# Metal center dependent coordination modes of a tricarbene ligand

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## Supporting Information

**General Procedures.** All reactions were carried out under an argon atmosphere using standard Schlenk techniques or in a glove box. Glassware was oven dried at 130 °C. Solvents were distilled by standard procedures prior to use. $^{1}$H and $^{13}$C{$^{1}$H} NMR spectra were recorded on Bruker AVANCE I 400 or Bruker AVANCE III 400 spectrometers. Chemical shifts ($\delta$) are expressed in ppm downfield from tetramethylsilane using the residual protonated solvent as an internal standard. All coupling constants are expressed in Hertz and only given for $^{1}$H,$^{1}$H couplings unless mentioned otherwise. Mass spectra were obtained with MicroTof (Bruker Daltonics, Bremen), Quattro LCZ (Waters-Micromass, Manchester, UK), Bruker Reflex IV or Varian MAT 212 spectrometers. Compounds [**1**](PF$_6$)$_3$,[1] [**1**]Br$_3$[1], [PdCl(allyl)]$_2$,[2] [Ir(Cp*)(Cl)$_2$]$_2$,[3] and [Rh(Cp*)(Cl)$_2$]$_2$[4] were prepared as described in the literature. $Cs_2CO_3$, $PdCl_2$, $IrCl_3 \cdot xH_2O$ and $RhCl_3 \cdot xH_2O$ were purchased from commercial sources and were used as received without further purification. For assignment of NMR resonances see Figure S1. Consistent microanalytical data for the complexes were difficult to obtain due to the large fluorine content in the hexafluorophosphate counterions. HRMS data are provided instead.

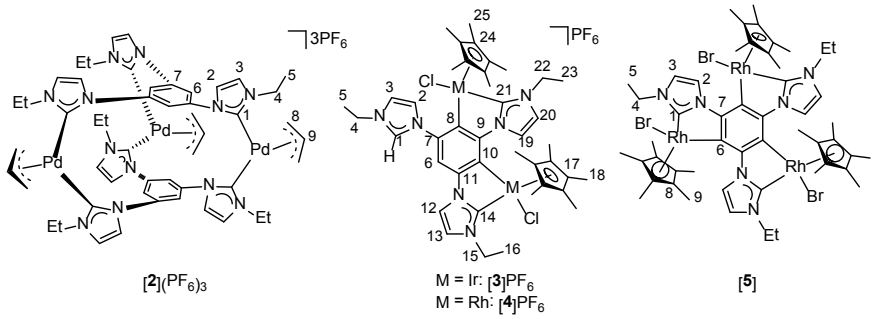


**Figure S1.** Assignment of NMR resonances for [**2**](PF$_6$)$_3$–[**4**]PF$_6$ and [**5**].

**Synthesis of [2](PF$_6$)$_3$.** Acetonitrile (10 mL) was added to a mixture of [**1**](PF$_6$)$_3$ (0.064 g, 0.08 mmol), $Cs_2CO_3$ (0.085 g, 0.26 mmol) and [PdCl(allyl)]$_2$ (0.022 g, 0.06 mmol). The reaction mixture was heated to 60 °C for 18 h. After cooling to ambient temperature, the obtained suspension was slowly filtered through Celite. The filtrate was concentrated to 3 mL and addition of diethyl ether (10 mL) led to the precipitation of slightly yellow solid. The solid was collected by filtration and dried *in vacuo*. Analytically pure [**2**](PF$_6$)$_3$ was obtained by recrystallization from an $CH_3CN/Et_2O$ solvent mixture at ambient temperature. Yield: 0.043 g (0.027 mmol, 68%, relative to [**1**](PF$_6$)$_3$). NMR data indicate that the complex is fluxional in solution leading to the observation of a major and a minor isomer (5%). HRMS data, however, clearly show the presence of only one compound with composition [**2**](PF$_6$)$_3$. $^1$H NMR (400 MHz, $CD_3CN$, major isomer): $\delta$ = 7.42 (d, $^3J$ = 1.94 Hz, 6H, H3), 7.34 (s, br, 6H, H7), 7.34 (s, br, 6H, H2), 4.94 (m, 3H, H9), 4.52 (m, 6H, H*H*4), 4.29 (m, 6H, *H*H4), 4.18 (d, $^3J$ = 7.1 Hz, 6H, H*H*8), 3.07 (d, $^3J$ = 13.4 Hz, 6H, *H*H8), 1.45 (m, 18H, H5) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CD_3CN$, major isomer): $\delta$ = 176.6 (C1), 141.9 (C6), 124.8 (C2), 124.0 (C3), 119.7 (C9), 118.1 (C7), 62.2 (C8), 48.3 (C4), 16.6 (C5) ppm. HRMS (ESI, positive ions): *m/z* = 1453.1702 (calcd for $[[\mathbf{2}](PF_6)_3-PF_6]^+$ 1453.1716), 654.1020 (calcd for $[[\mathbf{2}](PF_6)_3-2PF_6]^{2+}$ 654.1034), 387.7466 (calcd for $[[\mathbf{2}](PF_6)_3-3PF_6]^{3+}$ 387.7480).

**Synthesis of [3]PF$_6$.** To a mixture of [**1**](PF$_6$)$_3$ (0.320 g, 0.4 mmol), $Cs_2CO_3$ (0.391 g, 1.2 mmol) and [Ir(Cp*)(Cl)$_2$]$_2$ (0.318 g, 0.4 mmol) was added 10 mL of $CH_3CN$ and the reaction mixture was heated to 60 °C for 18 h. After cooling to ambient temperature, the suspension was filtered slowly through Celite. The filtrate was brought to dryness *in vacuo*. The residue was loaded on a silica gel column and eluted with dichloromethane:acetone (80:20, v:v) to give [**3**]PF$_6$ as a yellow solid. Yield: 0.369 g (0.3 mmol, 75%). $^1$H NMR (400 MHz, $CD_3CN$): $\delta$ = 10.04 (s, 1H, H1), 8.81 (d, $^3J$ = 2.1 Hz, 1H, H19), 8.12 (s, br, 1H, H2), 7.65 (d, $^3J$ = 2.2 Hz, 1H, H12), 7.54 (m, 1H, H3), 7.32 (d, $^3J$ = 2.2 Hz, 1H, H13), 7.19 (d, $^3J$ = 2.1 Hz, 1H, H20), 7.14 (s, 1H, H6), 4.36 (m, 2H, H15), 4.26 (m, 2H, H4), 4.26 (m, 2H, H22), 1.59 (s, 15H, H18), 1.55 (m, 3H, H5), 1.53 (s, 15H, H25), 1.50 (m, 3H, H23), 1.48 (m, 3H, H16) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CD_3CN$): $\delta$ = 165.5 (C14), 163.6 (C21), 156.1 (C9), 147.3 (C11), 138.4 (C1), 138.1 (C7), 131.0 (C8), 125.1 (C2), 124.9 (C10), 122.7 (C19), 122.0 (C3), 122.0 (C13), 119.1 (C20), 116.7 (C12), 105.3 (C6), 92.6 (C24), 92.5 (C17), 46.3 (C4), 46.1 (C15), 45.5 (C22), 17.5 (C16), 17.0

(C23), 15.1 (C5), 9.7 (C25), 9.2 (C18) ppm. MS (ESI, positive ions): *m/z* = 1085.2915 (calcd for $[[\mathbf{3}]PF_6–PF_6]^+$ 1085.2962).

**Synthesis of [4]$PF_6$.** Compound [**4**]$PF_6$ was synthesized as described for [**3**]$PF_6$ from [**1**]$(PF_6)_3$ (0.150 g, 0.188 mmol), $Cs_2CO_3$ (0.189 g, 0.580 mmol) and $[Rh(Cp^*)(Cl)_2]_2$ (0.116 g, 0.188 mmol) in 10 mL of $CH_3CN$. Yield: 0.130 g (0.124 mmol, 66%). $^1$H NMR (400 MHz, $CD_3CN$): $\delta$ = 10.19 (s, 1H, H1), 9.03 (d, $^3J$ = 2.1 Hz, 1H, H19), 8.15 (s, br, 1H, H2), 7.75 (d, $^3J$ = 2.1 Hz, 1H, H12), 7.52 (m, 1H, H3), 7.37 (d, $^3J$ = 2.1 Hz, 1H, H13), 7.26 (d, $^3J$ = 2.1 Hz, 1H, H20), 7.18 (s, 1H, H6), 4.37 (m, 2H, H15), 4.32 (m, 2H, H22), 4.23 (m, 2H, H4), 1.54 (s, 15H, H18), 1.54 (m, 3H, H5), 1.48 (m, 3H, H16), 1.50 (m, 3H, H23), 1.48 (s, 15H, H25) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CD_3CN$): $\delta$ = 182.7 ($^1J_{C,Rh}$ = 53.7 Hz, C14), 180.7 ($^1J_{C,Rh}$ = 51.8 Hz, C21), 156.9 (C9), 146.7 (C11), 145.8 ($^1J_{C,Rh}$ = 39.3 Hz, C8), 141.7 ($^1J_{C,Rh}$ = 39.7 Hz, C10), 139.6 (C7), 138.3 (C1), 124.9 (C2), 122.9 (C13), 122.7 (C19), 122.1 (C3), 120.1 (C20), 117.3 (C12), 106.3 (C6), 99.3 ($^1J_{C,Rh}$ = 5.0 Hz, C24), 99.2 ($^1J_{C,Rh}$ = 5.0 Hz, C17), 46.3 (C4, C15, C22), 17.1 (C16), 16.6 (C23), 15.1 (C5), 10.0 (C25), 9.6 (C18) ppm. MS (ESI, positive ions): *m/z* = 905.1794 (calcd for $[[\mathbf{4}]PF_6–PF_6]^+$ 905.1813).

**Synthesis of [5]**. Acetonitrile (20 mL) was added to a mixture of [**1**]$Br_3$ (0.050 g, 0.083 mmol), $CsCO_3$ (0.057 g, 0.175 mmol), $[Rh(Cp^*)(Cl)_2]_2$ (0.051 g, 0.082 mmol) and NaBr (excess). The suspension was heated to 65 °C for 18 h. The reaction mixture was then cooled to ambient temperature and filtered through Celite. A clear filtrate was obtained. To the filtrate was added $Ag_2O$ (0.023 g, 0.099 mmol). The resulting suspension was stirred for 48 h to 65 °C under exclusion of light. Subsequently, a mixture of $[Rh(Cp^*)(Cl)_2]$ (0.026 g, 0.042 mmol), NaOAc (0.008 g, 0.097 mmol) and NaBr (0.052 g, 0.505 mmol) was added to the suspension. The reaction mixture was heated with stirring for an additional 18 h to 65 °C. After cooling to ambient temperature the obtained suspension was filtered through Celite to get a clear solution. The solvent was removed *in vacuo* to give [**5**] as a reddish orange solid. Analytically pure [**5**] was obtained by column chromatography using a dichloromethane:methanol (95:5, v:v) solvent mixture. Yield: 0.058 g (0.044 mmol, 53%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 9.16 (d, $^3J$ = 2.0 Hz, 3H, H2), 6.94 (d, $^3J$ = 2.0 Hz, 3H, H3), 4.40 (m, 3H, *H*H4), 4.15 (m, 3H, H*H*4), 1.63 (s, 45H, H9), 1.54 (m, 9H, H5) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ = 177.7 (d, $^1J_{C\text{-}Rh}$ = 52.9 Hz,

C1), 149.7 (C7), 135.1 (d, $^{1}J_{C\text{-}Rh}$ = 38.2 Hz, C6), 123.1 (C2), 116.8 (C3), 97.4 (d, $^{1}J_{C\text{-}Rh}$ = 4.7 Hz, C8), 44.6 (C4), 16.0 (C5), 9.7 (C9) ppm. HRMS (ESI, positive ions): *m/z* = 1334.9903 (calcd for [[**5**]+Na]$^{+}$ 1334.9928). Anal. Calcd (%) for [**5**]·$CH_3OH$: C, 46.48; H, 5.25; N, 6.26. Found: C, 46.38; H, 5.26; N, 5.92 (the compound was obtained directly after column chromatography before recrystallization from acetonitrile).

**X-ray Crystallography:** X-ray diffraction data were collected at $T$ = 153(2) K with a Bruker AXS APEX CCD diffractometer equipped with a rotation anode using graphite-monochromated Mo-K$\alpha$ radiation ($\lambda$ = 0.71073 Å). Diffraction data were collected over the full sphere and were corrected for absorption. Structure solutions were found with the SHELXS-97 package using direct methods and were refined with SHELXL-97 against $|F^2|$ of all data using first isotropic and later anisotropic thermal parameters (for exceptions see description of the individual molecular structures). Hydrogen atoms were added to the structure models on calculated positions.

**[2](PF$_6$)$_3$·C$_4$H$_{10}$O·C$_2$H$_3$N:** Crystals of [**2**](PF$_6$)$_3$·C$_4$H$_{10}$O·C$_2$H$_3$N were obtained by slow vapor diffusion of diethyl ether into a saturated acetonitrile solution of the complex [**2**](PF$_6$)$_3$ at ambient temperature. $C_{57}H_{76}N_{13}F_{18}OP_3Pd_3$, $M$ = 1713.42 g·mol$^{-1}$, colorless crystal, 0.20 × 0.04 × 0.01 mm$^3$, orthorhombic, space group Pbam, $Z$ = 4, $a$ = 23.388(3), $b$ = 28.553(5), $c$ = 10.741(2) Å, $V$ = 7172.6(2) Å$^3$, $\rho_{calc}$ = 1.587 g·cm$^{-3}$, $\mu$ = 0.905 mm$^{-1}$, 70502 measured intensities (2.9° ≤ 2$\theta$ ≤ 55.8°), semiempirical absorption correction (0.840 ≤ $T$ ≤ 0.991), 8983 independent ($R_{int}$ = 0.119) and 5590 observed intensities ($I \geq 2\sigma(I)$), refinement of 470 parameters against $|F^2|$ of all measured intensities with hydrogen atoms on calculated positions. $R$ = 0.0642, $wR$ = 0.1894, $R_{all}$ = 0.1088, $wR_{all}$ = 0.2193.

The asymmetric unit contains 1/2 formula unit of the complex cation [**2**]$^{3+}$ related to each other half by a crystallographic mirror plane bisecting the three palladium atoms, three ½ formula units of hexafluorophosphate anions (located on special positions) and ½ molecule of each $Et_2O$ and $CH_3CN$ (both located on the crystallographic mirror plane).

**[3]PF$_6$:** Yellow crystals of [**3**]PF$_6$ were obtained by slow evaporation of the solvent from a saturated acetonitrile solution of the complex at room temperature. $C_{41}H_{53}N_6Cl_2F_6Ir_2P$, $M$ = 1230.16 g·mol$^{-1}$, yellow crystal, 0.09 × 0.08 × 0.05 mm$^3$, trigonal, space group $R$-3, $Z$ = 6, $a$ =

26.9202(6), $c$ = 34.3435(14) Å, $V$ = 21554.2(11) Å$^3$, $\rho_{calc}$ = 1.706 g·cm$^{-3}$, $\mu$ = 5.754 mm$^{-1}$, 85000 measured intensities (2.9° ≤ 2$\theta$ ≤ 60.0°), semiempirical absorption correction (0.626 ≤ $T$ ≤ 0.762), 13959 independent ($R_{int}$ = 0.0429) and 11398 observed intensities ($I \geq 2\sigma(I)$), refinement of 527 parameters against $|F^2|$ of all measured intensities with hydrogen atoms on calculated positions. $R$ = 0.0298, $wR$ = 0.0768, $R_{all}$ = 0.0400, $wR_{all}$ = 0.0798.

The asymmetric unit contains one formula unit of the cation [**3**]$^+$ and one hexafluorophosphate anion. The hexafluorophosphate anion is disordered and located on two special positions (SOF = 0.5 and SOF = 0.333). Thus 1/6 of the $PF_6^-$ anion could not be located. The missing 1/6 of a negative charge could also be contributed by a disordered fluoride anion in the asymmetric unit. However, the electron density associated with 1/6 of a negative charge could not be located. Remaining electron density (most likely arising from disordered solvent molecules and the missing 1/6 of a negative charge) was removed from the least-squares calculations by means of the SQEEZE program.

**[5]:** Crystals of [**5**]·2MeCN were obtained by slow evaporation of the solvent from a saturated acetonitrile solution of [**5**] at ambient temperature. $C_{55}H_{72}N_8Br_3Rh_3$, $M$ = 1393.67 g·mol$^{-1}$, red crystal, 0.34 × 0.31 × 0.24 mm$^3$, monoclinic, space group $P2_1/n$, $Z$ = 4, $a$ = 13.6282(2), $b$ = 23.4151(3), $c$ = 17.6118(3) Å, $V$ = 5568.05(14) Å$^3$, $\rho_{calc}$ = 1.663 g·cm$^{-3}$, $\mu$ = 3.075 mm$^{-1}$, 69471 measured intensities (3.6° ≤ 2$\theta$ ≤ 59.1°), semiempirical absorption correction (0.421 ≤ $T$ ≤ 0.526), 15605 independent ($R_{int}$ = 0.0304) and 13412 observed intensities ($I \geq 2\sigma(I)$), refinement of 642 parameters against $|F^2|$ of all measured intensities with hydrogen atoms on calculated positions. $R$ = 0.0255, $wR$ = 0.0625, $R_{all}$ = 0.0334, $wR_{all}$ = 0.0656. The asymmetric unit contains one formula unit of the complex [**5**] and two molecules of acetonitrile.

References

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