Supporting Information

Formal [2+2+2] Cycloaddition Reaction of Metal-Carbyne Complex with Nitriles: Synthesis of a Metallapyrazine Complex

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**Table of Contents**

1. Thermal Decomposition Data ................................................................. S3
2. NMR Spectra .......................................................................................... S3
3. X-ray crystallographic analysis .............................................................. S10
4. ACID Plot of 3’ ..................................................................................... S12
1. Thermal Decomposition Data

Table S1. Thermal decomposition data of 2, 3 and 4 in solid state\textsuperscript{[a]}.

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<tr>
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<th>100 °C</th>
<th>120 °C</th>
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\[a\] All reactions were carried out for 3 hours in air. ● = Stable. ▲ = Partly decomposed, major product is Ph$_3$PO. ■ = Completely decomposed, major product is Ph$_3$PO.

2. NMR Spectra

Figure S1. The $^1$H NMR (600.1 MHz, CD$_2$Cl$_2$) spectrum for complex 2.
Figure S2. The $^{31}\text{P} \{^{1}\text{H}\}$ NMR (242.9 MHz, CD$_2$Cl$_2$) spectrum for complex 2.

Figure S3. The $^{13}\text{C} \{^{1}\text{H}\}$ NMR 150.9 MHz, CD$_2$Cl$_2$) spectrum for complex 2.
Figure S4. The $^1$H NMR (600.1 MHz, CD$_2$Cl$_2$) spectrum for complex 2-BPh$_4$.

Figure S5. The $^{31}$P {$^1$H} NMR (242.9 MHz, CD$_2$Cl$_2$) spectrum for complex 2-BPh$_4$. 
**Figure S6.** The $^{13}$C ($^1$H) NMR 150.9 MHz, CD$_2$Cl$_2$) spectrum for complex 2-BPh$_4$.

**Figure S7.** The $^1$H NMR (600.1 MHz, CD$_2$Cl$_2$) spectrum for complex 3.
Figure S8. The $^{31}$P {$^{1}$H} NMR (242.9 MHz, CD$_2$Cl$_2$) spectrum for complex 3.

Figure S9. The $^{13}$C {$^{1}$H} NMR 150.9 MHz, CD$_2$Cl$_2$) spectrum for complex 3.
Figure S10. The $^1$H NMR (600.1 MHz, CD$_2$Cl$_2$) spectrum for complex 4.

Figure S11. The $^{31}$P {$^1$H} NMR (242.9 MHz, CD$_2$Cl$_2$) spectrum for complex 4.
Figure S12. The $^{13}$C/$^1$H NMR 150.9 MHz, CD$_2$Cl$_2$ spectrum for complex 4.
3. X-ray crystallographic analysis

**Figure S13.** X-ray molecular structure for the cation of complex 2-BPh₄ drawn with 50% probability level. The phenyl groups in PPh₃ are omitted for clarity. Selected bond lengths [Å] and angles [°]: Os1–C1 2.075(3), Os1–C4 2.097(3), Os1–C7 2.135(3), Os1–N2 1.894(3), C1–C2 1.354(4), C2–C3 1.454(4), C3–C4 1.369(4), C4–C5 1.436(4), C5–C6 1.353(4), C6–C7 1.443(4), C7–N1 1.306(4), N1–C8 1.375(4), C8–C10 1.383(4), C8–C9 1.517(4), C9–N2 1.278(4); Os1–C1–C2 121.3(2), C1–C2–C3 112.7(3), C2–C3–C4 112.3(3), C3–C4–Os1 120.1(2), C4–Os1–C1 73.52(11), Os1–C4–C5 117.0(2), C4–C5–C6 115.0(3), C5–C6–C7 116.8(3), C6–C7–Os1 114.3(2), C7–Os1–C4 76.15(11), Os1–C7–N1 127.6(2), C7–N1–C8 129.1(3), N1–C8–C9 118.0(3), C8–C9–N2 116.4(3), C9–N2–Os1 145.9(2), N2–Os1–C7 80.22(11).

**Crystal Data for 2-BPh₄:** C₁₁₇H₉₆Cl₄N₂O₂OsP₃ [C₉₁H₇₂N₂O₂OsP₃]BPh₄ · 2CH₂Cl₂ (M =1997.67 g mol⁻¹): triclinic, space group P-1 (no. 2), a = 13.25140(10) Å, b = 13.84720(10) Å, c = 26.3652(3) Å, α = 93.8960(10)°, β = 97.4610(10)°, γ = 98.4010(10)°, V = 4726.78(7) Å³, Z = 2, T = 100.00(10) K, μ(CuKα) = 4.493 mm⁻¹, Dcalc = 1.404 g cm⁻³, 57522 reflections measured (6.812° ≤ 2Θ ≤ 130°), 16044 unique (Rint = 0.0379, Rsigma = 0.0335) which were used in all calculations. The final R₁ was 0.0346 (I > 2σ(I)) and wR₂ was 0.0870 (all data). GOF = 1.031. Residual electron density (e Å⁻³) max/min: 2.38/-1.75.
Figure S14. X-ray molecular structure for the cation of complex 3 drawn with 50% probability level. The phenyl groups in PPh$_3$ are omitted for clarity. Selected bond lengths [Å] and angles [°]: Os1–C1 2.068(2), Os1–C4 2.110(2), Os1–C7 2.067(2), Os1–N2 1.882(2), C1–C2 1.373(3), C2–C3 1.428(3), C3–C4 1.382(3), C4–C5 1.393(3), C5–C6 1.384(3), C6–C7 1.414(3), C7–N1 1.367(3), N1–C8 1.277(3), C8–C9 1.493(3), C9–N2 1.263(3); Os1–C1–C2 121.19(17), C1–C2–C3 113.1(2), C2–C3–C4 112.6(2), C3–C4–Os1 119.57(16), C4–Os1–C1 73.47(9), Os1–C4–C5 118.14(16), C4–C5–C6 114.2(2), C5–C6–C7 114.1(2), C6–C7–Os1 118.82(16), C7–Os1–C4 74.66(9), Os1–C7–N1 126.71(16), C7–N1–C8 127.1(2), N1–C8–C9 114.1(2), C8–C9–N2 116.0(2), C9–N2–Os1 144.43(17), N2–Os1–C7 82.28(9).

Crystal Data for 3: C$_{93}$H$_{75}$B$_{2}$Cl$_{4}$F$_{8}$N$_{2}$O$_{2}$OsP$_{3}$ [C$_{91}$H$_{71}$N$_{2}$O$_{2}$OsP$_{3}$]$_{2}$BF$_{4}$· 2CH$_{2}$Cl$_{2}$ (M =1851.08 g/mol): triclinic, space group P-1 (no. 2), a = 13.04400(10) Å, b = 15.80610(10) Å, c = 22.01410(10) Å, α = 103.4130(10)°, β = 99.0530(10)°, γ = 109.8670(10)°, V = 4011.43(5) Å$^3$, Z = 2, T = 100.00(10) K, μ(CuKα) = 5.386 mm$^{-1}$, Dcalc = 1.533 g cm$^{-3}$, 56093 reflections measured (4.272° ≤ 2Θ ≤ 156.36°), 16555 unique (R$_{int}$ = 0.0295, R$_{sigma}$ = 0.0273) which were used in all calculations. The final $R_1$ was 0.0277 (I > 2σ(I)) and wR$_2$ was 0.0743 (all data). GOF = 1.055. Residual electron density (e Å$^{-3}$) max/min: 0.96/-1.18.
Figure S15. X-ray molecular structure for the cation of complex 4 drawn with 50% probability level. The phenyl groups in PPh$_3$ are omitted for clarity. Selected bond lengths [Å] and angles [°]: Os1–C1 2.097(4), Os1–C4 2.088(4), Os1–C7 2.081(4), Os1–N2 1.878(3), C1–C2 1.358(6), C2–C3 1.444(6), C3–C4 1.349(6), C4–C5 1.422(6), C5–C6 1.366(6), C6–C7 1.458(6), C7–N1 1.328(5), N1–C8 1.413(5), C8–Os1 2.130(6), C8–C9 1.491(6), C9–N2 1.283(5); Os1–C1–C2 119.5(3), C1–C2–C3 113.1(4), C2–C3–C4 113.4(4), C3–C4–Os1 120.0(3), C4–Os1–C1 73.79(16), Os1–C4–C5 116.9(3), C4–C5–C6 115.8(4), C5–C6–C7 114.2(4), C6–C7–Os1 116.5(3), C7–Os1–C4 76.5816(4), Os1–C7–N1 126.6(3), C7–N1–C8 131.9(4), N1–C8–C9 115.3(3), C8–Os1–C7 76.5816(4), C9–N2–Os1 148.0(3), N2–Os1–C7 80.64(15).

Crystal Data for 4: C$_{94}$H$_{106}$B$_2$Cl$_6$F$_8$N$_2$O$_5$OsP$_3$ [C$_{91}$H$_{73}$N$_2$O$_2$OsP$_3$]$_2$BF$_4$: 3CH$_2$Cl$_2$: 3H$_2$O ($M$ = 1992.07 g/mol): triclinic, space group P-1 (no. 2), $a = 12.44120(10)$ Å, $b = 13.2128(2)$ Å, $c = 30.4443(3)$ Å, $\alpha = 99.1000(10)^\circ$, $\beta = 93.8260(10)^\circ$, $\gamma = 117.2660(10)^\circ$, $V = 4336.90(9)$ Å$^3$, $Z = 2$, $T = 100.00(10)$ K, $\mu$(CuKα) = 5.604 mm$^{-1}$, $D_{calc} = 1.525$ g/cm$^3$, 54850 reflections measured (7.646° ≤ 2θ ≤ 156.452°), 17893 unique ($R_{int} = 0.0386$, $R_{sigma} = 0.0356$) which were used in all calculations. The final $R_1$ was 0.0478 (I > 2σ(I)) and $wR_2$ was 0.1278 (all data). GOF = 1.047. Residual electron density (eÅ$^{-3}$) max/min: 1.67/-1.68.

4. ACID Plot of 3’
Figure S16. ACID plot of model complex 3' with an isosurface value of 0.03. The magnetic field vector is orthogonal to the ring plane and is directed upward (aromatic species exhibit clockwise diatropic circulations).