Extension of Simmons–Smith Reaction to Metal-Carbynes: Efficient Synthesis of Metallacycloprenes with σ-Aromaticity

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1. Experimental Procedures

General Information: All syntheses were carried out under an inert atmosphere (N₂) using standard Schlenk techniques, unless otherwise stated. Solvents were distilled from sodium/benzophenone (hexane and diethyl ether) or calcium hydride (dichloromethane) under N₂ prior to use. The metallapentalyne was synthesized according to a previously published procedure.¹ Other reagents were used as received from commercial sources without further purification. Column chromatography was performed on alumina gel (200–300 mesh) in air. Nuclear magnetic resonance (NMR) spectroscopic experiments were performed on a Bruker AV-300, a Bruker AVIII-500 or a Bruker Ascend III 600 spectrometer at room temperature. ¹H and ¹³C NMR chemical shifts (δ) are relative to tetramethylsilane, and ³¹P NMR chemical shifts are relative to 85% H₃PO₄. The absolute values of the coupling constants are given in Hertz (Hz). Multiplicities are abbreviated as singlet (s), doublet (d), triplet (t), multiplet (m), and broad (br). High-resolution mass spectroscopy (HRMS) experiments were conducted on a Bruker En Apex Ultra 7.0T FT-MS. Elemental analyses were performed on a Vario EL III elemental analyzer.

Synthesis and characterization of S2

3-Butyn-2-one (63 μL, 0.80 mmol) was added to a suspension of compound S1 (300 mg, 0.27 mmol) in dichloromethane (15 mL). The mixture was stirred at RT for 5 min to give a yellow solution. The solution was evaporated under vacuum to a volume of ca. 2 mL and then purified by column chromatography (neutral alumina, eluent: dichloromethane/methanol = 20:1) to give complex S2 (270 mg, 85%) as a yellow solid. ¹H NMR plus HMQC (500.1 MHz, CD₂Cl₂): δ = 13.88 (s, 1H, C₇H), 9.43 (s, 1H, C₅H), 8.22 (s, 1H, C₃H), 1.78 (s, 3H, COC₃H₃), 7.84-7.10 ppm (m, 45H, other aromatic protons). ³¹P NMR (202.5 MHz, CD₂Cl₂): δ = 6.63 (t, Jₚ₋ₚ = 4.9 Hz, CPPh₃), 3.26 ppm (d, Jₚ₋ₚ = 4.9 Hz, OsPPh₃). ¹³C NMR plus DEPT-135 and HMQC (125.8 MHz, CD₂Cl₂): δ = 324.4 (dt, Jₚ₋ₜ = 14.4 Hz, 13.0 Hz, C₁), 226.5 (br, C₇), 193.8 (s, COCH₃, confirmed by HMBC), 182.4
(d, $J_{P-C} = 22.8$ Hz, C$^4$), 162.6 (s, C$^6$), 160.6 (d, $J_{P-C} = 15.4$ Hz, C$^3$), 152.7 (s, C$^5$), 119.2 (d, $J_{P-C} = 90.7$ Hz, C$^2$), 25.9 (s, COCH$_3$), 135.5-127.8 ppm (m, other aromatic carbons). HRMS (ESI): $m/z$ calcd for [C$_{63}$H$_{51}$ClOOsP$_3$]$^+$, 1143.2445; found: 1143.2460. Elemental analysis calcd (%) for C$_{63}$H$_{51}$Cl$_2$OP$_3$Os: C 64.23, H 4.36; found: C 64.56, H 4.70.

**Synthesis and characterization of 1d**

To a solution of compound S2 (295 mg, 0.25 mmol) in dichloromethane (15 mL) was added a solution of HBF$_4$·H$_2$O (85 μL, 0.50 mmol). The reaction mixture was stirred at RT for 3 h to give a reddish-brown solution. The solution was evaporated under vacuum to a volume of ca. 2 mL, then diethyl ether (20 mL) was added to the solution. The yellow precipitate was collected by filtration, washed with diethyl ether (2 × 5 mL) and dried under vacuum to give 1d (246 mg, 80%) as a yellow solid.

$^1$H NMR plus HMQC (500.1 MHz, CD$_2$Cl$_2$): $\delta$ = 13.44 (d, $J_{P-H} = 16.9$ Hz, 1H, C$^5$H), 8.92 (s, 1H, C$^3$H), 8.04 (s, 1H, C$^5$H), 1.98 (s, 3H, COC$_3$H$_3$), 7.91-6.95 ppm (m, 45H, other aromatic protons). $^{31}$P NMR (202.5 MHz, CD$_2$Cl$_2$): $\delta$ = 13.67 (t, $J_{P-P} = 4.9$ Hz, C$_3$PPh$_3$), 5.52 ppm (d, $J_{P-P} = 4.9$ Hz, OsPPh$_3$). $^{13}$C NMR plus DEPT-135 and HMQC (125.8 MHz, CD$_2$Cl$_2$): $\delta$ = 332.8 (dt, $J_{P-C} = 15.4$ Hz, 6.3 Hz, C$^7$), 224.5 (br, C$^1$), 189.0 (s, COCH$_3$), 180.7 (d, $J_{P-C} = 18.6$ Hz, C$^4$), 160.4 (s, C$^5$), 160.3 (s, C$^6$), 149.2 (d, $J_{P-C} = 21.4$ Hz, C$^3$), 118.9 (d, $J_{P-C} = 88.6$ Hz, C$^2$), 28.8 (s, COCH$_3$), 135.4-127.7 ppm (m, other aromatic carbons). HRMS (ESI): $m/z$ calcd for [C$_{63}$H$_{51}$ClOOsP$_3$]$^+$, 1143.2445; found: 1143.2456. Elemental analysis calcd (%) for C$_{63}$H$_{51}$Cl$_2$OF$_4$OP$_3$Os: C 64.54, H 4.18; found: C 64.28, H 4.36.

**Synthesis and characterization of 3a**

$^1$H NMR plus HMQC (500.1 MHz, CD$_2$Cl$_2$): $\delta$ = 13.44 (d, $J_{P-H} = 16.9$ Hz, 1H, C$^5$H), 8.92 (s, 1H, C$^3$H), 8.04 (s, 1H, C$^5$H), 1.98 (s, 3H, COC$_3$H$_3$), 7.91-6.95 ppm (m, 45H, other aromatic protons). $^{31}$P NMR (202.5 MHz, CD$_2$Cl$_2$): $\delta$ = 13.67 (t, $J_{P-P} = 4.9$ Hz, C$_3$PPh$_3$), 5.52 ppm (d, $J_{P-P} = 4.9$ Hz, OsPPh$_3$). $^{13}$C NMR plus DEPT-135 and HMQC (125.8 MHz, CD$_2$Cl$_2$): $\delta$ = 332.8 (dt, $J_{P-C} = 15.4$ Hz, 6.3 Hz, C$^7$), 224.5 (br, C$^1$), 189.0 (s, COCH$_3$), 180.7 (d, $J_{P-C} = 18.6$ Hz, C$^4$), 160.4 (s, C$^5$), 160.3 (s, C$^6$), 149.2 (d, $J_{P-C} = 21.4$ Hz, C$^3$), 118.9 (d, $J_{P-C} = 88.6$ Hz, C$^2$), 28.8 (s, COCH$_3$), 135.4-127.7 ppm (m, other aromatic carbons). HRMS (ESI): $m/z$ calcd for [C$_{63}$H$_{51}$ClOOsP$_3$]$^+$, 1143.2445; found: 1143.2456. Elemental analysis calcd (%) for C$_{63}$H$_{51}$Cl$_2$OF$_4$OP$_3$Os: C 64.54, H 4.18; found: C 64.28, H 4.36.
Propargyl alcohol (47 μL, 0.80 mmol) was added to a suspension of compound S1 (300 mg, 0.27 mmol) in dichloromethane (15 mL). The mixture was stirred at room temperature for 3 h to give a yellow solution. The solution was evaporated under vacuum to a volume of ca. 2 mL, then diethyl ether (20 mL) was added to the solution. The yellow precipitate was collected by filtration, washed with diethyl ether (2 × 5 mL) and dried under vacuum to give 3a (236 mg, 75%) as a yellow solid.

\[ \text{δ} = 13.08 \text{ (d, J}_{\text{P-H}} = 18.0 \text{ Hz, 1H, C}^1\text{H}) \]
\[ 8.60 \text{ (s, 1H, C}^3\text{H}) \]
\[ 8.08 \text{ (s, 1H, C}^5\text{H}) \]
\[ 4.05 \text{ (s, 2H, CH}_2\text{OH}) \]
\[ 1.94 \text{ (br, 1H, OH), 7.87-6.91 ppm (m, 45H, other aromatic protons).} \]

\[ \text{δ} = 13.41 \text{ (t, J}_{\text{P-P}} = 4.9 \text{ Hz, C}^\text{PPh}_3) \]
\[ 6.12 \text{ ppm (d, J}_{\text{P-P}} = 4.9 \text{ Hz, OsPPh}_3). \]

13C NMR plus DEPT-135 and HMQC (75.5 MHz, CDCl3): δ = 332.1 (br, C7), 219.5 (s, C1), 182.1 (d, J_{P-C} = 21.9 Hz, C4), 166.3 (s, C6), 161.3 (s, C5), 141.8 (d, J_{P-C} = 22.7 Hz, C5), 120.0 (d, J_{P-C} = 88.3 Hz, C2), 56.9 (s, CH2OH), 170.4 ppm (m, carbons of PPh3). Elemental analysis calcd (%) for C62H51Cl2OP3Os: C 63.86, H 4.41; found: C 63.74, H 4.55.

**Synthesis and characterization of 3b**

1-Phenyl-2-propyn-1-ol (97 μL, 0.80 mmol) was added to a suspension of compound S1 (300 mg, 0.27 mmol) in dichloromethane (15 mL). The mixture was stirred at room temperature for 3 h to give a yellow solution. The solution was evaporated under vacuum to a volume of ca. 2 mL, then diethyl ether (20 mL) was added to the solution. The yellow precipitate was collected by filtration, washed with diethyl ether (2 × 5 mL) and dried under vacuum to give 3b (225 mg, 67%) as a yellow solid.

\[ \text{δ} = 13.01 \text{ (d, J}_{\text{P-H}} = 18.0 \text{ Hz, 1H, C}^1\text{H}) \]
\[ 8.78 \text{ (s, 1H, C}^3\text{H}) \]
\[ 8.39 \text{ (s, 1H, C}^5\text{H}) \]
\[ 5.22 \text{ (s, 1H, CH(OH)Ph), 2.65 (br, 1H, OH), 7.86-6.78 ppm (m, 50H, other aromatic protons).} \]

\[ \text{δ} = 13.37 \text{ (t, J}_{\text{P-P}} = 4.9 \text{ Hz, C}^\text{PPh}_3) \]
\[ 6.41 \text{ ppm (d, J}_{\text{P-P}} = 4.9 \text{ Hz, OsPPh}_3). \]

13C NMR plus DEPT-135 and HMQC (75.5 MHz, CD2Cl2): δ = 329.6 (br, C7), 219.3 (s, C1), 181.8 (d, J_{P-C} = 19.1 Hz, C4), 170.4 ppm (m, carbons of PPh3).
(s, C\textsuperscript{6}), 162.5 (s, C\textsuperscript{5}), 142.9 (d, \(J_{P-C} = 21.5\) Hz, C\textsuperscript{3}), 120.0 (d, \(J_{P-C} = 88.3\) Hz, C\textsuperscript{2}), 69.1 (s, CH(OH)Ph), 144.3-126.7 ppm (m, other aromatic carbons). Elemental analysis calcd (%) for C\textsubscript{68}H\textsubscript{55}Cl\textsubscript{2}OP\textsubscript{3}Os: C 65.75, H 4.46; found: C 66.25, H 4.81.

**General Procedures A:** To a solution of metallapentalyne (1.0 equiv) in CH\textsubscript{2}Cl\textsubscript{2} (30 mL) was added CH\textsubscript{2}I\textsubscript{2} (5.0 equiv) and ZnEt\textsubscript{2} (1 M in hexane, 5.0 equiv). The reaction mixture was stirred at room temperature for 6 hours to give a brown solution. Excess zinc salt was removed by filtration. The solution was evaporated under vacuum to a volume of ca. 4 mL, then diethyl ether (40 mL) was added to the solution. The yellow precipitate was collected by filtration, washed with diethyl ether (2 \times 10 mL) and dried under vacuum.

**General procedures B:** CF\textsubscript{3}COOH (2.0 equiv) was added to a solution of metallapentalyne \(3\) (1.0 equiv) in dichloromethane (30 mL). CH\textsubscript{2}I\textsubscript{2} (5.0 equiv) and ZnEt\textsubscript{2} (1M in hexane, 5.0 equiv) were sequentially added to the reaction mixture and stirred at room temperature for 6 hours to give a brown yellow solution. Excess zinc salt was removed by filtration. The solution was evaporated under vacuum to a volume of ca. 4 mL, then diethyl ether (40 mL) was added to the solution. The yellow precipitate was collected by filtration, washed with diethyl ether (2 \times 10 mL) and dried under vacuum.

**Synthesis and characterization of complex 2a:** The product was prepared by General Procedure A using 1.00 g (0.79 mmol) of metallapentalyne (1a) with CH\textsubscript{2}I\textsubscript{2} (322 \(\mu\)L, 4.00 mmol) and ZnEt\textsubscript{2} (1 M, 4.00 mL, 4.00 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (30 mL), affording compound 2a (870 mg, 78%) as a yellow solid.

\(^1H\) NMR plus HSQC (500.1 MHz, CD\textsubscript{2}Cl\textsubscript{2}): \(\delta = 14.82\) (d, \(J_{P-H} = 16.5\) Hz, 1H, C\textsuperscript{1}H), 9.14 (s, 1H, C\textsuperscript{5}H), 8.67 (s, 1H, C\textsuperscript{3}H), 3.96 (q, \(J_{H-H} = 7.3\) Hz, 2H, COOCH\textsubscript{2}CH\textsubscript{3}), 3.21 (t, \(J_{P-H} = 4.7\) Hz, 2H, C\textsuperscript{8}H), 1.15 (t, \(J_{H-H} = 7.1\) Hz, 3H, COOCH\textsubscript{2}CH\textsubscript{3}), 7.83-6.93 ppm (m, 45H, other aromatic protons); \(^{31}P\) NMR (202.5 MHz, CD\textsubscript{2}Cl\textsubscript{2}): \(\delta = 11.88\) (s, CPPh\textsubscript{3}), -20.87 ppm (s, OsPPh\textsubscript{3}); \(^{13}C\) NMR plus DEPT-135, HSQC and HMBC (125.8 MHz, CD\textsubscript{2}Cl\textsubscript{2}): \(\delta = 238.8\)
(t, \( J_{P-C} = 4.5 \text{ Hz}, C^7 \)), 238.1 (m, C^1), 191.1 (d, \( J_{P-C} = 22.7 \text{ Hz}, C^4 \)), 164.6 (s, C^5), 160.3 (s, COOCH2CH3), 153.5 (d, \( J_{P-C} = 22.5 \text{ Hz}, C^3 \)), 146.8 (s, C^6), 139.3 (d, \( J_{P-C} = 71.8 \text{ Hz}, C^2 \)), 60.5 (s, COOCH2CH3), 18.8 (s, C^8), 14.3 (s, COOCH2CH3), 135.1-118.8 ppm (m, other aromatic carbons); HRMS (ESI): \( m/z \) calcld for \([C_{65}H_{55}I_2OsP_3]^+\), 1279.2075; found, 1279.2174. Elemental analysis calcld (%) for \(C_{65}H_{55}I_2OsP_3\): C, 55.56; H, 3.95; found: C, 55.38; H, 3.82.

Synthesis and characterization of complex 2b: The product was prepared by General Procedure A using 1.00 g (0.78 mmol) of metallapentalyne (1b) with CH2I2 (314 \( \mu \text{L}, 3.90 \text{ mmol}) and ZnEt2 (1 M, 3.90 mL, 3.90 mmol), affording compound 2b (845 mg, 76%) as a yellow solid.

\(^1H\) NMR plus HSQC (500.1 MHz, CD2Cl2): \( \delta = 14.83 \) (d, \( J_{P-H} = 17.0 \text{ Hz}, 1\text{H}, C^1\text{H} \)), 9.13 (s, 1H, C^5H), 8.70 (s, 1H, C^3H), 3.28 (s, 2H, C^8H), 1.38 (s, 9H, COOC(CH3)_3), 7.90-6.93 ppm (m, 45H, other aromatic protons); \(^31\text{P}\) NMR (202.5 MHz, CD2Cl2): \( \delta = 13.75 \) (s, C\text{PPh}_3), -18.97 ppm (s, Os\text{PPh}_3); \(^{13}\text{C}\) NMR plus DEPT-135, HSQC, and HMBC (125.8 MHz, CD2Cl2): \( \delta = 240.9 \) (t, \( J_{P-C} = 4.6 \text{ Hz}, C^7 \)), 239.6 (m, C^1), 192.9 (d, \( J_{P-C} = 22.0 \text{ Hz}, C^4 \)), 166.7 (s, C^5), 161.5 (s, COOC(CH3)_3), 154.9 (d, \( J_{P-C} = 21.8 \text{ Hz}, C^3 \)), 150.4 (s, C^6), 141.0 (d, \( J_{P-C} = 72.9 \text{ Hz}, C^2 \)), 82.9 (s, COOC(CH3)_3), 29.8 (s, COOC(CH3)_3), 20.4 (s, C^8), 137.7-120.8 ppm (m, other aromatic carbons); HRMS (ESI): \( m/z \) calcld for \([C_{67}H_{59}I_2OsP_3]^+\), 1307.2388; found, 1307.2467. Elemental analysis calcld (%) for \(C_{67}H_{59}I_2OsP_3\): C, 56.15; H, 4.15; found: C, 56.55; H, 3.76.

Synthesis and characterization of complex 2c: The product was prepared by General Procedure A using 1.00 g (0.80 mmol) of metallapentalyne (1c) with CH2I2 (322 \( \mu \text{L}, 4.00 \text{ mmol}) and ZnEt2 (1 M, 4.00 mL, 4.00 mmol), affording compound 2c (837 mg, 75%) as a yellow solid.

\(^1H\) NMR plus HSQC (600.1 MHz, CD2Cl2): \( \delta = 14.91 \) (dd, \( J_{P-H} = 16.3 \text{ Hz}, 1\text{H}, C^1\text{H} \)), 9.25 (s, 1H, C^5H, confirmed by HSQC), 8.76 (t, \( J_{P-H} = 2.7 \text{ Hz}, 1\text{H}, C^3\text{H}, \text{ confirmed by HSQC} \)), 3.58 (s, 3H, COOCH3), 3.29 (t, \( J_{P-H} = 5.0 \text{ Hz}, 2\text{H}, C^8\text{H} \)), 7.91-6.90 ppm (45H, other aromatic protons); \(^31\text{P}\) NMR (242.9 MHz, CD2Cl2): \( \delta = 11.83 \) (s, C\text{PPh}_3), -20.89 ppm (s, Os\text{PPh}_3); \(^{13}\text{C}\) NMR plus DEPT-135, HSQC, and HMBC (150.9 MHz, CD2Cl2): \( \delta = 239.5 \) (t, \( J_{P-C} = 4.5 \text{ Hz}, C^7 \)), 239.3 (m, C^1), 191.5 (d, \( J_{P-C} = 23.7 \text{ Hz}, C^4 \)), 165.5 (s, C^5), 161.7 (s, COOCH3), 154.7 (d, \( J_{P-C} = 21.9 \text{ Hz}, C^3 \)), 147.0 (s, C^6), 140.3 (dt, \( J_{P-C} = 4.5 \text{ Hz}, C^7 \)), 140.2 (m, C^1), 139.3 (d, \( J_{P-C} = 71.8 \text{ Hz}, C^2 \)).
72.7 Hz, $J_{P-C} = 3.7$ Hz, C$^2$), 135.9-119.5 (other aromatic carbons), 52.4 (s, COOCH$_3$), 19.2 ppm (s, C$^8$); HRMS (ESI): $m/z$ calcd for [C$_{64}$H$_{53}$I$_2$OsP$_3$]$^+$, 1265.1918; found 1265.1971. Elemental analysis calcd (%) for C$_{64}$H$_{53}$I$_2$OsP$_3$: C 55.26, H 3.84; found: C 55.58, H 3.89.

**Synthesis and characterization of complex 2d:** The product was prepared by General Procedure A using 1.00 g (0.81 mmol) of metallapentalyne (1d) with CH$_2$I$_2$ (378 μL, 4.55 mmol) and ZnEt$_2$ (1 M, 2.03 mL, 2.03 mmol), affording compound 2d (805 mg, 72%) as a yellow solid.

$^1$H NMR plus HSQC (600.1 MHz, CD$_2$Cl$_2$/CD$_3$OD = 4/1): $\delta = 14.95$ (d, $J_{P-H} = 16.2$ Hz, 1H, C$_1$H), 9.30 (s, 1H, C$_5$H, confirmed by HSQC), 8.81 (s, 1H, C$_3$H, confirmed by HSQC), 3.29 (t, $J_{P-H} = 4.5$ Hz, 2H, C$_8$H), 1.93 (s, 3H, COCH$_3$), 7.88-6.95 ppm (45H, other aromatic protons);

$^{31}$P NMR (242.9 MHz, CD$_2$Cl$_2$/CD$_3$OD = 4/1): $\delta = 11.87$ (s, C$_P$Ph$_3$), -20.60 ppm (s, Os$_2$PPh$_3$);

$^{13}$C NMR plus DEPT-135, HSQC, and HMBC (150.9 MHz, CD$_2$Cl$_2$/CD$_3$OD = 4/1): $\delta = 240.4$ (m, C$_1$), 239.0 (t, $J_{P-C} = 4.8$ Hz, C$_7$), 192.0 (s, COCH$_3$), 191.4 (d, $J_{P-C} = 24.0$ Hz, C$_4$), 164.0 (s, C$_3$), 156.0 (d, $J_{P-C} = 21.6$ Hz, C$_5$), 153.9 (s, C$_6$), 140.7 (dt, $J_{P-C} = 72.6$ Hz, $J_{P-C} = 3.7$ Hz, C$_2$), 135.3-119.6 (other aromatic carbons), 27.8 (s, COCH$_3$), 19.0 ppm (s, C$_8$); HRMS (ESI): $m/z$ calcd for [C$_{64}$H$_{53}$I$_2$OsP$_3$]$^+$, 1249.1969; found: 1249.1990. Elemental analysis calcd (%) for C$_{64}$H$_{53}$I$_2$OsP$_3$: C 55.90, H 3.89; found: C 55.52, H 3.80.

$^{1}$H NMR plus HSQC (600.1 MHz, CD$_2$Cl$_2$/CD$_3$OD = 4/1): $\delta = 14.95$ (d, $J_{P-H} = 16.2$ Hz, 1H, C$_1$H), 9.30 (s, 1H, C$_5$H, confirmed by HSQC), 8.81 (s, 1H, C$_3$H, confirmed by HSQC), 3.29 (t, $J_{P-H} = 4.5$ Hz, 2H, C$_8$H), 1.93 (s, 3H, COCH$_3$), 7.88-6.95 ppm (45H, other aromatic protons);

$^{31}$P NMR (202.5 MHz, CD$_2$Cl$_2$/CD$_3$OD = 4/1): $\delta = 11.59$ (s, C$_P$Ph$_3$), -19.43 ppm (s, Os$_2$PPh$_3$);

$^{13}$C NMR plus DEPT-135, HSQC and HMBC (125.8 MHz, CD$_2$Cl$_2$/CD$_3$OD = 4/1): $\delta = 232.9$ (s, C$^7$),

**Synthesis and characterization of complex 4a:** The product was prepared by General Procedure B using 1.00 g (0.82 mmol) of metallapentalyne (3a) with CF$_3$COOH (122 μL, 1.64 mmol), CH$_2$I$_2$ (330 μL, 4.10 mmol) and ZnEt$_2$ (1 M, 4.10 mL, 4.10 mmol), affording compound 4a (784 mg, 70%) as a yellow solid.

$^1$H NMR plus HSQC (500.1 MHz, CD$_2$Cl$_2$/CD$_3$OD = 4/1): $\delta = 14.73$ (d, $J_{P-H} = 15.7$ Hz, 1H, C$_1$H), 9.03 (s, 1H, C$_5$H), 8.39 (s, 1H, C$_3$H), 4.13 (br, 1H, CH$_2$OH), 3.33 (s, 2H, CH$_2$OH), 3.04 (s, 2H, C$_8$H), 7.90-6.99 ppm (m, 45H, other aromatic protons); $^{31}$P NMR (202.5 MHz, CD$_2$Cl$_2$/CD$_3$OD = 4/1): $\delta = 11.59$ (s, C$_P$Ph$_3$), -19.43 ppm (s, Os$_2$PPh$_3$); $^{13}$C NMR plus DEPT-135, HSQC and HMBC (125.8 MHz, CD$_2$Cl$_2$/CD$_3$OD = 4/1): $\delta = 232.9$ (s, C$^7$),
232.3 (m, C1), 193.3 (d, J_P-C = 27.8 Hz, C4), 163.6 (s, C5), 157.6 (s, C6), 148.2 (d, J_P-C = 22.3 Hz, C3), 137.4 (d, J_P-C = 68.2 Hz, C2), 60.0 (s, CH2OH), 19.4 (s, C8), 135.3-119.3 ppm (m, other aromatic carbons); HRMS (ESI): m/z calcd for [C_{63}H_{53}IOOsP_3]^+, 1237.2069; found: 1237.2037. Elemental analysis calcd (%) for C_{63}H_{53}I_{2}OOsP_3: C, 55.51; H, 3.92; found: C, 55.26; H, 4.22.

**Synthesis and characterization of complex 4b:** The product was prepared by General Procedure B using 1.00 g (0.77 mmol) of metallapentalyne (3b) with CF3COOH (114 μL, 1.54 mmol), CH2I2 (310 μL, 3.85 mmol) and ZnEt2 (1 M, 3.85 mL, 3.85 mmol), affording compound 4b (812 mg, 73%) as a yellow solid.

1H NMR plus HSQC (500.1 MHz, CD2Cl2/CD3OD): δ = 14.76 (d, J_P-H = 16.1 Hz, 1H, H1), 9.45 (s, 1H, H5), 8.25 (s, 1H, H3), 5.66 (s, 1H, CH(OH)Ph), 3.91 (s, 1H, CH(OH)Ph), 3.32 (s, 2H, H8), 7.87-6.94 ppm (m, 50H, other aromatic protons); 31P NMR (202.5 MHz, CD2Cl2/CD3OD): δ = 11.61 (s, PPh3), -21.00 ppm (d, J_P-P = 28.5 Hz, OsPPh3); 13C NMR plus DEPT-135, HSQC and HMBC (125.8 MHz, CD2Cl2/CD3OD): δ = 230.62 (m, C1), 229.1 (t, J_P-C = 5.28 Hz, C7), 194.4 (d, J_P-C = 24.8 Hz, C4), 164.4 (s, C5), 157.6 (s, C6), 149.3 (d, J_P-C = 23.1 Hz, C3), 137.2 (dt, J_P-C = 70.5 Hz, J_P-C = 3.31 Hz, C2), 72.8 (s, CH(OH)Ph), 27.2 (s, C8), 143.6, 135.3-119.3 ppm (m, other aromatic carbons); HRMS (ESI): m/z calcd for [C_{69}H_{57}IOOsP_3]^+, 1313.2283; found: 1313.2286. Elemental analysis calcd (%) for C_{69}H_{57}I_{2}OOsP_3: C, 57.59; H, 3.99; found: C, 57.45; H, 3.62.

**Synthesis and characterization of complex 7:** CF3COOH (119 μL, 1.60 mmol) was added to a solution of 6 (1.00 g, 0.83 mmol) in dichloromethane (30 mL) and stirred at 0°C for 20 min. A solution of CH2I2 (168 μL, 2.08 mmol) and ZnEt2 (1 M, 2.08 mL, 2.08 mmol) were sequentially added to the reaction mixture and stirred at 0°C for 24 hours to give a red solution. Excess zinc salt was removed by filtration. nBu4NCl (4.62 g, 16.6 mmol) was added to the filtrate and stirred at room temperature for 1 hour to give a red solution. The solution was evaporated under vacuum to a volume of approximately 3 mL and washed with n-hexane (3 × 30 mL) to give a brown solid, the solid was purified by column
chromatography (silicone, eluent: dichloromethane/methanol = 15:1) to give a brown solution. Brown solid 7 (556 mg, 55%) was collected after solvent evaporation under vacuum.

$^1$H NMR (600.1 MHz, CD$_2$Cl$_2$): $\delta$ = 13.91 (ddd, $J_{P-H} = 17.34$ Hz, $J_{P-H} = 5.34$ Hz, $J_{H-H} = 2.52$ Hz, 1H, C$^1$H), 7.72 (dd, $J_{H-H} = 2.52$ Hz, $J_{H-H} = 1.26$ Hz, 1H, C$^3$H), 6.90-7.81 (m, 46H, the above-mentioned C$^3$H and other aromatic protons), 3.71 (s, 6H, COOCH$_3$), 3.67(s, 2H, C$^8$H), 3.06 (s, C$^{11}$H), 2.38 ppm (s, C$^9$H); $^{31}$P NMR (242.9 MHz, CD$_2$Cl$_2$): $\delta$ = 21.71 (s, RuPPh$_3$), 9.85 ppm (s, CPPh$_3$); $^{13}$C NMR (150.9 MHz, CD$_2$Cl$_2$, plus HSQC and HMBC): $\delta$ = 269.4 (br, C$^1$), 250.6 (t, $J_{P-C} = 5.33$ Hz, C$^7$), 202.4 (dt, $J_{P-C} = 26.75$ Hz, $J_{P-C} = 5.65$ Hz, C$^4$), 194.4 (s, C$^5$), 171.2 (s, COOCH$_3$), 153.7 (s, C$^6$), 150.0 (d, $J_{P-C} = 22.97$ Hz, C$^3$), 129.9 (dt, $J_{P-C} = 67.25$ Hz, $J_{P-C} = 3.68$ Hz, C$^2$), 128.3-135.5 (m, the above-mentioned C$^2$ and other aromatic carbons), 119.7 (d, $J_{P-C} = 88.05$ Hz, Ph), 65.5 (s, C$^{10}$), 54.4 (s, COOCH$_3$), 53.9 (s, COOCH$_3$), 45.8 (s, C$^8$), 39.2 (s, C$^9$), 35.1 ppm (s, C$^{11}$); HRMS (ESI): m/z calcd for [C$_{69}$H$_{59}$ClO$_4$P$_3$Ru$^+$] + 1181.2368, found: 1181.2372. Elemental analysis calcd (%) for C$_{69}$H$_{59}$ClO$_4$P$_3$Ru: C, 68.09; H, 4.89; found: C, 67.68; H, 5.27.
2. X-ray Crystallographic Analysis

Single-Crystal X-Ray Diffraction Experiments. Single-crystal X-ray diffraction data were collected on a Rigaku XtaLAB Synergy, Dualflex, HyPix diffractometer with mirrormonochromated Cu Kα radiation (λ = 1.54184 Å) for 2a and 2b. The crystal was kept at 100.00 K during data collection. And single-crystal X-ray diffraction data were collected on an Oxford Gemini S Ultra CCD area detector with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) for 1d, 3a, 3b and 7. With Olex2, the structure was solved using the SHELXT\textsuperscript{3} structure solution program and refined with the SHELXL\textsuperscript{4} refinement package using least-squares minimization. Non-hydrogen atoms were refined anisotropically unless otherwise stated. Hydrogen atoms were introduced at their geometric positions and refined as riding atoms unless otherwise stated. The diffuse electron densities resulting from the residual solvent molecules in 2a, 2b and 6 were removed from the data set using the SQUEEZE routine of PLATON. Single crystals suitable for X-ray diffraction were grown from a solution of CH\textsubscript{2}Cl\textsubscript{2} (for 1d) or CHCl\textsubscript{3} (for 2a, 2b, 3a, 3b and 7) layered with hexane. In solution, complex 3a is easily oxidized to transform into 3a’ with an oxygen atom to the original carbyne carbon, therefore, in our extension attempts to grow crystals of 3a, the cocrystals of 3a and 3a’ were always obtained only, owing to the partially oxidation of 3a. the composition of the cocrystal was defined as 0.7·3a·0.3·3a’ by the X-ray diffraction analysis. Due to the similarity between the overall structure of 3a and 3a’, the structure of the cocrystal showed a disorder between 3a and 3a’ with the O2 atom refined with 30% site occupancies. Further details on the crystal data, data collection, and refinements are provided in Tables S1 and S2. X-ray crystal structures have been deposited in the Cambridge Crystallographic Database under the deposition numbers CCDC 2005482 (1d), CCDC 2005483 (2a), CCDC 2005484 (2b), CCDC 2005479 (3a), CCDC 2005480 (3b), CCDC 2005481 (7). The data can be obtained free of charge from the CCDC (www.ccdc.cam.ac.uk/data_request/cif).
Table S1. Crystal data and structure refinement of 1d, 2a and 2b.

|                          | 1d·3CHCl₂                    | 2a                                | 2b                                |
|--------------------------|------------------------------|-----------------------------------|-----------------------------------|
| **Empirical formula**    | C₆₆H₅₇BOF₄Cl₇OsP₆           | C₆₅H₅₅I₂O₂OsP₃                    | C₆₇H₅₉I₂O₂OsP₃                    |
| **Mol. weight**          | 1484.18                      | 1405.00                           | 1433.05                           |
| **Temperature [K]**      | 173                          | 100.00(10)                        | 100.00(10)                        |
| **Crystal system**       | Triclinic                    | Monoclinic                        | Monoclinic                        |
| **Space group**          | P-1                          | P₂₁/n                             | P₂₁/n                             |
| **a [Å]**                | 13.7995(6)                   | 13.57170(10)                      | 18.5224(2)                        |
| **b [Å]**                | 15.4786(6)                   | 12.22040(10)                      | 12.6665(2)                        |
| **c [Å]**                | 18.2124(7)                   | 38.22804(6)                       | 29.5255(4)                        |
| **α [°]**                | 65.1950(10)                  | 90                                | 90                                |
| **β [°]**                | 73.6760(10)                  | 96.8380(10)                       | 102.2220(10)                      |
| **γ [°]**                | 73.0050(10)                  | 90                                | 90                                |
| **V [Å³]**               | 3370.8(2)                    | 6295.08(10)                       | 6770.09(16)                       |
| **Z**                    | 2                            | 4                                 | 4                                 |
| **ρ_{calcld} [g cm⁻³]** | 1.462                        | 1.482                             | 1.406                             |
| **μ [mm⁻¹]**             | 2.291                        | 12.551                            | 11.681                            |
| **F(000)**               | 1484.0                       | 2752.0                            | 2816.0                            |
| **Crystal size [mm³]**   | 0.08 × 0.08 × 0.07           | 0.3 × 0.3 × 0.2                   | 0.35 × 0.35 × 0.2                 |
| **Radiation**            | MoKα (λ = 0.71073)           | CuKα (λ = 1.54184)                | CuKα (λ = 1.54184)                |
| **2θ range [°]**         | 6.07 to 50                   | 6.694 to 150.308                  | 5.184 to 129.996                  |
| **Coll. refl.**          | 42713                        | 71539                             | 46265                             |
| **Indep. refl.**         | 11805                        | 12830                             | 11456                             |
| **data/restraints/params** | 11805/40/822                  | 12830/0/659                       | 11456/0/667                       |
| **GOF on F²**            | 1.049                        | 1.061                             | 1.047                             |
| **R_1/wR_2 [I ≥ 2σ(I)]** | 0.0449/0.1131                | 0.0347/0.0880                     | 0.0316/0.0774                     |
| **R_1/wR_2 (all data)**  | 0.0504/0.1179                | 0.0350/0.0882                     | 0.0328/0.0781                     |
| **Largest peak/hole [e Å³]** | 2.54/-1.87                  | 0.90/-2.98                        | 1.29/-1.59                        |
Table S2. Crystal data and structure refinement of 3a, 3b and 7.

|                        | 0.7·3a·0.3·3a'*·2CHCl$_3$·H$_2$O | 3b·2CHCl$_3$ | 2·7 C$_{138}$H$_{118}$Cl$_8$O$_8$Ru$_2$P$_6$ |
|------------------------|----------------------------------|--------------|------------------------------------------|
| **Empirical formula**  | C$_{64}$H$_{55}$Cl$_8$O$_2$OsP$_3$ | C$_{70}$H$_{57}$Cl$_8$OosP$_3$ | C$_{138}$H$_{118}$Cl$_8$O$_8$Ru$_2$P$_6$ |
| **Mol. weight**        | 1427.59                          | 1480.86      | 2434.08                                  |
| **Temperature [K]**    | 173(2)                           | 173(2)       | 173.00(10)                               |
| **Crystal system**     | Triclinic                        | Triclinic    | Triclinic                                |
| **Space group**        | P-1                              | P-1          | P-1                                      |
| **a [Å]**              | 12.5033(6)                       | 12.0312(5)   | 18.0079(6)                               |
| **b [Å]**              | 14.0801(5)                       | 17.2019(10)  | 18.6935(7)                               |
| **c [Å]**              | 18.7173(8)                       | 19.2444(11)  | 24.9721(9)                               |
| **α [°]**              | 80.333(3)                        | 106.991(5)   | 95.726(3)                                |
| **β [°]**              | 80.005(4)                        | 103.843(4)   | 110.761(3)                               |
| **γ [°]**              | 72.223(4)                        | 105.956(4)   | 102.104(3)                               |
| **V [Å$^3$]**          | 3066.3(2)                        | 3433.9(3)    | 7545.1(5)                                |
| **Z**                  | 2                                | 2            | 2                                        |
| **ρ$_{c}$alcd [g cm$^{-3}$]** | 1.546                           | 1.432        | 1.071                                    |
| **μ [mm$^{-1}$]**      | 2.550                            | 2.279        | 0.381                                    |
| **F(000)**             | 1429.0                           | 1484.0       | 2512.0                                   |
| **Crystal size [mm$^3$]** | 0.20 × 0.10 × 0.05              | 0.6 × 0.3 × 0.2 | 0.4 × 0.3 × 0.3 |
| **Radiation**          | MoKα ($λ = 0.71073$)             | MoKα ($λ = 0.71073$) | MoKα ($λ = 0.71073$) |
| **2θ range [°]**       | 5.65 to 50                       | 4.548 to 58.398 | 3.138 to 58.162 |
| **Coll. refl.**        | 25229                            | 35894        | 78787                                    |
| **Indep. refl.**       | 10777                            | 15765        | 34379                                    |
| **data/restraints/params** | 10777/6/753                    | 15765/1/796  | 34379/0/1427                             |
| **GOF on F$^2$**       | 0.757                            | 0.936        | 1.064                                    |
| **R$_I$/wR$_{p}$ [I ≥ 2σ(I)]** | 0.0369/0.0411               | 0.0332/0.0639 | 0.0673/0.1356                           |
| **R$_I$/wR$_{p}$ (all data)** | 0.0609/0.0434           | 0.0464/0.0654 | 0.0993/0.1499                           |
| **Largest peak/hole [e Å$^{-3}$]** | 0.71/-0.56                   | 1.65/-0.97   | 0.99/-0.84                              |
Crystal Structures

**Figure S1.** X-ray molecular structure of the cation of complex 1d (ellipsoids are drawn at the 50% probability level). The phenyl groups of PPh$_3$ are omitted for clarity. Selected bond lengths (Å) and angles (°): Os1–C1 2.040(5), C1–C2 1.384(7), C2–C3 1.411(7), C3–C4 1.385(7), C4–C5 1.411(7), C5–C6 1.390(8), C6–C7 1.441(8), C7–Os1 1.800(6), Os1–C4 2.088(5); Os1–C1–C2 119.8(4), C1–C2–C3 113.6(4), C2–C3–C4 113.3(4), C3–C4–Os1 118.2(4), C4–Os1–C1 74.99(19), Os1–C4–C5 117.9(4), C4–C5–C6 111.4(5), C5–C6–C7 106.9(5), C6–C7–Os1 130.7(4), C7–Os1–C4 73.1(2).

**Figure S2.** X-ray molecular structure for the cation of complex 2a drawn at the 50% probability level. The phenyl groups are omitted for clarity. Selected bond lengths (Å) and angles (°): Os1–C1 2.034(4), Os1–C4 2.089(4), Os1–C7 1.991(4), Os1–C8 2.288(4), C1–C2 1.387(6), C2–C3 1.416(5), C3–C4 1.380(5), C4–C5 1.401(5), C5–C6 1.388(6), C6–C7 1.381(6), C7–C8 1.361(6); Os1–C1–C2 119.8(3), C1–C2–C3 113.5(3), C2–C3–C4 113.3(3), C3–C4–Os1 118.3(3), C4–Os1–C1 75.12(15), Os1–C4–C5 119.5(3), C4–C5–C6 111.4(5), C5–C6–C7 110.5(3), C6–C7–Os1 125.3(3), C7–Os1–C4 72.24(16), Os1–C7–C8 83.9(3), C7–C8–Os1 59.9(2), C7–Os1–C8 36.24(16).
**Figure S3.** X-ray molecular structure of complex 2b (ellipsoids are drawn at the 50% probability level). The phenyl groups of PPh₃ are omitted for clarity. Selected bond lengths (Å) and angles (°): Os1–C1 2.039(4), Os1–C4 2.083(4), Os1–C7 1.979(4), Os1–C8 2.297(4), C1–C2 1.391(5), C2–C3 1.411(6), C3–C4 1.395(5), C4–C5 1.411(6), C5–C6 1.393(5), C6–C7 1.380(6), C7–C8 1.384(5); Os1–C1–C2 119.6(3), C1–C2–C3 113.7(3), C2–C3–C4 113.3(3), C3–C4–Os1 118.0(3), C4–Os1–C1 75.43(15), Os1–C4–C5 119.3(3), C4–C5–C6 111.9(3), C5–C6–C7 110.9(3), C6–C7–Os1 125.1(3), C7–Os1–C4 72.78(15), Os1–C7–C8 84.2(2), C7–C8–Os1 59.0(2), C7–Os1–C8 36.83(15).

**Figure S4.** X-ray molecular structure of the cation of 0.7 3 0.3 3a’ (ellipsoids are drawn at the 50% probability level). The phenyl groups of PPh₃ are omitted for clarity. Selected bond lengths (Å) and angles (°): Os1–C1 2.035(3), C1–C2 1.367(5), C2–C3 1.426(5), C3–C4 1.373(5), C4–C5 1.415(5), C5–C6 1.362(5), C6–C7 1.426(6), C7–Os1 1.852(4), Os1–C4 2.071(4); Os1–C1–C2 119.9(3), C1–C2–C3 113.7(3), C2–C3–C4 112.3(4), C3–C4–Os1 119.1(3), C4–Os1–C1 74.87(16), Os1–C4–C5 118.6(3), C4–C5–C6 112.9(4), C5–C6–C7 105.7(4), C6–C7–Os1 131.2(3), C7–Os1–C4 71.52(17). The structure of the cocrystal showed a disorder between 3a (Os1–C7 carbyne bond) and 3a’ (metallacycle Os1–C7–O2), which were refined with 0.7 and 0.3 site occupancies, respectively.
Figure S5. X-ray molecular structure of the cation of complex 3b (ellipsoids are drawn at the 50% probability level). The phenyl groups of PPh$_3$ are omitted for clarity. Selected bond lengths (Å) and angles (°): Os1–C1 2.039(3), C1–C2 1.367(4), C2–C3 1.428(4), C3–C4 1.369(4), C4–C5 1.415(4), C5–C6 1.379(4), C6–C7 1.414(4), C7–Os1 1.847(3), Os1–C4 2.092(3); Os1–C1–C2 119.9(2), C1–C2–C3 113.7(3), C2–C3–C4 113.1(3), C3–C4–Os1 118.2(2), C4–Os1–C1 75.03(13), Os1–C4–C5 117.3(2), C4–C5–C6 113.0(3), C5–C6–C7 106.5(3), C6–C7–Os1 130.9(2), C7–Os1–C4 72.26(13).

Figure S6. X-ray molecular structure for the cation of complex 7 drawn at the 50% probability level. The phenyl groups are omitted for clarity. Selected bond lengths (Å) and angles (°): Ru1–C1 2.012(4), Ru1–C4 2.067(4), Ru1–C7 2.027(4), Ru1–C8 2.315(4), C1–C2 1.385(5), C2–C3 1.412(5), C3–C4 1.375(5), C4–C5 1.411(5), C5–C6 1.379(6), C6–C7 1.377(6), Ru1–C1–C2 119.5(3), C1–C2–C3 113.6(3), C2–C3–C4 113.0(4), C3–C4–Ru1 118.2(3), C4–Ru1–C1 75.72(15), Ru1–C4–C5 117.9(3), C4–C5–C6 113.7(4), C5–C6–C7 112.6(3), C6–C7–Ru1 121.4(3), C7–Ru1–C4 74.40(16), Ru1–C7–C8 83.9(3), C7–C8–Ru1 60.5(2), C7–Ru1–C8 35.62(16).
3. Theoretical Calculations

Computational details.
Structure 2a' and structure 7' were optimized at the B3LYP/6-311++G** level of DFT with an SDD basis set describing P, Cl, Ru, I and Os atoms. Whereas the other structures were optimized at the B3LYP/6-31G* level with an SDD basis set to describe P, Cl, Zn, Ru, I and Os atoms; our single-point energy calculations were then performed on the mechanism at the ωB97XD/def2-TZVP level with the Solvation Model based on Density (SMD) in dichloromethane. Frequency calculations were performed to identify all the stationary points as minima (zero imaginary frequency). The energies are given in kcal/mol and include the zero-point energy corrections. NBO calculations were carried out at the B3LYP/6-31G* level with an SDD basis set to describe P, Cl, Zn, Ru, I and Os atoms with the NBO 6.0 program. Nucleus-independent chemical shift (NICS) values were calculated at the B3LYP/6-311++G** level of theory. All the above calculations were performed with the Gaussian 09 software package. The anisotropy of the induced current density (AICD) calculations were carried out with the AICD program.

\[
\text{[Os]} = \text{Os}(\text{PPh}_3)_2
\]

\[
\text{[Ru]} = \text{RuCl}(\text{PPh}_3)_2
\]

\[
\begin{array}{c}
\text{1a} \\
0.052 \\
0.193 \\
\text{EtO} \\
\text{PPh}_3
\end{array}
\quad
\begin{array}{c}
\text{B1} \\
\text{Et} \\
\text{Cl} \\
\text{Zn} \\
\text{O} \\
\text{O}
\end{array}
\quad
\begin{array}{c}
-0.536 \\
0.122
\end{array}
\]

\[
\begin{array}{c}
\text{A3} \\
\text{MeOOC} \\
\text{MeOOC} \\
\text{F}_3\text{C}
\end{array}
\quad
\begin{array}{c}
\text{A4} \\
\text{MeO} \\
\text{MeOOC} \\
\text{O}
\end{array}
\quad
\begin{array}{c}
-0.204 \\
-0.204 \\
-0.184
\end{array}
\]

Figure S7. The natural bond orbital (NBO) charges calculated for 1a, B1 (at 298 K) and A3, A4 (at 273 K). The B3LYP/6-31G* level with an SDD basis set was used.
**Figure S8. Aromaticity Evaluation.** A) NICS(0) values for the model complex 2a'; B) Key occupied \( \pi \) MOs and their energies together with contributions to NICS(0): the eigenvalues of the MOs are given within parentheses in the first line whereas the NICS(0) values of rings a, b, and c are given in the second line; C) AICD isosurfaces of 2a' separated into the \( \sigma \) and \( \pi \) contribution. Current density vectors are plotted onto the AICD isosurface of 0.025 to indicate dia- and paratropic ring currents. The magnetic field vector is orthogonal with respect to the ring plane and points upward (clockwise currents are diatropic).
4. NMR Spectra

**Figure S9.** The $^1$H NMR (500.1 MHz, CD$_2$Cl$_2$) spectrum for complex 1d'.

**Figure S10.** The $^{31}$P{$^1$H} NMR (202.5 MHz, CD$_2$Cl$_2$) spectrum for complex 1d'.
Figure S11. The $^{13}$C{${}^1$H} NMR (125.8 MHz, CD$_2$Cl$_2$) spectrum for complex 1d'.

Figure S12. The $^1$H NMR (500.1 MHz, CD$_2$Cl$_2$) spectrum for complex 1d.
Figure S13. The $^{31}$P{$^1$H} NMR (202.5 MHz, CD$_2$Cl$_2$) spectrum for complex 1d.

Figure S14. The $^{13}$C{$^1$H} NMR (125.8 MHz, CD$_2$Cl$_2$) spectrum for complex 1d.
Figure S15. The $^1$H NMR (300.1 MHz, CDCl$_3$) spectrum for complex 3a.

Figure S16. The $^{31}$P{$^1$H} NMR (121.5 MHz, CDCl$_3$) spectrum for complex 3a.
Figure S17. The $^{13}$C{H} NMR (75.5 MHz, CD$_2$Cl$_2$) spectrum for complex 3a.

Figure S18. The $^1$H NMR (300.1 MHz, CDCl$_3$) spectrum for complex 3b.
Figure S19. The $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, CDCl$_3$) spectrum for complex 3b.

Figure S20. The $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CD$_2$Cl$_2$) spectrum for complex 3b.
Figure S21. The $^1$H NMR (500.1 MHz, CD$_2$Cl$_2$) spectrum for complex 2a.

Figure S22. The $^{31}$P{$^1$H} NMR (202.5 MHz, CD$_2$Cl$_2$) spectrum for complex 2a.
**Figure S23.** The $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, CD$_2$Cl$_2$) spectrum for complex 2a.

**Figure S24.** The $^1\text{H}$ NMR (500.1 MHz, CD$_2$Cl$_2$) spectrum for complex 2b.
Figure S25. The $^{31}$P{$^{1}$H} NMR (205.5 MHz, CD$_2$Cl$_2$) spectrum for complex 2b.

Figure S26. The $^{13}$C{$^{1}$H} NMR (125.8 MHz, CD$_2$Cl$_2$) spectrum for complex 2b.
Figure S27. The $^1$H NMR (600.1 MHz, CD$_2$Cl$_2$) spectrum for complex 2c.

Figure S28. The $^{31}$P{$^1$H} NMR (242.9 MHz, CD$_2$Cl$_2$) spectrum for complex 2c.
Figure S29. The $^{13}$C{$^1$H} NMR (150.9 MHz) spectrum for complex 2c.

Figure S30. The $^1$H NMR (600.1 MHz, CD$_2$Cl$_2$/CD$_3$OD = 4/1) spectrum for complex 2d.
Figure S31. The $^{31}$P{${}^1$H} NMR (242.9 MHz, CD$_2$Cl$_2$/CD$_3$OD = 4/1) spectrum for complex 2d.

Figure S32. The $^{13}$C{${}^1$H} NMR (150.9 MHz, CD$_2$Cl$_2$/CD$_3$OD = 4/1) spectrum for complex 2d.
Figure S33. The $^1$H NMR (500.1 MHz, CD$_2$Cl$_2$/CD$_3$OD = 4/1) spectrum for complex 4a.

Figure S34. The $^{31}$P{$^1$H} NMR (202.5 MHz, CD$_2$Cl$_2$/CD$_3$OD = 4/1) spectrum for complex 4a.
Figure S35. The $^{13}$C{$^{1}$H} NMR (125.8 MHz, CD$_2$Cl$_2$/CD$_3$OD = 4/1) spectrum for complex 4a.

Figure S36. The $^1$H NMR (500.1 MHz, CD$_2$Cl$_2$/CD$_3$OD = 4/1) spectrum for complex 4b.
Figure S37. The $^{31}$P{¹H} NMR (202.5 MHz, CD$_2$Cl$_2$/CD$_3$OD = 4/1) spectrum for complex 4b.

Figure S38. The $^{13}$C{¹H} NMR (125.8 MHz, CD$_2$Cl$_2$/CD$_3$OD = 4/1) spectrum for complex 4b.
Figure S39. The $^1$H NMR (600.1 MHz, CD$_2$Cl$_2$) spectrum for complex 6.

Figure S40. The $^{31}$P{$^1$H} NMR (242.9 MHz, CD$_2$Cl$_2$) spectrum for complex 7.
Figure S41. The $^{13}$C{$^{1}$H} NMR (150.9 MHz, CD$_2$Cl$_2$) spectrum for complex 7.

Figure S42. The in situ $^{31}$P{$^{1}$H} NMR (202.5 MHz, CD$_2$Cl$_2$) spectrum for the reaction of 6 with CF$_3$COOH.
**Figure S43.** The *in situ* $^1$H NMR (500.1 MHz, CD$_2$Cl$_2$) spectrum for the reaction of 6 with CF$_3$COOH.

**Figure S44.** The *in situ* $^{31}$P{$^1$H} NMR (202.5 MHz, CD$_2$Cl$_2$) spectrum for the reaction of 1b with CH$_3$I$_2$. 

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Figure S45. The in situ $^1$H NMR (500.1 MHz, CD$_2$Cl$_2$) spectrum for the reaction of 1b with CH$_2$I$_2$. 
5. HRMS spectra

Figure 46. Positive ion ESI-MS spectrum of [2a]$^+$ [C_{65}H_{55}IO_2OsP_3]$^+$ measured in methanol.

Figure 47. Positive ion ESI-MS spectrum of [2b]$^+$ [C_{67}H_{59}IO_2OsP_3]$^+$ measured in methanol.
Figure 48. Positive ion ESI-MS spectrum of [2c]+ [C$_{64}$H$_{53}$IO$_2$OsP$_3$]+ measured in methanol.

Figure 49. Positive ion ESI-MS spectrum of [2d]+ [C$_{64}$H$_{53}$IOOsP$_3$]+ measured in methanol.
Figure 50. Positive ion ESI-MS spectrum of [4a]+ [C_{63}H_{53}IOOsP_{3}]^+ measured in methanol.

Figure 51. Positive ion ESI-MS spectrum of [4b]+ [C_{69}H_{57}IOOsP_{3}]^+ measured in methanol.
Figure 52. Positive ion ESI-MS spectrum of $[7]^{+}$ [C$_{69}$H$_{39}$ClO$_4$OsP$_3$]$^{+}$ measured in methanol.
6. Cartesian Coordinates

\[ \text{[Os] = OsCl(PPh}_3\text{)}_2 \]

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1a* E = -4196.28116761 a.u.

Os 1.000360 0.020883 -0.511234
P 1.091645 -2.481412 -0.739120
P 1.177053 2.523261 -0.642638
P -3.619603 0.019593 0.667938
Cl 1.173228 0.051695 -3.039439
O 5.051214 -0.117884 2.025881
O 3.847895 -0.152878 3.948372
C -1.060424 0.078872 -0.596861
H -1.581558 0.142010 -1.552126
C -1.776734 0.033389 0.583000
C -0.979655 -0.053604 1.764325
H -1.390643 -0.134117 2.770227
C 0.376165 -0.045655 1.497977
C 1.397847 -0.096261 2.486940
C 1.217235 -0.143669 3.559708
H 2.671012 -0.078793 1.921483
C 2.517353 -0.030482 0.518770
C 3.983965 -0.117839 2.607716
C -0.436384 -3.313946 -1.446569
C -0.915003 -4.530036 -0.939924
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C 2.020676 -5.150783 -1.529777
H -2.376669 -6.099253 -1.136246
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H -3.500828 -5.056583 -3.094864
C -2.163660 -3.362681 -3.146457
H -2.635995 -2.910257 -4.013882
C -1.062105 -2.736019 -2.560814
H -0.669103 -1.816242 -2.983907
C 2.475288 -3.048622 -1.869182
C 2.324556 -4.201245 -2.649902
C 1.392244 -4.755893 -2.639938
C 3.376979 -4.642644 -3.454019
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C 4.583751 -3.942113 -3.477974
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H 5.670495 -2.241970 -2.714001
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H 3.802718 -1.443195 -1.305322
C 1.421385 -3.392392 0.869010
C 0.445299 -3.411257 1.876204
H -0.507964 -2.916657 1.720688
C 0.687977 -4.068177 3.082706
H -0.080475 -4.083581 3.851101
C 1.913784 -4.701599 3.302927
H 2.103281 -5.211543 4.243259
C 2.891049 -4.677710 2.308453
H 3.846861 -5.168261 2.469092
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H 3.413444 -4.026167 0.327377
C 1.496281 3.346469 1.012675
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H 3.502944 3.977624 0.526737
C 2.969258 4.527696 2.535551
C 3.930474 4.993578 2.732954
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C 2.599579 3.113251 -1.709740
C 3.725471 2.305778 -1.904370
H 3.760582 1.309676 -1.479094
C 4.801585 2.782518 -2.655578
H 5.670825 2.148825 -2.805965
C 4.756950 4.058233 -3.219301
H 5.935157 4.423051 -3.806612
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H -6.225088 1.359172 0.510734
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H -4.095717 3.355396 3.070020
H -3.497336 3.918769 3.779762
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H -5.573140 -0.429606 2.872122
C -3.541339 2.248733 2.424919
H -2.517359 1.959881 2.635502
\[
\text{EtO} = \text{OsCl(PPh}_3\text{)}_2
\]

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A1* E = -6392.08031215 a.u.

Os  -0.183348  0.202445  -0.473050
P   -4.803548  -0.374395  0.559001
P   -0.144291  -2.233683  -1.013882
P   -0.264988  2.709274  -0.283545
O    3.825742  0.028859  2.153274
O    2.572462  -0.305153  4.009189
C    -2.237400  0.083472  -0.604667
C    -4.736064  -0.116571  2.693119
C    -2.181850  -0.385391  1.993811
C    -5.232653  -2.444492  1.235808
C    -2.596790  -0.653218  2.682559
C    -0.828191  -0.211282  1.486983

C    2.116342  -4.508103  1.858210
H     3.132013  -4.857109  2.019541
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H     2.753685  -4.830088  -4.390297
C    -1.948910  -2.453967  -2.910097
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H    -1.880069  2.419581  2.178681
H    -6.973739  1.235880  1.346647
H    -7.505945  0.763054  0.526978
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H    -2.131077  3.353540  -2.301199
C    -5.610343  -1.153309  -2.757406
H    -6.168353  -2.019912  -3.099028
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C    -5.873275  -0.053136  -4.592210
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H    -4.600163  1.928680  -3.795672
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H    5.649670  -1.079063  4.401256
H    5.625031  -0.262140  6.785183
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C    4.113241  -1.113130  6.411165

H    -1.500815  2.722269  -2.919873
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C    6.223531  -2.194928  2.122261
H    6.751480  -1.330326  2.600641
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C    1.823678  -3.759181  0.714911
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C    1.600414  -2.539742  -2.152557
C    2.329816  2.933813  -1.436001
H    2.475187  1.911783  -1.105805
H    -6.093780  -1.281345  -1.795774
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C    1.103713  3.573488  -1.221918
H    2.685690  -1.656153  -2.160325
H    2.661022  -0.759340  -1.552557
C    6.698149  0.968877  0.833666
C   -0.881092  3.491245  3.753768
C    -1.631085  3.241683  4.500040
C    -7.625582  2.177267  2.143730
H    -8.663721  2.423972  1.942627
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H    -4.948715  1.543367  2.650642
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H  -4.933555  1.897320  -1.286369
C  -5.908275  1.203290  -3.070359
H  -5.830706  2.167669  -3.652198
C  0.920689  4.891850  -1.663600
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C  3.825682  -3.064573  -3.764786
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H  -2.97246  -6.094469  -1.983336
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H  -0.977327  -4.575958  3.268558
C  1.112298  -4.806497  2.778977
H  1.338436  -5.397516  3.662073
C  -5.853380  -4.586849  2.197119
H  -6.095412  -5.576946  2.572181
C  1.959035  5.560682  -2.313079
H  1.809028  6.581196  -2.654201
C  -6.515628  0.125019  -3.719628
H  -6.917432  0.251986  -4.720622
C  0.225557  4.266971  4.107475
H  0.338262  4.624049  5.127222
C  -1.640808  -4.426035  -1.537841
C  -1.117373  -4.957467  -0.750388
C  0.175176  -0.308075  2.487809
H  -0.017896  -0.527423  3.536734
C  -6.943631  2.802818  3.189918
H  -7.452565  3.538004  3.806225
C  -3.337301  -4.408763  -3.266786
H  -4.127917  -4.914156  -3.814716
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H  -7.085846  -1.951075  -3.582699
C  -2.630749  4.360595  -0.156264
H  -2.391640  4.534630  0.886835
C  3.182565  4.920981  -2.522554
H  3.989314  5.442351  -3.030038
C  -3.747056  4.990842  -0.715699
H  -4.364175  5.635204  -0.095515
C  1.182875  4.581908  3.143547
H  2.046442  5.185542  3.408033
C  -4.051156  4.815072  -2.066251

H  -4.905678  5.324622  -2.503482
Zn  6.031439  -0.817188  1.295059
I  6.879462  1.055571  -1.408456
H  4.397079  -1.172606  4.847799
H  4.328345  0.589691  4.662278
H  6.028667  1.797738  1.065414
H  7.708131  1.218075  1.162558
Cl  0.008283  0.586329  -2.965966
C  5.727158  -2.728776  1.615437
C  6.982761  -3.615234  1.526353
H  4.978397  -3.067737  0.885585
H  5.255614  -2.841071  2.602218
H  6.752728  -4.675743  1.704968
H  7.456012  -3.551635  0.539470
H  7.740862  -3.324421  2.264025

\[ \text{E} = -6392.06100246 \text{ a.u.} \]

\[ \text{TSA}^+ \]

\[ [\text{Os}] = \text{OsCl(PPh}_3)_2 \]
|   |   |   |   |
|---|---|---|---|
| **H** | -1.432167 | 2.383556 | -2.856438 |
| **C** | 1.376009 | -4.444236 | -2.421206 |
| **H** | 0.554656 | -5.083372 | -2.112417 |
| **C** | -5.248302 | 1.531954 | 1.259582 |
| **C** | -6.060433 | -1.271536 | 2.604943 |
| **H** | -6.507450 | -0.297279 | 2.772565 |
| **C** | -2.704262 | 0.007881 | 0.495613 |
| **C** | -1.415412 | -3.267426 | -1.471028 |
| **C** | 1.752315 | -3.986752 | 1.012606 |
| **H** | 2.509655 | -3.963400 | 0.237227 |
| **C** | 1.451846 | -3.117190 | -1.975026 |
| **C** | 2.193156 | 2.842593 | -2.564116 |
| **H** | 2.110967 | 1.773105 | -2.698333 |
| **C** | -5.984664 | -1.373457 | -1.494698 |
| **H** | -6.123442 | -2.176502 | -0.779291 |
| **C** | 1.411513 | 3.493812 | -1.608094 |
| **C** | 2.508490 | -2.305119 | -2.394602 |
| **H** | 2.556915 | -1.274232 | -2.073623 |
| **C** | 3.616848 | 0.503847 | -0.297612 |
| **C** | 0.92666 | 3.591268 | 3.555918 |
| **H** | -0.639975 | 3.562621 | 4.358268 |
| **C** | -7.097917 | 3.074531 | 1.477896 |
| **H** | -8.102131 | 3.381546 | 1.201605 |
| **C** | -3.07272 | 3.839589 | -2.734102 |
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| **C** | -4.508642 | 2.283127 | 2.179924 |
| **C** | -3.502000 | 1.983296 | 2.450022 |
| **C** | 3.671620 | -0.108867 | 5.100435 |
| **C** | -4.512059 | -2.707309 | 1.397739 |
| **H** | -3.762709 | 2.849327 | 0.624212 |
| **H** | -5.265945 | -0.224367 | -1.147762 |
| **C** | 3.050215 | 3.581432 | -3.385971 |
| **H** | 3.655530 | 3.064049 | -4.124102 |
| **C** | 3.490102 | -2.817264 | -3.247220 |
| **H** | 4.305450 | -2.176398 | -3.569605 |
| **C** | 0.657949 | 3.221458 | 1.221671 |
| **H** | -5.068284 | 3.428840 | 2.746843 |
| **H** | -4.492228 | 4.012878 | 3.458353 |
| **C** | 0.506450 | -3.383103 | 0.805275 |
| **C** | -0.452446 | -3.427274 | 1.828112 |
| **H** | -1.420026 | -2.955998 | 1.689977 |
| **C** | -3.091300 | -3.339468 | -3.220396 |
| **C** | -3.521696 | -2.912511 | -4.121736 |
| **Zn** | 3.090104 | 0.191193 | 6.467610 |
| **H** | 2.648722 | 1.192491 | 6.494865 |
| **H** | 3.884461 | 0.145392 | 7.219833 |
| **C** | 2.319746 | -0.538041 | 6.738126 |
| **C** | 1.958755 | 3.671420 | 1.483503 |
| **H** | 2.692133 | 3.722533 | 0.685942 |
| **C** | -5.092523 | 0.814028 | -2.074913 |
| **H** | -4.546252 | 1.714213 | -1.809917 |
| **C** | -5.634686 | 0.689306 | -3.353419 |
| **H** | -5.497831 | 1.490630 | -4.073205 |
H 7.370675 -3.774208 1.112447
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H 7.004918 -2.280186 1.984522

[Os] = OsCl(PPh3)3

B1 E = -6392.17765302 a.u.

Et

Zn

O

[Os]

PPh3

S41

E = -6356.146 -0.437679 -0.853676
H -6.543930 -1.190399 -0.096001
C 1.859146 2.745472 -2.150560
C 1.102596 -3.319545 -3.052933
H 1.021119 -2.263129 -3.276355
C 2.154944 -0.645175 -1.155247
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C 3.744821 0.596139 5.823809
H 4.983124 -0.585894 6.288400
C 3.295751 -1.102455 6.098756
C 2.206346 2.917241 1.117938
H 2.998055 2.519001 0.490887
C -5.158715 1.531992 -1.628962
H -4.417763 2.311171 -1.478136
C -5.887180 1.499831 -2.817240
H -5.702531 2.252852 -3.577127
C 2.607849 3.904084 -1.902149
C 2.433525 4.496993 -1.011027
H -5.253876 -2.992772 2.690547
H -5.034329 -4.034419 2.477109
C 1.808009 -5.545200 -3.705289
H 2.307793 -6.206031 -4.407864
C -6.294300 -1.305320 4.077426
H -6.880608 -1.030364 4.949607
C -3.941994 -4.988842 -0.587547
C -4.320041 -5.858871 -0.057052
C -0.357108 -3.778408 3.358377
H -1.041387 -3.716386 4.200362
C 0.926827 -4.298561 3.534610
\[ \text{Os}^+ = \text{OsI}(\text{PPh}_3)_2 \]
| Atom | X      | Y      | Z      |
|------|--------|--------|--------|
| H    | -3.693466 | 4.450555 | 2.509342 |
| C    | 2.399346  | -3.291289 | -1.729171 |
| C    | -0.762068 | 3.470149  | -0.791278 |
| C    | -2.313844 | 5.310548  | -0.465311 |
| H    | -2.594859 | 6.213651  | 0.070219  |
| C    | 3.642186  | -3.291289 | -1.729171 |
| H    | 4.270054  | 5.763448  | -3.276155 |
| C    | 3.642186  | 3.633476  | 1.464239 |
| H    | 4.270054  | 3.616715  | 0.650951 |
| C    | 2.544801  | -4.686063 | -1.657064 |
| H    | 1.984032  | -5.260743 | -0.926430 |
| C    | -2.170130 | -3.997021 | -2.383771 |
| H    | -2.719318 | -3.765426 | -3.293001 |
| C    | -4.467410 | 0.016806  | -0.816803 |
| C    | 2.740144  | 3.633476  | 1.464239 |
| H    | -0.819622 | -2.338063 | -2.625472 |
| C    | 3.203303  | -3.401672 | -3.554825 |
| H    | 4.542432  | -2.680476 | -2.299153 |
| C    | -5.540427 | -0.121968 | 3.126150 |
| C    | 4.141724  | -4.631069 | -3.472053 |
| H    | 4.816819  | -5.149097 | -4.147764 |
| C    | 3.991606  | -3.248328 | -3.554825 |
| H    | 2.512271  | -5.108984 | -1.614605 |
| C    | -3.55942 | -5.739192 | -1.911629 |
| H    | 1.495104  | -3.604703 | 3.484942  |
| C    | 0.823407  | -3.685772 | 4.335521  |
| C    | 5.505861  | -0.984750 | 5.205949  |
| H    | 6.331208  | -0.883768 | 5.919709  |
| H    | 5.906714  | -1.390838 | 4.273117  |
| H    | 4.778036  | -1.690144 | 5.618486  |
| C    | -5.993426 | -3.456843 | 1.785489  |

CH$_2$E = -634.876560049 a.u.

CH$_3$ClE = -797.305246600 a.u.

Et$_2$E = -377.0192201 a.u.

EtZnIE = -2156.5581584 a.u.
H  -3.060926 -1.125147  0.879834
H  -3.060858 -1.124992 -0.880121
H  -4.731606  0.556832  0.879834
H  -3.454506  1.398116  0.883424
H  -3.454518  1.398187 -0.883389
I   1.572396  0.087694 -0.000012
15
ZnEt₂ E = -1937.91545370 a.u.
Zn  0.000003  0.000013 -0.050660
C   1.843934  0.677774 -0.050083
C   2.936905 -0.393235  0.129367
H   1.929264  1.432055  0.745130
H   2.007487  1.221055 -0.991696
H   3.944736 -0.046069  0.121664
H   2.830274  0.931674  1.079391
H   2.909447 -1.144024 -0.670256
C  -1.843919 -0.677770 -0.050091
C  -2.936931  0.393194  0.129370
H  -1.929222 -1.432065  0.745113
H  -2.007451 -1.221049 -0.991710
H  -3.944744  0.046149  0.121659
H  -2.830322 -0.931674  1.079391
H  -2.909499  1.143995 -0.670243

[Os]' PH₃

I  2.777276 -1.763096  0.301557
C   4.175599 -1.737378  0.290418
O   0.825321  1.585504  0.078183
C   2.566104  0.015781  0.175036
C   1.748327  1.506552 -0.049665
H   2.831896  1.400360 -0.104529
C  -0.241382  2.841582  0.043900
H  -0.804562  3.772179  0.068622
C  -3.945647 -0.553397  0.258661
C  -0.777685 -2.011678  0.082076
H  -0.762930 -2.003024 -0.829137
H  -0.667735 -2.604395  0.985749
C  -1.432037 -0.797249  0.116010
I   1.175185  2.769596 -0.027457
C  -2.223639  1.366946  0.152287

H  -2.964677  2.159491  0.189486
C  -6.862006 -0.237084 -0.984708
H  -7.926172 -0.465913 -0.882007
H  -6.381314 -1.085346 -1.474991
H  -6.765312  0.647008 -1.618974
C  -6.270328  0.010767  0.390358
H  -6.751943  0.848533  0.893322
H  -6.327804 -0.876282  1.020856
H   0.010986 -1.443226 -2.967540
H  -0.295223  0.697351 -3.174694
H   1.725301 -0.108010 -3.036619
H   0.303737 -1.437091  3.035783
H   0.002959  0.701915  3.267436
H   2.007620 -0.088886  2.944656
H   2.105853  5.138762  1.025289
H   3.567526  3.924227 -0.162730
H   1.982575  5.128769 -1.192626

Temperature = 273.15 K
6¹ E = -4505.74797628 a.u.
C  -1.313282 -0.096887 -0.368954
C  -1.585553 -0.153909  0.997122
C  -0.380155  0.021343  1.724947
H  -0.313842  0.021463  2.813852
C   0.702097  0.172255  0.861697
C   2.031306  0.400428  1.221150
C   2.927294  0.461037  0.137840
C   2.327474  0.293879 -1.094434
C   2.924089  0.249716 -2.008566
C   2.742437  0.620078  2.530974
C   2.460220 -0.085013  3.316373
C   2.534681  1.635267  2.895033
C   4.257618  0.469088  2.157305
C   4.341273  0.711458  0.611433
H   4.648966  1.749726  0.441280
H   5.090775  0.072261  0.136034
C   4.729167 -0.955756  2.478322
C   6.616920 -2.374042  2.532286
C   6.443439 -2.668689  3.569961
C   7.683003 -2.269232  2.333485
C   6.170303 -3.115577  1.865348
C   5.100843  1.484559  2.936751
C   5.959615  2.005766  5.073508
C   5.488458  2.991372  5.101746
H   6.982405  2.106964  4.703005
H   5.950232  1.544937  6.060939
\[ [\text{Ru}] = \text{RuCl}(\text{PPh}_3)_2 \]

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Temperature = 273.15 K

\[ \text{E} = -4506.19180472 \text{ a.u.} \]

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S47

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Temperature = 273.15 K

A3+ \( E = -450.74863959 \) a.u.

C 1.500647 0.071412 -0.493647
C 1.661932 -0.034449 0.868261

C 0.445793 -0.151784 1.620064
H 0.419270 -0.218335 2.707609
C -0.673730 -0.149049 0.824928
H -2.052642 -0.310122 1.242813
C -2.927955 -0.259413 0.186741
C -2.205676 -0.057969 -0.992067
C -2.728043 -0.576724 2.548882
H -2.454666 0.125696 3.341032
H -2.497052 -1.590585 2.899174
C -4.250326 -0.434633 2.188883
C -4.349081 -0.489539 0.620332
C -4.711913 -1.478757 0.321205
H -5.057018 0.246439 0.228378
C -4.777558 0.920581 2.684518
C -6.721358 2.245422 2.902536
H -6.562389 2.164047 3.969803
H -7.781697 2.123643 2.684060
C -6.302740 3.080011 2.334924
C -5.060109 -1.564162 2.838669
C -5.850312 -2.387868 4.905854
C -5.378486 -3.365207 4.777670
H -6.884780 -2.439765 4.558313
H -5.808102 -2.072499 5.948031
C -1.988713 3.206542 -2.177867
H -2.642459 4.369830 -1.752123
C -2.285235 4.917057 -0.886493
C -3.764611 4.835949 -2.441856
P -4.266901 5.737044 -2.100705
P -4.232561 4.152854 -3.564942
P -5.103341 4.516844 -4.102028
C -3.572394 3.001490 -4.000020
C -3.923794 2.470728 -4.880581
C -2.456689 2.524238 -3.310233
C -1.937056 1.639245 -3.662471
C 0.966355 3.082758 -2.228317
C 0.738229 4.154725 -3.357988
P 0.365885 0.131042 -1.282511
O 5.033531 -1.586144 3.869585
O 4.492814 -2.433144 1.845223
H -2.208995 0.107973 -1.115936
C 5.112265 0.959335 3.005815
O 4.685835 1.815846 3.748915
O 6.399991 0.784464 2.691482
C 7.342545 1.663524 3.349103
H 7.283237 1.531159 4.431407
H 8.321455 1.367610 2.974902
H 7.127274 2.703914 3.095903

\[ \text{MeOOC} \]
\[ \text{MeOOC} \]

\[ \text{[Ru] = RuCl(PPh}_3\text{)]}_2 \]
| C     | 2.092536   | 4.539793   | 5.307893   |
|-------|-------------|-------------|-------------|
| C     | 0.894950   | 4.133682   | 5.899533   |
| H     | -0.825400  | 2.844108   | 5.731289   |
| C     | 0.505221   | 2.611327   | 4.057467   |
| C     | 1.701931   | 3.021293   | 3.459946   |
| C     | 4.820015   | 3.472334   | 1.245704   |
| C     | 6.210198   | 3.536076   | 1.381398   |
| H     | 7.965679   | 2.642585   | 2.258311   |
| C     | 6.887002   | 2.582178   | 2.141570   |
| H     | 6.681188   | 0.829058   | 3.385657   |
| C     | 6.166875   | 1.561220   | 2.768449   |
| H     | 5.740959   | 3.385657   | 0.305823   |
| C     | -0.39706   | 3.431538   | 0.284238   |
| H     | -1.86177   | 4.54250   | -3.775192   |
| C     | -1.580361  | -2.791192  | -2.400168   |
| H     | -2.310240  | -2.237497  | -3.935053   |
| C     | -1.123323  | -2.259740  | -1.194477   |
| H     | -1.509936  | -1.308523  | -0.853344   |
| C     | 4.097906   | 2.442087   | 1.860818   |
| H     | 4.779601   | 4.851999   | 2.628760   |
| H     | 4.22153    | 0.701652   | 3.133927   |
| C     | 6.166875   | 1.561220   | 2.768449   |
| H     | 6.681188   | 0.829058   | 3.385657   |
| C     | 6.887002   | 2.582178   | 2.141570   |
| H     | 3.497906   | 3.431538   | 0.284238   |
| H     | -0.39706   | 3.431538   | 0.284238   |
| C     | 3.514533   | 4.769591   | 1.975882   |
| H     | 4.477802   | 4.969864   | 1.515126   |
| C     | 2.674171   | -3.803943  | 1.421839   |
| H     | 2.994504   | -3.263870  | 0.536567   |
| C     | -0.197041  | -2.964809  | -0.411322  |
| H     | 0.258171   | -4.212238  | -0.855079  |
| H     | 0.952009   | -4.787038  | -0.251889  |
| H     | -0.200141  | -4.741998  | -2.067175  |
| H     | 0.147486   | -5.720612  | -2.387924  |
| C     | -1.118644  | -4.034156  | -2.842838  |
| H     | -1.486177  | -4.454250  | -3.775192  |
| C     | -1.580361  | -2.791192  | -2.400168  |
| H     | -2.310240  | -2.237497  | -3.935053  |
| C     | -1.123323  | -2.259740  | -1.194477  |
| H     | -1.509936  | -1.308523  | -0.853344  |
| C     | 4.097906   | 2.442087   | 1.860818   |
| H     | 4.779601   | 4.851999   | 2.628760   |
| H     | 4.22153    | 0.701652   | 3.133927   |
| C     | 6.166875   | 1.561220   | 2.768449   |
| H     | 6.681188   | 0.829058   | 3.385657   |
| C     | 6.887002   | 2.582178   | 2.141570   |
| H     | 7.965679   | 2.642585   | 2.258311   |
| C     | 6.210198   | 3.536076   | 1.381398   |
| H     | 6.758302   | 4.342769   | 0.902347   |
| C     | 4.820015   | 3.472334   | 1.245704   |
| H     | 4.307985   | 4.236102   | 0.670917   |
| C     | 1.701931   | 3.021293   | 3.459946   |
| C     | 0.505221   | 2.611327   | 4.057467   |
| H     | 0.103271   | 1.850318   | 3.582882   |
| C     | 0.102819   | 3.171618   | 5.271564   |
| H     | -0.825400  | 2.844108   | 5.731289   |
| C     | 0.894950   | 4.133682   | 5.899533   |
| H     | 0.583399   | 4.562123   | 6.847992   |
| C     | 2.092536   | 4.539793   | 5.307893   |
| O     | -3.685586  | 0.166880   | -1.818805  |
Temperature = 273.15 K

TSA4$^+$ $E = -7148.61844020$ a.u.

C -2.903021 -3.213208 -2.130458

H -2.907471 3.198993 5.352782

C -2.324929 6.861470 4.651778

C -2.584034 -1.942276 -4.164361

H -2.006977 -1.253741 -4.771245

C 1.489280 1.071200 -0.273050

C 1.109169 -0.220096 0.102232

C 0.691287 3.217944 -0.986124

H 0.153878 4.000867 -0.438923

H 0.454333 3.352833 -2.048355

C 2.248496 3.312970 -0.795914

C 2.755022 1.855464 -0.484220

H 3.341583 1.463445 -1.320989

H 3.396769 1.867831 0.401385

C 2.503534 4.235355 0.397856

C 0.996555 -0.973325 3.537105

C 1.885738 -0.063632 4.117991

H 1.656340 0.994449 4.154221

C 3.085452 -0.515109 4.679087

H 3.767971 0.202378 5.125790

C 3.97603 -1.874350 4.675444

H 4.327609 -2.223181 5.114711

C 2.503830 -2.786503 4.107119

H 2.736781 -3.847291 4.101396

C 1.310811 -2.342516 3.535170

H 0.627277 -3.057369 3.087466

C -1.875096 -1.389928 3.827912

C -1.537455 -1.709860 5.150777

H -0.557023 -1.460602 5.541479

C -2.458824 -2.354087 5.979943

H -2.180678 -2.600138 6.998810

C -3.726792 -2.681971 5.495894

C -4.440440 -3.189645 6.138777

H -4.070917 -2.355996 4.183585

C -5.053060 -2.609466 3.795013

C -3.149519 -1.714158 3.354118

H -3.426618 -1.475618 2.336454

C -9.036261 1.321791 3.331258

C -1.948046 1.651386 4.206442

H -2.629042 0.884838 4.558130

C -2.105295 2.965843 4.657178

C -2.907471 3.198993 5.352782

C -1.219943 3.963014 4.244978

H -1.328881 4.978752 4.615545

C -0.180272 3.641740 3.369777

C 0.536094 4.393978 3.055340

C -0.028866 2.333290 2.907724

H 0.795063 2.109803 2.240607

C -2.161682 -2.282204 -2.873700

C -2.903021 -3.213208 -2.130458

H -2.561883 -3.515856 -1.144223

C -4.057432 -3.782228 -2.672980

H -4.607549 -4.522857 -2.097896

C -4.488631 -3.424251 -3.953147

H -5.383528 -3.873191 -4.375235

C -3.748331 -2.504686 -4.695823

H -4.063473 -2.232631 -5.699468

C -2.584034 -1.942276 -4.164361

C -2.006977 -1.253741 -4.771245

C 0.565559 -3.160028 -2.585561

C 1.103390 -4.010506 -1.615598

H 0.900090 -3.838374 -0.566451

C 1.866029 -5.118414 -2.002154

H 2.280424 -5.770309 -1.238963

C 2.087981 -5.385260 -3.351827

H 2.681906 -6.245125 -3.648064

C 1.536188 -4.546057 -4.323939

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Temperature = 273.15 K
\[ \Delta E = -4545.07942884 \text{ a.u.} \]

Ru 0.371020 -0.073834 -1.318194
P 0.116058 2.421654 -1.663291
Cl -0.816275 -0.510928 -3.576327
P 0.449522 -2.618080 -1.274621
P -3.117480 0.011143 1.891344
C -1.541586 0.025967 0.920125
C -0.290924 0.180104 1.581030
H -0.191493 0.269990 2.663133
C -1.459750 -0.108209 -0.461955
H -2.370736 -0.218758 -1.049421
C 0.713574 -3.517855 0.364617
C 0.845376 2.499675 -4.410242
H 0.390034 1.514022 -2.447339
C 2.316050 0.021749 -2.565439
H 2.543075 -0.916384 -3.065268
H 2.328001 0.900229 -3.205513
C 0.919834 3.192555 -3.193607

\[
\begin{align*}
\text{MeOOC} & \rightarrow \text{RuCl(PPh}_3)_2 \\
\text{MeOOC} & \quad \text{MeOOC}
\end{align*}
\]

S51
C  -3.355849  -4.908181  -2.806751  
H  -4.238429  -5.442676  -3.147000  
C  -3.525965  -1.806862   5.574832  
H  -4.059241  -1.614545   6.501049  
C  -3.634808  -0.905139   4.516084  
H  -4.248497  -0.016417   4.623877  
C  -5.222041   3.311530   3.232545  
H  -6.258929   3.633016   3.257887  
C  -4.893163   2.092470   2.635600  
H  -5.675213   1.477621   2.203220  
C  -4.224459   4.109423   3.793639  
H  -4.483249   5.055639   4.259554  
C  -2.892515   3.689631   3.757447  
H  -2.115123   4.305807   4.199563  

7 Temperature = 273.15 K

CF₃C=O⁻E = -526.420939699 a.u.
C  -1.066804   0.009776  -0.000022  
O  -1.592252   1.139976  -0.000042  
O  -1.532909  -1.147993  -0.000096  
C   0.513669   0.013435   0.000024  
F   1.080968   1.250871  -0.000025  
F   1.032822  -0.629553  1.089004  
F   1.032887  -0.629666 -1.088858  

8 Temperature = 273.15 K

CF₃COOH E = -526.884339105 a.u.
C  -0.934653   0.160088  -0.000050  
O  -1.498219   1.222252  -0.000067  
O  -1.523209  -1.147993  -0.000096  
C   0.513669   0.013435  0.000024  
F   1.080968   1.250871  -0.000025  
F   1.032822  -0.629553  1.089004  
F   1.032887  -0.629666 -1.088858  

9 Temperature = 273.15 K

CF₃COOZnI E = -2603.64237173 a.u.
Zn   0.394077  -0.005083  -0.000036  
O  -1.355849  -0.803006  -0.000021  
C  -1.963015   0.268161  -0.000002  
C  -1.346214   1.126739  -0.000023  
C  -3.508295   0.005300   0.000082  
F  -4.027225  1.245846  -0.000427  
F  -3.960631  -0.644707   1.096369  
F  -3.960791  -0.645671  -1.095558  
I   2.833258   0.000202  -0.000048  

CH₂I₂ E = -634.876560049 a.u.
C   0.000000   0.000000  1.057325  
H  -0.899514   0.000000  1.664053  
H   0.899514   0.000000  1.664053  
I   1.000000  1.852908  -0.091246  
I   1.000000 -1.852908  -0.091246  

8 Temperature = 273.15 K

Ethane E = -79.8349434909 a.u.
C  -0.765067   0.000001  -0.000005  
C   0.765067   0.000001  0.000005  
H  -1.164334  -0.963801  -0.336678  
H  -1.164264   0.190321  1.003025  
H  -1.164292   0.773515  -0.666291  
H   1.164332   0.963809  0.336655  
H   1.164293  -0.773499  0.666310  
H   1.164265 -0.190344 -1.003020  

8 Temperature = 273.15 K

EtI E = -377.019220101 a.u.
C   2.451769  -0.434584  0.000070  
C   1.446596   0.700086  0.000051  
H   3.463477  -0.007336  0.000094  
H   2.349107  -1.065492  0.887504  
H   2.349149  -1.065485 -0.887374  
H   1.503435   1.322976  0.891832  
H   1.503490  1.322995 -0.891713  
I  -0.652071  -0.039635  0.000020  

15 Temperature = 273.15 K

ZnEt₂ E = -1937.91545370 a.u.
Zn  -0.000003  -0.000013  0.050660  
C  -1.843934  -0.677774  -0.050083  
C  -2.936905  0.393235   0.129367  
H  -1.929264  -1.432055  0.745130  
H  -2.007487  -1.221055  -0.991696  
H  -3.944736  -0.460696  0.121664  
H  -2.830274   0.931722  1.079381  
H  -2.909447  1.144024  -0.670256  
C   1.843919   0.677770  -0.050091  
C   2.936931  -0.393194   0.129370  
H   1.929222  1.432065  0.745113  
H   2.007451  1.221049  -0.991710  
H   3.944744   0.46149  0.121659  
H   2.830322  -0.931674  1.079391  
H   2.909499  -1.143995  -0.670243  

5 Temperature = 273.15 K
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\[
\text{[Ru\(\text{II}\)} = \text{RuCl(PH}_3\text{)}_2
\]

7"" \(E = -2.654.414.007.59 \text{ a.u.}\)

\[
\begin{array}{ccc}
\text{Ru} & -2.007989 & 0.602401 \\
\text{P} & -2.517231 & 0.312272 \\
\text{Cl} & -4.225020 & 1.833364 \\
\text{P} & -1.871268 & 1.605374 \\
\text{P} & 3.229135 & 3.819700 \\
\text{C} & -2.387963 & 2.234820 \\
\text{C} & 0.975796 & 2.170965 \\
\text{H} & -0.318021 & 3.034888 \\
\text{C} & 0.977023 & 1.605478 \\
\text{H} & -1.179023 & 1.025223 \\
\text{C} & -1.096889 & 2.640676 \\
\text{H} & -1.198694 & 3.329409 \\
\text{H} & -1.423612 & 3.043838 \\
\text{C} & 3.733369 & 1.259469 \\
\text{H} & 2.586771 & 1.406869 \\
\text{H} & 2.682360 & 2.169761 \\
\text{C} & -0.260632 & 1.560520 \\
\text{C} & 0.933875 & 1.761532 \\
\text{H} & 2.120686 & 1.183224 \\
\text{H} & 2.271358 & 1.888428 \\
\end{array}
\]

\[
\begin{array}{ccc}
\text{C} & 0.788983 & 0.488910 \\
\text{O} & 4.567014 & -1.113351 \\
\text{C} & -0.551019 & 0.889427 \\
\text{C} & 3.572001 & -0.223225 \\
\text{O} & 4.614188 & -0.217900 \\
\text{O} & 3.047290 & 0.294783 \\
\text{O} & 5.113639 & 1.276293 \\
\text{C} & 4.375621 & 0.304716 \\
\text{C} & 6.303393 & 1.673966 \\
\text{H} & 6.977559 & 0.823986 \\
\text{H} & 6.757120 & 2.456590 \\
\text{H} & 6.035073 & 2.049415 \\
\text{C} & 3.149327 & 0.003141 \\
\text{C} & 5.063954 & -1.432706 \\
\text{H} & 5.443054 & -0.532448 \\
\text{H} & 5.863115 & -2.151298 \\
\text{H} & 4.268861 & -1.866902 \\
\text{H} & -3.107620 & -1.084889 \\
\text{H} & -1.350162 & -2.318978 \\
\text{H} & -1.113209 & -0.222690 \\
\text{H} & -3.885615 & -1.510109 \\
\text{H} & -2.198511 & -1.388226 \\
\text{H} & -1.958787 & 0.753580 \\
\text{H} & -4.608491 & 3.598179 \\
\text{H} & -2.820701 & 4.434922 \\
\text{H} & -3.107480 & 4.840598
\end{array}
\]

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