.0955        |
| Diff. density: rms, max, min (e·Å⁻³) | 0.099, 1.596, −0.892 | 0.144, 1.757, −2.082 | 0.099, 0.905, −0.646 |
| Absolute structure parameter    |              |                      | −0.005(9)             |
| Diffractometer                  | Bruker AXS Smart 1000 | Bruker AXS Smart 1000 | Agilent SuperNova-E   |
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