Supporting Information

Diverse Coordination Modes of Bidentate COC and Trideterminate CNC Ligands Comprising 1,2,3-Triazol-5-ylidenes

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S1. General Methods

a. Method

All synthetic manipulations, unless otherwise stated, were performed under a \( \text{N}_2 \) (g) or Ar (g) atmosphere using oven or flame dried glassware and standard Schlenk or vacuum line techniques. Air sensitive solids were stored and handled in an InertLab glove box. Preparations of NMR and crystallization samples that also require an inert atmosphere were performed in a glove box.

b. Materials

The following ligand and metal precursors were synthesized in this study according to known synthetic procedures: 1,3-bis-(2,6-diisopropylphenyl)triaz-1-ene,
\(^1\) sodium hypochlorite,
\(^2\) N-(tert-butylxoy)carbonyl dipropargylamine,
\(^3\) di-µ-chloro-bis(1,5-cyclooctadiene)dirhodium(I),
\(^4\) di-µ-chlorotetracarbonyldirhodium(I),
\(^5\) and di-µ-chloro-bis(1,5-cyclooctadiene)diiridium(I).
\(^6\) All other reagents were obtained from commercial sources and were used without any further purification. Unless otherwise stated, only anhydrous solvents were used for the experimental procedures. Anhydrous THF (tetrahydrofuran) and DEE (diethyl ether) were obtained after distillation over sodium wire Na(s) and benzophenone under a \( \text{N}_2 \) (g) atmosphere. Anhydrous toluene and hexane were obtained after distillation over sodium wire under a \( \text{N}_2 \) (g) atmosphere. Anhydrous DCM (dichloromethane) was obtained after distillation over calcium hydride (CaH\(_2\)) under a \( \text{N}_2 \) (g) atmosphere. Deuterated benzene was dried over sodium and distilled under an Ar (g) atmosphere. Deuterated acetonitrile, chloroform and dichloromethane were dried over calcium hydride under an Ar (g) atmosphere.

b. Characterization Techniques

Nuclear magnetic resonance (NMR) spectra were obtained using either a Bruker AVANCE-III-300 operating at 300.13 MHz for \(^1\)H, 75.47 MHz for \(^{13}\)C, 121.49 MHz for \(^{31}\)P and 282.40 MHz for \(^{19}\)F; or AVANCE-III-400 operating at 400.21 MHz for \(^1\)H, 100.64 MHz for \(^{13}\)C, 162.01 MHz for \(^{31}\)P and 376.57 MHz for \(^{19}\)F; or AVANCE-III-500 operating at 500.13 MHz for \(^1\)H, 125.31 MHz for \(^{13}\)C, 202.46 MHz for \(^{31}\)P and 470.59 MHz for \(^{19}\)F. \(^1\)H Chemical shifts are reported as \( \delta \) (ppm) values downfield from Me\(_4\)Si and chemical shifts were referenced to residual non-deuterated solvent peaks (CDCl\(_3\): 7.260 ppm, C\(_6\)D\(_6\): 7.160 ppm; CD\(_2\)Cl\(_2\): 5.32 ppm; and CD\(_3\)CN: 1.940 ppm). \(^{13}\)C chemical shifts are also reported as \( \delta \) (ppm) values
downfield from Me₃Si and chemical shifts were referenced to residual non-deuterated solvents peaks (CDCl₃: 77.160 ppm, C₆D₆: 128.060 ppm; CD₂Cl₂: 54.00 ppm; and CD₃CN: 118.260 ppm. Proton coupling constants (J) are given in Hz. The spectral coupling patterns are designated as follows: s - singlet; d - doublet; t - triplet; q- quartet; quint – quintet; sept - septet; m - multiplet; dd- doublet of doublets; dt – doublet of triplets; td – triplet of doublets; br - broad signal. Quaternary carbons are designated as C₄.

Chemical shift assignment in the ¹H NMR spectra is based on first-order analysis experiments. The ¹³C shifts were obtained from proton-decoupled ¹³C NMR spectra. Where necessary, the multiplicities of the ¹³C signals were deduced from proton-decoupled DEPT-135 spectra. The resonances of the proton-bearing carbon atoms were correlated with specific proton resonances using 2D (¹³C-¹H) heteronuclear single-quantum coherence (HSQC) experiments. Standard Bruker pulse programs (298 K) were used in the experiments, while low temperature (243 K) NMR experiments were run for all of the fluxional 1,5-cyclooctadiene metal complexes.

Solution IR spectra (ν(CO)) were recorded on a Bruker ALPHA FT–IR spectrophotometer in CH₂Cl₂ as solvent. The range of absorption measured was from 4000–400 cm⁻¹.

Electrospray mass spectra (ESI-MS) were recorded on a Bruker QTOF Mass spectrometer with positive electron spray as the ionization techniques; nitrogen was employed as drying and nebulizing gas at a flow of 4 L/min. The m/z values were measured in the range of 100-1500 with acetonitrile as solvent. Accurate mass measurements were performed by use of a Q-TOF premier mass spectrometer with electrospray source (Waters, Manchester, UK) operating at a resolution of ca. 16 000 (fwhm).
S2. Synthesis and characterization of ligand precursors

Synthesis of \([\text{H}_2(\text{COC})](\text{PF}_6)_2\)

A round-bottom flask was loaded with dry 1,3-bis-(2,6-diisopropylphenyl)triaz-1-ene (14.62 g, 0.04 mol), KPF\(_6\) (7.36 g, 0.04 mol), and degassed CH\(_2\)Cl\(_2\) (ca. 500 mL). Whilst stirring, dipropargyl ether (0.69 mL, 6.69 mmol) was added to the reaction vessel and cooled to -78°C. \(\text{tBuOCl}\) (4.55 mL, 0.04 mol) was added dropwise in the absence of light, and allowed to warm to room temperature (RT) overnight. The solvent was evaporated under reduced pressure, and the residue was washed with dichloromethane (DCM) to yield a pinkish-white solid. Excess KPF\(_6\) was removed by performing multiple H\(_2\)O/DCM (50/50) liquid-liquid extractions. Combined organic fractions were then evaporated to dryness and the resulting solid washed with diethyl ether to yield \([\text{H}_2(\text{COC})](\text{PF}_6)_2\) (6.46 g, 5.8 mmol, 87%), as a white solid after vacuum filtration. Crystallization from DCM yielded single crystals suitable for XRD analysis.

**\(^1\)H NMR** \(\delta\) (CD\(_3\)CN, 500.13 MHz) 8.91 (s, 2H, CH\(_{\text{Trz}}\)), 7.76 (td, 4H, J = 7.9 Hz, ArCH\(_{\text{Dipp}}\)), 7.54 (dd, 8H, J = 7.9 Hz, 7.85 Hz, ArCH\(_{\text{Dipp}}\)), 4.58 (s, 4H, O(\text{CH}_2)_2)), 2.21 (sept, 4H, J = 6.9 Hz, CH(CH\(_3\))_2)), 2.10 (sept, 4H, J = 6.7 Hz, CH(CH\(_3\))_2)), 1.29 (d, 12H, J = 6.8 Hz, CH(CH\(_3\))_2)), 1.18 (dd, 24H, J = 7.9 Hz, 7.85 Hz, ArCH\(_{\text{Dipp}}\)), 1.10 (d, 12H, J = 6.8 Hz, CH(CH\(_3\))_2)), 1.10 (d, 12H, J = 6.7 Hz, CH(CH\(_3\))_2)).

**\(^{13}\)C NMR** \(\delta\) (CD\(_3\)CN,125.31 MHz) \(\delta\) C(CH\(_3\))_2) 146.54 (ArC\(_q\)), 146.27 (ArC\(_q\)), 143.43 (C\(_q\)\(_{\text{Trz}}\)), 134.92 (CH\(_{\text{Trz}}\)), 134.82, (ArCH) 134.58 (ArCH), 131.19 (ArC\(_q\)), 128.78 (ArC\(_q\)), 126.47 (ArCH), 126.13 (ArCH), 62.17 (O(\text{CH}_2)_2)), 30.02 (CH(CH\(_3\))_2), 25.60 (CH(CH\(_3\))_2)).

**\(^{19}\)F NMR** \(\delta\) (CD\(_3\)CN, 470.59 MHz) -72.81 (d, J = 707.4 Hz, PF\(_6\)).

**\(^{31}\)P NMR** \(\delta\) (CD\(_3\)CN, 202.46 MHz) -144.58 (sept, J = 707.0 Hz, PF\(_6\)).

**HRMS** (FIA-ESI): Calculated for \([\text{C}_{54}\text{H}_{74}\text{N}_6\text{O}]^{2+}\) [M – 2PF\(_6\)]\(^{2+}\): 411.2962; found: 411.2946, [C\(_{54}\text{H}_{74}\text{N}_6\text{OPF}_6\)]\(^+\) [M – PF\(_6\)]\(^+\): 967.5565; found: 967.5456.
Synthesis of [H₂(C₈O₃NC)][PF₆]₂

Compound [H₂(C₈O₃NC)][PF₆]₂ was prepared by a similar procedure as employed for the synthesis of [H₂(COC)][PF₆]₂. A round bottom flask (RBF) was loaded with 1,3-bis-(2,6-diisopropylphenyl)triaz-1-ene (28.4 g, 0.08 mol), KPF₆ (17.2 g, 0.09 mol), N-(tert-butyl)carbonyl dipropargylamine (5.0 g, 0.03 mol) and degassed, anhydrous DCM (ca. 500 mL). After cooling the reaction mixture to -78°C, tBuOCl (8.8 mL, 0.08 mmol) was added dropwise in the absence of light and allowed to warm to RT overnight. The solvent was evaporated under reduced pressure, and the resulting solid was repeatedly washed with hexane, followed by diethyl ether (DEE), to yield [H₂(C₈O₃NC)][PF₆]₂ (16.9 g, 0.014 mol, 54%) as a cream-coloured solid. Crystallization from DCM yielded single crystals suitable for XRD analysis.

¹H NMR δH (CD₃CN, 500.13 MHz) 8.97 (s, 1H, CH₃), 8.83 (s, 1H, CH₃), 7.77 (m, 3H, ArH), 7.54 (m, 9H, ArH), 4.60 (s, 2H, N(CH₃)₂), 3.71 (s, 2H, N(CH₃)₂), 2.25 (Sept, 6H, ArH), 1.28 (dd, 18H, ArH). ¹³C NMR δC (CD₃CN, 125.31 MHz) δ154.58 (BOC-CO), 146.64 (ArCH), 146.30 (ArCH), 146.18 (ArC₆), 145.99, (ArC₆), 145.18 (Cq, 135.11 (ArCH), 134.49 (ArCH), 133.67 (ArCH), 131.17 (ArC₆), 130.98 (ArC₆), 128.99 (ArC₆), 126.53 (ArC₆), 126.63 (ArCH), 126.10 (ArCH), 85.25 (OC(CH₃)₂), 45.28 (N(CH₂)₂), 44.86 (N(CH₂)₂), 30.22 (CH(CH₃)₂), 29.96 (CH(CH₃)₂), 28.83 (CH(CH₃)₂), 29.81 (CH(CH₃)₂), 28.31 (CH(CH₃)₂), 26.45 (CH(CH₃)₂), 26.13 (CH(CH₃)₂), 25.09 (CH(CH₃)₂), 24.64 (CH(CH₃)₂), 24.02 (CH(CH₃)₂), 22.75 (CH(CH₃)₂), 22.47 (CH(CH₃)₂). ¹⁹F NMR δF (CD₃CN, 470.59 MHz) -72.85 (d, J = 705.8 Hz, PF₆). ³¹P NMR δP (CD₃CN, 202.46 MHz) -144.60 (d, J = 706.4 Hz, PF₆). HRMS (FIA-ESI): Calculated for [C₉H₆₊₂N₂O₂]²⁺ [M – 2PF₆]²⁺: 460.8304; found: 460.8295, [C₉H₆₊₂N₂O₂PF₆]⁺ [M – PF₆]⁺ : 1066.6250; found: 1066.6184.
Synthesis of $[\text{H}_2(\text{C}^{\text{H}}\text{NC})](\text{PF}_6)_2$

Compound $[\text{H}_2(\text{C}^{\text{H}}\text{NC})](\text{PF}_6)_2$ was obtained by a simple deprotection strategy whereby compound $[\text{H}_2(\text{C}^{\text{Boc}}\text{NC})](\text{PF}_6)_2$ (16.9 g, 0.014 mol) was treated with 3N methanolic HCl (60 mL, 0.181 mol) and was stirred for 2 days at 50°C. The solution was neutralized with saturated NaHCO$_3$ (aq), further basified with KOH (aq) until pH tested above 9 before frit filtration and solvent removal. Excess KPF$_6$ was removed by performing multiple H$_2$O/DCM (50/50) liquid-liquid extractions. The organic fractions were combined and then evaporated to dryness. The product was washed with hexane, DEE and DCM, consecutively, to yield $[\text{H}_2(\text{C}^{\text{H}}\text{NC})](\text{PF}_6)_2$ (13.2 g, 0.012 mol, 85%) as a pure white solid. Crystallization from DCM yielded single crystals suitable for XRD analysis.

$^1$H NMR $\delta_H$(CD$_3$CN, 500.13 MHz) 10.46 (s, 2H, CH$_{\text{Trz}}$), 7.71 (td, 4H, $J$= 7.8, ArH$_{\text{Dipp}}$), 7.51 (dd, 8H, $J$= 7.8 Hz, ArH$_{\text{Dipp}}$), 4.44 (pent, 1H, N-H), 3.82 (d, 4H, $J$= 6.9 Hz, N(CH$_2$)$_2$), 2.23 (sept, 4H, $J$= 6.7 Hz, CH(CH$_3$)$_2$), 2.11 (Sept, 4H, $J$= 6.7 Hz, CH(CH$_3$)$_2$), 1.15 (d, 12H, $J$= 6.8 Hz, CH(CH$_3$)$_2$), 1.08 (d, 12H, $J$= 6.8 Hz, CH(CH$_3$)$_2$). $^{13}$C NMR $\delta_C$(CD$_3$CN,125.31 MHz) $\delta$147.16 (ArC$_q$), 146.51 (ArC$_q$), 146.32 (C$_q$Trz), 136.26 (CH$_{\text{Trz}}$), 134.46 (ArCH), 134.16 (ArCH), 131.62 (ArC$_q$), 129.02 (ArC$_q$), 126.31 (ArCH), 125.93 (ArCH), 43.59 (N(CH$_2$)$_2$), 29.95 (CH(CH$_3$)$_2$), 29.88 (CH(CH$_3$)$_2$), 25.42 (CH(CH$_3$)$_2$), 24.56 (CH(CH$_3$)$_2$), 24.20 (CH(CH$_3$)$_2$), 23.04 (CH(CH$_3$)$_2$). $^{19}$F NMR $\delta_F$(CD$_3$CN, 470.59 MHz) -72.81 (d, $J$= 706.4 Hz, PF$_6$). $^{31}$P NMR $\delta_P$(CD$_3$CN, 202.46 MHz) -144.58 (d, $J$= 707.0 Hz, PF$_6$). HRMS (FIA-ESI): Calculated for [C$_{54}$H$_{75}$N$_7$]$^{2+}$ [M – 2PF$_6$]$^{2+}$: 410.8041 found: 410.8075, and also [C$_{54}$H$_{75}$N$_7$PF$_6$]$^{+}$ [M – PF$_6$]$^{+}$: 966.5725 found: 966.5674.
Figure S1: $^1$H NMR spectrum of $[\text{H}_2(\text{COC})][\text{PF}_6]_2$ in CD$_3$CN. [* annotates residual DCM (CH$_2$Cl$_2$)]

Figure S2: $^{13}$C NMR spectrum of $[\text{H}_2(\text{COC})][\text{PF}_6]_2$ in CD$_3$CN
Figure S3. $^1$H NMR spectrum of [H$_2$(C$^{Boc}$NC)](PF$_6$)$_2$ in CD$_3$CN

Figure S4. $^{13}$C NMR spectrum of [H$_2$(C$^{Boc}$NC)](PF$_6$)$_2$ in CD$_3$CN
Figure S5: $^1$H NMR spectrum of [H$_2$(C$^\text{HNC}$)](PF$_6$)$_2$ in CD$_3$CN

Figure S6: $^{13}$C NMR spectrum of [H$_2$(C$^\text{HNC}$)](PF$_6$)$_2$ in CD$_3$CN
Figure S7: $^1$H NMR spectrum of 1a [Rh(cod)(COC)](PF$_6$) in CDCl$_3$ [* annotates grease]

Figure S8: $^{13}$C NMR spectrum of 1a [Rh(cod)(COC)](PF$_6$) in CDCl$_3$ [* annotates grease]
Figure S9: $^1$H NMR spectrum (243 K) of 1b [Ir(cod)(COC)](PF$_6$) in CD$_2$Cl$_2$ [* annotates grease]

Figure S10: $^{13}$C NMR spectrum (243 K) of 1b [Ir(cod)(COC)](PF$_6$) in CD$_2$Cl$_2$ [* annotates grease]
Figure S11: $^1$H NMR spectrum of 2a [Rh(CO)$_2$(COC)](PF$_6$) in CDCl$_3$

[* annotates residual DCM (CH$_2$) and grease]

Figure S12: $^{13}$C NMR spectrum of 2a [Rh(CO)$_2$(COC)](PF$_6$) in CDCl$_3$ [* annotates grease]
Figure S13: $^1$H NMR spectrum of 2b [Ir(CO)$_2$(COC)](PF$_6$) in CD$_2$Cl$_2$ 
[* annotates residual chloroform (CH), toluene (CH$_3$), and acetone (CH$_3$)]

Figure S14: $^{13}$C NMR spectrum of 2b [Ir(CO)$_2$(COC)](PF$_6$) in CD$_2$Cl$_2$ 
[* annotates residual chloroform (CH) and grease]
Figure S15: $^1$H NMR spectrum (243 K) of 3a [Rh$_2$(cod)$_2$Cl$_2$(µ-COC)] in CDCl$_3$
[* annotates residual DCM (CH$_2$Cl$_2$) and grease]

Figure S16: $^{13}$C NMR spectrum (243 K) of 3a [Rh$_2$(cod)$_2$Cl$_2$(µ-COC)] in CDCl$_3$
[* annotates residual DCM (CH$_2$Cl$_2$) and grease]
Figure S17: $^1$H NMR spectrum of 4a [Rh$_2$(CO)$_4$Cl$_2$(µ-COC)] in CDCl$_3$

[* annotates residual toluene (CH$_3$) and grease]

Figure S18: $^{13}$C NMR spectrum of 4a [Rh$_2$(CO)$_4$Cl$_2$(µ-COC)] in CDCl$_3$
Figure S19: $^1$H NMR spectrum of 4b [Ir$_2$(CO)$_4$Cl$_2$(µ-COC)] in solvent CDCl$_3$ [* annotates residual toluene (CH$_3$) and grease]

Figure S20: $^{13}$C NMR spectrum of 4b [Ir$_2$(CO)$_4$Cl$_2$(µ-COC)] in CDCl$_3$ [* annotates grease]
**Figure S21:** $^1$H NMR spectrum of $[\text{Ag}_2\text{Cl}_2(\mu-\text{COC})]$ in CDCl₃

[* annotates residual DCM (CH$_2$)$_2$, diethyl ether (CH$_2$)$_2$ and grease*]

**Figure S22:** $^{13}$C NMR spectrum of $[\text{Ag}_2\text{Cl}_2(\mu-\text{COC})]$ in CDCl₃

[* annotates residual diethyl ether (CH$_2$)$_2$ and grease*]
Figure S23: $^1$H NMR spectrum (243 K) of 6 $[\text{Rh}_2(\text{cod})_2(\mu-\text{CNC})](\text{PF}_6)$ in CD$_2$Cl$_2$ [* annotates grease]

Figure S24: $^{13}$C NMR spectrum (243 K) of 6 $[\text{Rh}_2(\text{cod})_2(\mu-\text{CNC})](\text{PF}_6)$ in CD$_2$Cl$_2$ [* annotates residual chloroform (CH)]
Figure S25: $^1$H NMR spectrum of 7a [Ir(cod)(HCNC)](PF$_6$) in CD$_2$Cl$_2$ 

[* annotates residual DCM (CH$_2$) and acetone (CH$_3$)]

Figure S26: $^{13}$C NMR spectrum of 7a [Ir(cod)(HCNC)](PF$_6$) in CD$_2$Cl$_2$
Figure S27: $^1$H NMR spectrum of 7b [Ir(CO)$_2$HNC]$_2$(PF$_6$) in CD$_2$Cl$_2$ [\* annotates free 1,5-cod, water (H$_2$O) and grease]

Figure S28: $^{13}$C NMR spectrum of 7b [Ir(CO)$_2$HNC]$_2$(PF$_6$) in CD$_2$Cl$_2$ [\* annotates free 1,5-cod and grease]
Figure S29: $^1$H NMR spectrum of 8a [Rh$_2$(CO)$_3$Cl($\mu$-CNC)] in C$_6$D$_6$ [* annotates grease]

Figure S30: $^{13}$C NMR spectrum of 8a [Rh$_2$(CO)$_3$Cl($\mu$-CNC)] in C$_6$D$_6$
Figure S31: $^1$H NMR spectrum of intractable mixture of 8a $[\text{Rh}_2(\text{CO})_3\text{Cl}(\mu-\text{CNC})]$ (red) and 8b $[\text{Rh}(\text{CO})(\text{C}^\text{HNC})](\text{PF}_6)$ (blue) in $\text{C}_6\text{D}_6$ [* annotates grease]

Figure S32: $^{13}$C NMR spectrum of intractable mixture of 8a $[\text{Rh}_2(\text{CO})_3\text{Cl}(\mu-\text{CNC})]$ (red) and 8b $[\text{Rh}(\text{CO})(\text{C}^\text{HNC})](\text{PF}_6)$ (blue) in $\text{C}_6\text{D}_6$ [* annotates grease]
Figure S33: $^1$H NMR spectrum of 8b [Rh(CO)(CH=N)(C)](PF$_6$) in C$_6$D$_6$
[* annotates residual DCM (CH$_2$) and acetone (CH$_3$)]

Figure S34: $^{13}$C NMR spectrum of 8b [Rh(CO)(CH=N)(C)](PF$_6$) in C$_6$D$_6$
[* annotates residual CDCl$_3$ & diethyl ether (CH$_2$ & CH$_3$)]
Figure S35: $^1$H NMR spectrum of 9 [Ag$_2$Cl$_2$(µ-C$_6$H$_4$NC)] in CDCl$_3$ [* annotates residual acetone (CH$_3$) and grease]

Figure S36: $^{13}$C NMR spectrum of 9 [Ag$_2$Cl$_2$(µ-C$_6$H$_4$NC)] in CDCl$_3$ [* annotates residual grease]
S4. Crystal Structure Details

Single crystal X-ray diffraction data were collected on Bruker D8 Venture kappa geometry diffractometers using Mo-Kα radiation (λ = 0.71073 Å) (Iµs for 1a and sealed tube for 3a and [H₂(COC)][PF₆]₂), Photon 100 CMOS detectors and Apex3 control software.⁷ A Bruker Apex II three circle diffractometer using sealed tube Mo-Kα radiation (λ = 0.71073 Å), CCD detector and Apex2 control software⁷ was used to collect data for [H₂(C⁺NC)][PF₆]₂, [H₂(C⁺BocNC)][PF₆]₂, 1b, 2b, 4a, 6, 7b and 8a. Crystals were selected under oil, mounted on nylon loops and then immediately placed in a cold stream of N₂ at 173 K or 150 K (for 1a). Data reductions were performed using SAINT,⁷ and multiscan absorption corrections were applied using SADAB⁷ with the exception of 1b where the raw data was used, and 1a and 7a where face-indexed absorption corrections using XPREP⁷ were used. Structures were solved using SHELXT-2018/2⁸ and refined using SHELX-2018/3⁹ and Olex2.¹⁰ The crystal structures of [H₂(COC)][PF₆]₂, 3a, 6, 7b and 8a contained badly disordered solvent molecules. The contributions of these disordered molecules to the structure factors in these structures were calculated using PLATON SQUEEZE.¹¹

S4.1 Crystal data for ligand salt [H₂(COC)][PF₆]₂

Suitable crystals of compound [H₂(COC)][PF₆]₂ for an X-ray diffraction analysis were obtained by slow solvent evaporation from DCM. C₅₄H₇₄N₆O₂P₂F₁₂ (M = 1113.13 g/mol): monoclinic, space group P2₁/n (no.14), a = 12.3474(7) Å, b = 19.7123(10) Å, c = 13.7256(6) Å, α = 90°, β = 99.325(2)°, γ = 90°, V = 3296.6(3) Å³, Z = 2, T = 173.15 K, μ(MoKα) = 0.137 mm⁻¹, Dcalc = 1.121 g/cm³, 90921 reflections measured (5.836 ≤ Θ ≤ 50.996°), 5793 unique (6117 with I > 2σ(I)) (Rint = 0.0488, Rsigma = 0.0179) which were used in all calculations. The final R₁ was 0.0829 (I >2σ(I)) and wR₂ was 0.2246 (all data).

Figure S37. X-ray crystal structure of complex [H₂(COC)][PF₆]₂. (50% displacement ellipsoids)
S4.2 Crystal data for ligand salt \([\text{H}_2(\text{C}^\text{Boc}\text{NC})](\text{PF}_6)_2\)

Suitable crystals of compound \([\text{H}_2(\text{C}^\text{Boc}\text{NC})](\text{PF}_6)_2\) for an X-ray diffraction analysis were obtained by slow solvent evaporation from DCM. \(C_{59}H_85N_7O_3P_2F_{12}\) (Incl. solvent \(H_2O\)) (\(M = 1230.27\) g/mol): monoclinic, space group \(P2_1/n\) (no. 14), \(a = 19.8012(13)\) Å, \(b = 12.6035(9)\) Å, \(c = 26.5305(19)\) Å, \(\alpha = 90°, \beta = 105.6995(18)°, \gamma = 90°, V = 6247.1(8)\) Å\(^3\), \(Z = 4, T = 173.15\) K, \(\mu(\text{MoK}_\alpha) = 0.151\) mm\(^{-1}\), \(D_{\text{calc}} = 1.282\) g/cm\(^3\), 72816 reflections measured (\(5.614 \leq \Theta \leq 51.456°\)), 12121 unique (6117 with \(I > 2\sigma(I)\)) (\(R_{\text{int}} = 0.0482, R_{\text{sigma}} = 0.0395\) which were used in all calculations. The final \(R_1\) was 0.0619 (I >\(2\sigma(I)\)) and \(wR_2\) was 0.1552 (all data).

\textbf{Figure S38.} X-ray crystal structure of complex \([\text{H}_2(\text{C}^\text{Boc}\text{NC})](\text{PF}_6)_2\). (50% displacement ellipsoids) [Counteranions (2PF\(_6\)), hydrogen atoms (except for H1 and H6) and solvent molecules (H\(_2O\)) omitted for clarity]

Selected bond distances (Å) and angles (°): C1-C2 1.358(3), C1-N1 1.352(3), C2-C3 1.493(3), C2-N3 1.364(3), C3-N7 1.460(3), C4-C5 1.491(3), C4-N7 1.454(3), C5-C6 1.361(3), C5-N6 1.363(3), C6-N4 1.354(3), C55-N7 1.366(3), C55-O1 1.207(3), C55-O2 1.332(3), C56-O2 1.482(3), N1-N2 1.327(3), N2-
S3.2 N 1.328(3), N4-N5 1.325(3), N5-N6 1.326(3); C1-C2-C3 129.9(2), C2-C3-N7 112.97(19), C3-N7-C4 118.63(19), C4-C5-C6 132.9(2), C3-N7-C55 124.41(19).

S4.3 Crystal data for ligand salt [H₂(C₃H₇NC)][PF₆]₂

Suitable crystals of compound [H₂(C₃H₇NC)][PF₆]₂ for an X-ray diffraction analysis were obtained by slow solvent evaporation from DCM / CH₃CN mixture. C₅₂H₇₈N₈P₂F₁₂ (incl. CH₃CN) (M = 1153.20 g/mol): triclinic, space group P-1 (no.2), a = 11.0352(2) Å, b = 12.3798(2) Å, c = 24.3690(4) Å, α = 81.3850(10)°, β = 89.281(10)°, γ = 65.5350(10)°, V = 2991.51(9) Å³, Z = 2, T = 173.15 K, µ(MoKα) = 0.153 mm⁻¹, Dcalc = 1.280 g/cm³, 122057 reflections measured (3.386 ≤ Θ ≤ 56.71°), 14937 unique (6117 with I > 2σ(I)) which were used in all calculations. The final R₁ was 0.0443 (I >2σ(I)) and wR₂ was 0.1226 (all data).

Figure S39. X-ray crystal structure of complex [H₂(C₃H₇NC)][PF₆]₂. (50% displacement ellipsoids) [Counteranions (2PF₆), hydrogen atoms (except for H1, H6 and H7) and solvent molecules (CH₃CN) omitted for clarity] Selected bond distances (Å) and angles (°): C1-C2 1.3670(17), C1-N1 1.3518(16), C2-C3 1.4901(18), C2-N3 1.3606(16), C3-N7 1.4553(17), C4-C5 1.4987(17), C4-N7 1.4652(16), C5-C6 1.3636(18), C5-N4 1.3688(16), C6-N6 1.3521(16), N1-N2 1.3258(14), N2-N3 1.3280(15), N4-N5 1.3264(14), N5-N6 1.3240(14), C1-C2-C3 132.14(12), C2-C3-N7 109.64(10), C3-N7-C4 112.46(10), C4-C5-C6 131.50(12).

S4.4 Crystal data for complex 1b [Ir(cod)(COC)][PF₆].

Suitable crystals of compound 1b [Ir(cod)(COC)][PF₆] for an X-ray diffraction analysis were obtained by slow solvent evaporation from a toluene / DCM mixture. C₆₅H₉₀O₆IrPF₆ (Incl. 6 DCM) (M = 1521.29
g/mol): triclinic, space group $P\overline{1}$ (no.2), $a = 15.0178(9)$ Å, $b = 15.1067(9)$ Å, $c = 18.2934(10)$ Å, $\alpha = 76.729(3)^\circ$, $\beta = 69.064(3)^\circ$, $\gamma = 65.711(3)^\circ$, $V = 3516.4(4)$ Å$^3$, $Z = 2$, $T = 173.15$ K, $\mu$(MoKα) = 2.209 mm$^{-1}$, $D_{calc} = 1.437$ g/cm$^3$, 144803 reflections measured (2.972 ≤ Θ ≤ 57.152°), 17852 unique (6117 with I > 2σ(I)) ($R_{int}$ = 0.0358, $R_{sigma}$ = 0.0226) which were used in all calculations. The final $R_1$ was 0.0264 (I > 2σ(I)) and $wR_2$ was 0.0687 (all data).

Figure S40. X-ray crystal structure of complex 1b [Ir(cod)(COC)](PF$_6$). (50% displacement ellipsoids) [Counteranion (PF$_6^-$), hydrogen atoms and solvent molecules (DCM) omitted for clarity]

Selected bond distances (Å) and angles (º): Ir1-C1 2.102(2), Ir1-C6 2.055(2), Ir1-C55 2.223(2), Ir1-C56 2.162(2), Ir1-C59 2.177(2), Ir1-C60 2.152(2), C1–Ir1–C6 92.74(8), C1–Ir1–C55 98.27(8), C1–Ir1–C56 91.90(9), C1–Ir1–C59 159.12(10), C1–Ir1–C60 163.36(10), C6–Ir1–C55 168.04(9), C6–Ir1–C56 147.91(10), C6–Ir1–C59 84.29(9), C6–Ir1–C60 89.29(9).

S4.5 Crystal data for complex 2a [Rh(CO)$_2$(COC)](PF$_6$).

Suitable crystals of compound 2a [Rh(CO)$_2$(COC)](PF$_6$) for an X-ray diffraction analysis were obtained by slow solvent evaporation from DCM. C$_{56}$H$_{72}$N$_6$O$_3$RhPF$_6$ ($M$ =1125.07 g/mol): monoclinic, space group $Pc$ (no. 7), $a = 21.5202(11)$ Å, $b = 10.7072(5)$ Å, $c = 24.8940(13)$ Å, $\beta = 105.722(2)^\circ$, $V = 5521.5(5)$ Å$^3$, $Z = 4$, $T = 150.0$ K, $\mu$(MoKα) = 0.407 mm$^{-1}$, $D_{calc} = 1.353$ g/cm$^3$, 209908 reflections measured (4.364° ≤ 2Θ ≤ 53.554°), 23488 unique ($R_{int}$ = 0.0588, $R_{sigma}$ = 0.0365) which were used in all calculations. The final $R_1$ was 0.0313 (I > 2σ(I)) and $wR_2$ was 0.0643 (all data).
Figure S41. X-ray crystal structure of complex 2a [Rh(CO)₂(COC)](PF₆). (50% displacement ellipsoids) [Counteranion (PF₆⁻) and hydrogen atoms omitted for clarity]

Selected bond distances (Å) and angles (°): Rh1-C1 2.122(4), Rh1-C6 2.110(4), Rh1-C55 1.878(4), Rh1-C56 1.878(4), C1–Rh1–C6 95.24(14), C1–Rh1–C55 93.09(15), C1–Rh1–C56 167.67(17), C6–Rh1–C55 167.76(15), C6–Rh1–C56 90.90(16).

S4.6 Crystal data for complex 2b [Ir(CO)₂(COC)](PF₆)

Suitable crystals of compound 2b [Ir(CO)₂(COC)](PF₆) for an X-ray diffraction analysis were obtained by slow solvent evaporation from C₆D₆. C₅₆H₇₂N₆O₃IrPF₆ (M =1214.36 g/mol): monoclinic, space group P2₁/c (no.14), a = 21.527(3) Å, b = 10.6934(14) Å, c = 24.942(3) Å, α = 90°, β = 105.386(9)°, V = 5535.7(13) Å³, Z = 4, T = 150.15 K, μ(MoKα) = 2.509 mm⁻¹, Dcalc = 1.457 g/cm³, 72636 reflections measured (3.388° ≤ 2Θ ≤ 50°), 9747 unique (Rint = 0.5670, Rsigma = 0.5490) which were used in all calculations. The final R₁ was 0.0895 (I > 2σ(I)) and wR₂ was 0.1964 (all data).
Figure S42. X-ray crystal structure of complex 2b [Ir(CO)₂(COC)](PF₆). (50% displacement ellipsoids) [Counteranion (PF₆⁻) and hydrogen atoms omitted for clarity]

Selected bond distances (Å) and angles (°): Ir1-C1 2.110(16), Ir1-C6 2.059(15), Ir1-C55 1.824(17), Ir1-C56 1.868(19), C1–Ir1–C6 93.7(6), C1–Ir1–C55 91.5(7), C1–Ir1–C56 169.2(8), C6–Ir1–C55 172.6(7), C6–Ir1–C56 92.7(7).

S4.7 Crystal data for complex 3a [Rh₂(cod)₂Cl₂(µ-COC)]

Suitable crystals of compound 3a [Rh₂(cod)₂Cl₂(µ-COC)] for an X-ray diffraction analysis were obtained by slow solvent evaporation from CDCl₃. C₇₁H₉₈Cl₄N₆ORh₂ (M =1399.17 g/mol): monoclinic, space group P2₁/c (no. 14), a = 15.4130(8) Å, b = 35.913(2) Å, c = 15.0642(8) Å, β = 111.6130(10)°, V = 7752.2(7) Å³, Z = 4, T = 173.15 K, μ(MoKα) = 0.605 mm⁻¹, Dcalc = 1.199 g/cm³, 113394 reflections measured (5.686° ≤ 2Θ ≤ 55.996°), 18698 unique (Rint = 0.0458, Rsigma = 0.0264) which were used in all calculations. The final R₁ was 0.0411 (I > 2σ(I)) and wR₂ was 0.0968 (all data).

Figure S43. X-ray crystal structure of complex 3a [Rh₂(cod)₂Cl₂(µ-COC)]. (50% displacement ellipsoids) (Hydrogen atoms and solvent molecules (DCM) omitted for clarity)

Selected bond distances (Å) and angles (°): Rh1-C1 2.030(2), Rh1-C11 2.3927(7), Rh1-C55 2.197(3), Rh1-C56 2.177(3), Rh1-C59 2.099(3), Rh1-C60 2.089(2), Rh2-C6 2.043(2), Rh2-Cl2 2.3741(7), Rh2-C63 2.167(3), Rh2-C64 2.205(2), Rh2-C67 2.087(3), C1–Rh1–C11 86.46(7), C55–Rh1–C1 165.77(10), C56–Rh1–C1 157.78(10), C59–Rh1–C1 94.40(10), C60–Rh1–C1 93.06(9), C6–Rh2–Cl2 87.31(7), C6–Rh2–C63 155.92(11), C6–Rh2–C64 167.10(10), C6–Rh2–C67 95.81(10), C6–Rh2–C68 93.60(11)
**S4.8 Crystal data for complex 4a [Rh\(_2\)(CO)\(_4\)Cl\(_2\)(µ-COC)]**

Suitable crystals of compound 4a [Rh\(_2\)(CO)\(_4\)Cl\(_2\)(µ-COC)] for an X-ray diffraction analysis were obtained by slow solvent evaporation from CDCl\(_3\). C\(_{58}\)H\(_{72}\)N\(_6\)O\(_5\)Cl\(_2\)Rh\(_2\) (M = 1209.93 g/mol): triclinic, space group P -1 (no. 2), a = 10.4449(4) Å, b = 15.9061(6) Å, c = 17.7631(7) Å, \(\alpha = 87.305(2)^{\circ}\), \(\beta = 76.657(2)^{\circ}\), \(\gamma = 88.372(2)^{\circ}\), \(V = 2867.81(19) \text{ Å}^3\), \(Z = 2\), \(T = 173.15 \text{ K}\), \(\mu(\text{MoK}\alpha) = 0.720 \text{ mm}^{-1}\), \(D_{\text{calc}} = 1.401 \text{ g/cm}^3\), 35559 reflections measured (2.564 \(\leq \Theta \leq 51.564^{\circ}\)), 10990 unique (6117 with I > 2\(\sigma(I)\)) (\(R_{\text{int}} = 0.084\), \(R_{\sigma} = 0.1074\)) which were used in all calculations. The final \(R_1\) was 0.0568 (I >2\(\sigma(I)\)) and \(wR_2\) was 0.1402 (all data).

**Figure S44.** X-ray crystal structure of complex 4a [Rh\(_2\)(CO)\(_4\)Cl\(_2\)(µ-COC)]. (50% displacement ellipsoids) (Hydrogen atoms omitted for clarity)

Selected bond distances (Å) and angles (°): Rh1-C1 2.054(5), Rh1-C11 2.3434(16), Rh1-C55 1.831(7), Rh1-C56 1.899(7), Rh2-C6 2.041(5), Rh2-C12 2.3672(17), Rh2-C57 1.812(7), Rh2-C58 1.905(6), C1–Rh1–C11 87.50(15), C55–Rh1–C1 93.1(2), C56–Rh1–C1 172.9(2), C6–Rh2–C12 85.70(15), C6–Rh2–C57 91.6(2), C6–Rh2–C58 174.0(2).

**S4.9 Crystal data for complex 6 [Rh\(_2\)(cod)\(_2\)(µ-CNC)](PF\(_6\))**

Suitable crystals of compound 6 [Rh\(_2\)(cod)\(_2\)(µ-CNC)](PF\(_6\)) for an X-ray diffraction analysis were obtained by slow solvent evaporation from a toluene / DCM mixture. C\(_{73}\)H\(_{102}\)N\(_7\)Cl\(_2\)Rh\(_2\)PF\(_6\) (Incl. 3 DCM) (M = 1641.10 g/mol): triclinic, space group P -1 (no.2), a = 12.4173(11) Å, b = 16.7357(16) Å, c = 20.3867(18) Å, \(\alpha = 81.880(6)^{\circ}\), \(\beta = 85.642(6)^{\circ}\), \(\gamma = 86.607(6)^{\circ}\), \(V = 4177.0(7) \text{ Å}^3\), \(Z = 2\), \(T = 173.15 \text{ K}\), \(\mu(\text{MoK}\alpha) = 0.661 \text{ mm}^{-1}\), \(D_{\text{calc}} = 1.302 \text{ g/cm}^3\), 59766 reflections measured (2.022 \(\leq \Theta \leq 50^{\circ}\), 14704
unique (6117 with I > 2σ(I)) \((R_{int} = 0.0858, R_{sigma} = 0.0824)\) which were used in all calculations. The final \(R_1\) was 0.1040 (I >2σ(I)) and \(wR_2\) was 0.2779 (all data).

**Figure S45.** X-ray crystal structure of complex 6 [Rh₂(cod)(μ-CNC)](PF₆). (50% displacement ellipsoids) [Counteranion (PF₆⁻), hydrogen atoms and solvent molecules (DCM) omitted for clarity]

Selected bond distances (Å) and angles (°): Rh1-Rh2 3.1963(12), Rh1-C1 2.035(11), Rh2-C6 2.037(10), Rh1-N7 2.209(8), Rh2-N7 2.217(8), Rh1-C55 2.125(12), Rh1-C56 2.136(11), Rh1-C59 2.223(11), Rh1-C60 2.191(11), Rh2-C63 2.207(11), Rh2-C64 2.179(12), Rh1–N7–Rh2 92.5(3), C1–Rh1–N7 80.8(4), C1–Rh1–C55 93.9(4), C1–Rh1–C56 94.7(4), C1–Rh1–C59 169.6(4), C1–Rh1–C60 153.9(4), C6–Rh2–C63 167.9(4), C6–Rh2–C64 156.4(4), C6–Rh2–C67 95.4(5), C6–Rh2–C68 95.3(4).

**S4.10 Crystal data for complex 7b [Ir(CO)₂(HCNC)](PF₆)**

Suitable crystals of compound 7b [Ir(CO)₂(HCNC)](PF₆) for an X-ray diffraction analysis were obtained from DCM / Hexane by slow vapour diffusion. **C₅₈H₇₇Cl₄F₆IrN₇O₂P (Incl. 2 DCM) \((M = 1383.23 \text{ g/mol})\):** triclinic, space group P-1 (no. 2), \(a = 12.0336(7)\) Å, \(b = 13.6319(9)\) Å, \(c = 22.5444(15)\) Å, \(\alpha = 96.465(5)^°, \beta = 104.140(4)^°, \gamma = 97.574(4)^°, V = 3514.3(4) \text{ Å}^3, Z = 2, T = 173.15 \text{ K, µ(MoKα) = 2.131 mm}^{-1, D_{calc} = 1.307 \text{ g/cm}^3, 34784} \text{ reflections measured (3.048° ≤ 2Θ ≤ 50°), 12322 unique (R_{int} = 0.1339, R_{sigma} = 0.1557) which were used in all calculations. The final R_1 was 0.0770 (I > 2σ(I)) and wR_2 was 0.1845 (all data).}**
**Figure S46.** X-ray crystal structure of complex 7b [Ir(CO)$_2$(HCNC)](PF$_6$). (50% displacement ellipsoids) (Hydrogen atoms, counteranion (PF$_6^-$) and solvent molecules (DCM) omitted for clarity)

Selected bond distances (Å) and angles (°): Ir1-C1 2.032(9), Ir1-N7 2.048(7), Ir1-C55 1.865(9), Ir1-C56 1.866(11), C1–Ir1–N7 78.0(3), C1–Ir1–C55 97.2(3), C1–Ir1–C56 174.3(4), N7–Ir1–C55 175.3(3), N7–Ir1–C56 96.3(3).

**S4.10 Crystal data for complex 8a [Rh$_2$(CO)$_3$Cl(µ-CNC)]**

Suitable crystals of compound 8a [Rh$_2$(CO)$_3$Cl(µ-CNC)] for an X-ray diffraction analysis were obtained by slow solvent evaporation from toluene. C$_{57}$H$_{72}$N$_7$O$_3$ClRh$_2$ (M = 1144.48 g/mol): triclinic, space group $P\overline{1}$ (no.2), $a = 10.7323(18)$ Å, $b = 13.222(2)$ Å, $c = 21.491(3)$ Å, $α = 82.115(3)^\circ$, $β = 78.984(4)^\circ$, $γ = 86.235(3)^\circ$, $V = 2962.7(8)$ Å$^3$, $Z = 2$, $T = 173.15$ K, $μ(\text{MoKα}) = 0.648$ mm$^{-1}$, $Dcalc = 1.283$ g/cm$^3$, 18554 reflections measured ($3.112\leq Θ\leq 51^\circ$), 10960 unique (6117 with $I>2σ(I)$) ($R_{int} = 0.0869$, $R_{sigma} = 0.1565$) which were used in all calculations. The final $R_1$ was 0.0758 ($I>2σ(I)$) and $wR_2$ was 0.2273 (all data).
Figure S47. X-ray crystal structure of complex 8a [Rh₂(CO)₃Cl(μ-CNC)]. (50% displacement ellipsoids) (Hydrogen atoms omitted for clarity)

Selected bond distances (Å) and angles (°): Rh1-Rh2 2.9698(12), Rh1-C1 2.046(8), Rh1-C6 2.029(8), Rh1-N7 2.113(6), Rh1-C55 1.846(10), Rh1-C56 2.211(10), Rh2-N7 2.189(7), Rh2-C56 1.909(11), Rh2-C57 1.819(15), Rh2-C11 2.385(3), C1–Rh1–C6 157.3(3), C1–Rh1–N7 79.3(3), C1–Rh1–C55 100.0(3), N7–Rh1–C56 87.3(3), Rh1–N7–Rh2 56 47.41(18), N7–Rh2–C57 177.7(4).

S5. References


