Electronic Supplementary Information

For

Halogenation of Carbyne Complexes: Isolation of Unsaturated Matallaiodirenium Ion and Matallabromirenium Ion

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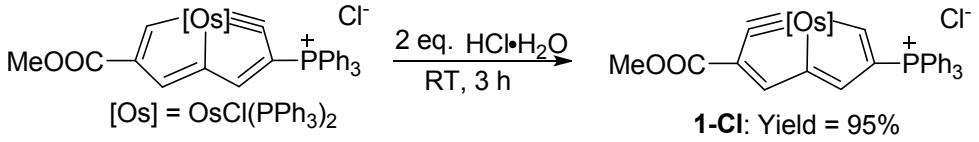
Contents

1. Experimental Procedures

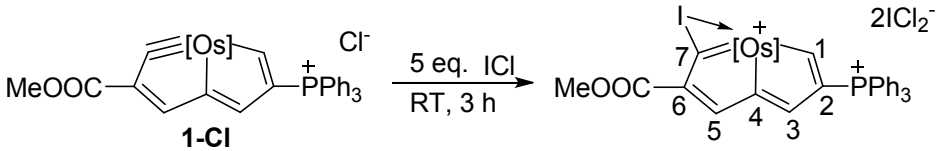
General Procedures: All syntheses were carried out under an inert atmosphere (N_2) by means of standard Schlenk techniques, unless otherwise stated. Solvents were distilled from sodium/benzophenone (hexane and diethyl ether) or calcium hydride (dichloromethane) under N_2 prior to use. The metallapentalyne was synthesized according to the previously published procedure.[1] Other reagents were used as received from commercial sources without further purification. NMR spectroscopic experiments were performed on a Bruker AVIII-600 (^{1}H 600.2 MHz; ^{31}P 242.9 MHz; ^{13}C 150.9 MHz) or a Bruker AVII-400 (^{1}H 400.1 MHz; ^{31}P 162.0 MHz; ^{13}C 100.6 MHz) spectrometer at room temperature. ^{1}H and ^{13}C NMR chemical shifts (δ) are relative to tetramethylsilane, and ^{31}P NMR chemical shifts are relative to 85% H_3PO_4. Two-dimensional and one-dimensional NMR are abbreviated as heteronuclear single quantum coherence (HSQC), heteronuclear multiple bond correlation (HMBC), and distortionless enhancement by polarization transfer (DEPT). The absolute values of the coupling constants are given in Hertz (Hz). Multiplicities are abbreviated as singlet (s), doublet (d) and broad (br). Elemental analyses were performed on a Vario EL III elemental analyzer.

Synthesis and characterization of 1-Cl:



According to the previously reported procedure,[1] **1-Cl** was achieved by mixing the metallapentalyne (300 mg, 0.25 mmol) with concentrated HCl solution (43 μL, 0.50 mmol) in dichloromethane (10 mL). The reaction mixture was stirred at room temperature for 3 hours to give a yellow solution. The solution was evaporated under vacuum to a volume of approximately 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 **1-Cl** (285 mg, 95%) as an orange solid. The NMR spectroscopic data is associated with the published literature. Anal. Calcd (%) for $C_{63}H_{51}Cl_2O_2OsP_3$: C 63.37, H 4.30; Found: C 63.48, H 4.65.

Synthesis and characterization of 2-$(ICl_2)_2$:



1-Cl

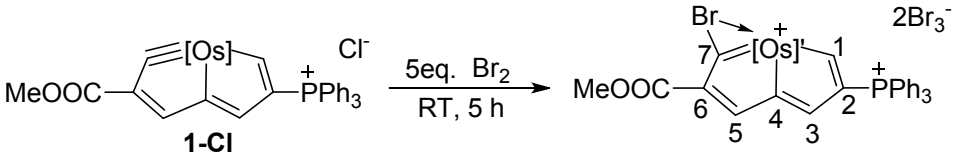
[Os] = $OsCl(PPh_3)_2$

2-$(ICl_2)_2$: Yield = 95%

To a solution of **1-Cl** (300 mg, 0.24 mmol) in dichloromethane (10 mL), a solution of ICl (195 mg, 1.20 mmol) was added. The reaction mixture was stirred at room temperature for 3 hours to give a reddish−yellow solution. The solution was evaporated under vacuum to a volume of approximately 2 mL, then diethyl ether (20 mL) was added to the solution. The orange precipitate was collected by filtration, washed with diethyl ether (2 × 5 mL) and dried under vacuum to give **2-$(ICl_2)_2$** (380 mg, 95%) as an orange solid.

^{1}H NMR plus HSQC (600.2 MHz, CD_2Cl_2): δ = 14.5 (d, $J_{P\text{-}H}$ = 10.2 Hz, 1H, H1), 9.7 (s, 1H, H3), 9.2 (s, 1H, H5), 3.6 (s, 3H, COOC*H*$_3$), 8.0-7.0 ppm (m, 45H, other aromatic protons). ^{31}P NMR (242.9 MHz, CD_2Cl_2): δ = 13.9 (s, C*P*Ph_3), −15.2 ppm (s, Os*P*Ph_3). ^{13}C NMR plus DEPT-135 and HSQC (150.9 MHz, CD_2Cl_2): δ = 236.4 (br, C1), 231.1 (s, C7), 185.1 (d, $J_{P\text{-}C}$ = 16.5 Hz, C4), 166.4 (s, C5), 164.6 (br, C3), 157.1 (s, *C*$OOCH_3$, confirmed by HMBC), 156.7 (s, C6), 116.5 (d, $J_{P\text{-}C}$ = 90.0 Hz, C2), 53.4 (s, COO*C*H_3), 138.2-127.8 ppm (m, other aromatic carbon atoms). Anal. Calcd (%) for $C_{63}H_{51}Cl_5I_3O_2OsP_3$: C 45.01, H 3.06; Found: C 44.83, H 3.46.

Synthesis and characterization of 3-$(Br_3)_2$:



1-Cl

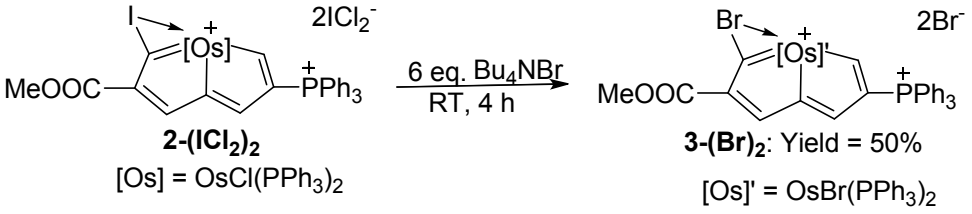
[Os]' = $OsBr(PPh_3)_2$

3-$(Br_3)_2$: Yield = 90%

To a solution of **1-Cl** (300 mg, 0.24 mmol) in dichloromethane (10 mL), a solution of Br_2 (192 mg, 1.20 mmol) was added. The reaction mixture was stirred at room temperature for 5 hours to give a red solution. The solution was evaporated under vacuum to a volume of approximately 2 mL, then diethyl ether (20 mL) was added to the solution. The red precipitate was collected by filtration, washed with diethyl ether

(3 × 5 mL) and dried under vacuum to give **3-(Br$_3$)$_2$** (379 mg, 90%) mg as a red solid. ^{1}H-NMR plus HSQC (400.1 MHz, CD_2Cl_2): δ = 13.9 (d, $J_{P\text{-}H}$ = 8.9 Hz, 1H, H1), 9.6 (s, 1H, H3), 9.1 (s,1H, H5), 3.6 (s, 3H, COOC*H$_3$*), 7.9-6.9 ppm (m, 45H, other aromatic protons).^{31}P NMR (162.0 MHz, CD_2Cl_2): δ = 13.4 (s, C*P*Ph$_3$), −4.7 ppm (s, Os*P*Ph$_3$). ^{13}C NMR plus DEPT-135 and ^{1}H-^{13}C HSQC (100.6 MHz, CD_2Cl_2): δ = 229.3 (br, C1), 226.9 (s, C7), 186.2 (d, $J_{P\text{-}C}$ = 18.3 Hz, C4), 165.2 (s, C5), 163.1 (d, $J_{P\text{-}C}$ = 16.7 Hz, C3), 157.2 (s, *C*OOCH$_3$, confirmed by HMBC), 152.4 (s, C6), 116.5 (d, $J_{P\text{-}C}$ = 91.0 Hz, C2), 53.4 (s, COO*C*H$_3$), 136.9-129.6 ppm (m, other aromatic carbon atoms). Anal. Calcd (%) for $C_{63}H_{51}Br_8O_2OsP_3$: C 42.93, H 2.92; Found: C 43.16, H 3.31.

Conversion of 2-(ICl$_2$)$_2$ to 3-(Br)$_2$ starting from complex:

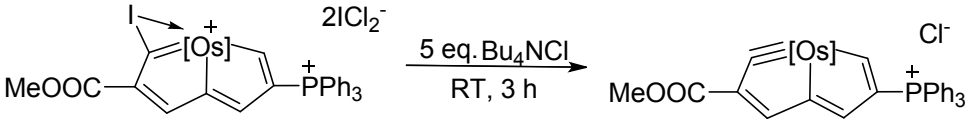


2-(ICl$_2$)$_2$
[Os] = OsCl(PPh$_3$)$_2$

3-(Br)$_2$: Yield = 50%
[Os]' = OsBr(PPh$_3$)$_2$

A mixture of **2-(ICl$_2$)$_2$** (16.8 mg, 0.01 mmol) reacted with Bu_4NBr (19.3 mg, 0.06 mmol) in CD_2Cl_2 (0.5 mL) in an NMR tube, after 4 hours at room temperature, through the NMR analysis, **2-(ICl$_2$)$_2$** transformed into **3-(Br)$_2$** in 50% NMR yield.

Conversion of 1-Cl to 2-(ICl$_2$)$_2$:

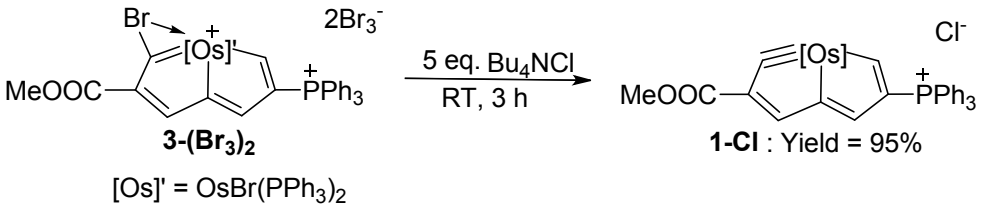


2-(ICl$_2$)$_2$
[Os] = OsCl(PPh$_3$)$_2$

1-Cl : Yield = 95%

A mixture of **2-(ICl$_2$)$_2$** (16.8 mg, 0.01 mmol) reacted with Bu_4NCl (13.9 mg, 0.05 mmol) in CD_2Cl_2 (0.5 mL) in an NMR tube, after 3 hours at room temperature, through the NMR analysis, **2-(ICl$_2$)$_2$** transformed into complex **1-Cl** in 95% NMR yield.

Conversion of 3-$(Br_3)_2$ to 1-Cl:



A mixture of **3-$(Br_3)_2$** (17.5 mg, 0.01 mmol) reacted with Bu_4NCl (13.9 mg, 0.05 mmol) in CD_2Cl_2 (0.5 mL) in an NMR tube, after 3 hours at room temperature, through the NMR analysis, **3-$(Br_3)_2$** transformed into complex **1-Cl** in 95% NMR yield.

Time-evolved ^{31}P NMR spectra of reactions of complex 2-$(ICl_2)_2$ with Bu_4NCl:

The reaction of complex **2-$(ICl_2)_2$** (16.8 mg, 0.01 mmol) with Bu_4NCl (13.9 mg, 0.05 mmol) was traced in an NMR tube in CD_2Cl_2 (0.5 mL). As shown in Figure S1, the reaction of **2-$(ICl_2)_2$** with Bu_4NCl can produce **1-Cl** via an intermediate. Unfortunately, the intermediate is very unstable and the pure sample of the intermediate could not be obtained.

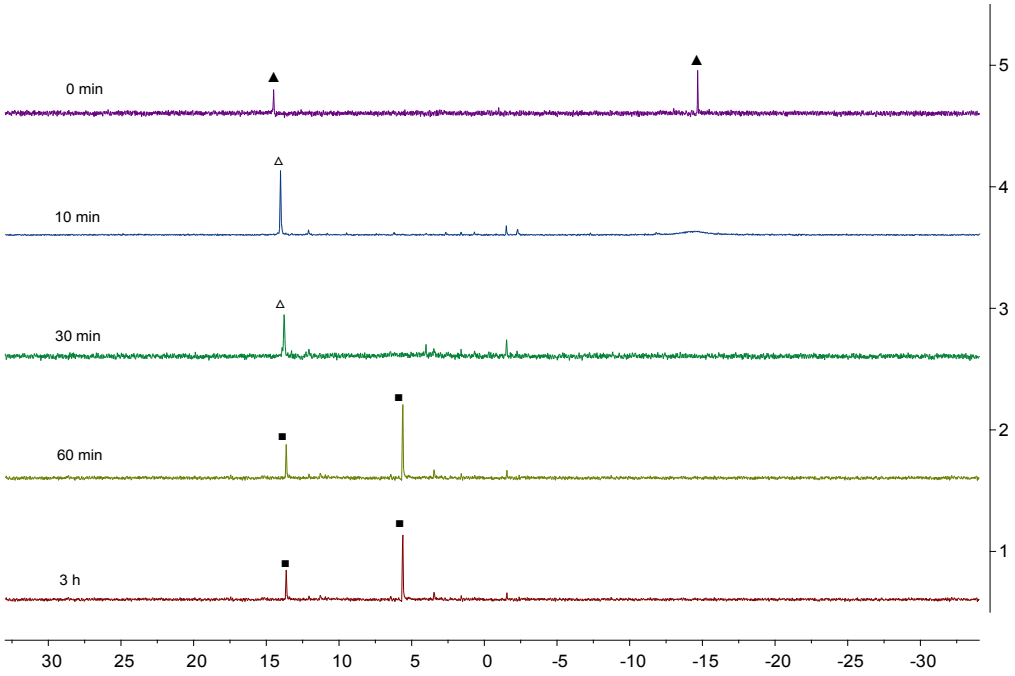


Figure S1. Time-evolved ^{31}P NMR spectra of the reaction of complex **2-$(ICl_2)_2$** with Bu_4NCl at room temperature. The symbol ▲, ■ and △ were used to label the

characteristic signals of **2-$(ICl_2)_2$**, **1-Cl** and unidentified products respectively.

Reactions of complex 2-$(ICl_2)_2$ with different equivalents of Bu_4NCl:

Complex **2-$(ICl_2)_2$** (16.8 mg, 0.01 mmol) with 0.5 equivalents Bu_4NCl (1.4 mg, 0.005 mmol), 1 equivalent Bu_4NCl (2.8 mg, 0.01 mmol), 3 equivalents Bu_4NCl (8.3 mg, 0.03 mmol) or 5 equivalents Bu_4NCl (13.9 mg, 0.05 mmol) were reacted for 3 hours in CD_2Cl_2 (0.5 mL) respectively. As shown in Figure S2, the regeneration of **1-Cl** depended on the amount of Bu_4NCl. When the solution of **2-$(ICl_2)_2$** was treated with 5 equivalents of Bu_4NCl for 3 hours at room temperature, the conversion to **1-Cl** was completely achieved.

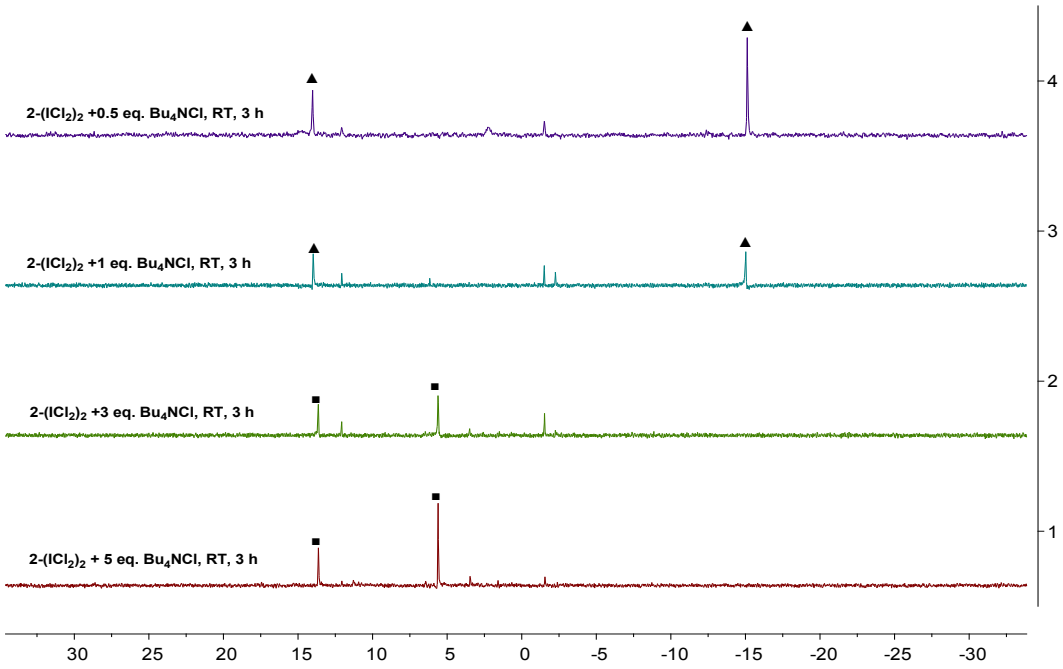


Figure S2. Reactions of complex **2-$(ICl_2)_2$** with different equivalents of Bu_4NCl for 3 hours at room temperature. The symbol ▲ and ■ were used to label the characteristic signals of **2-$(ICl_2)_2$** and **1-Cl** respectively.

Reactions of complex 2-$(ICl_2)_2$ with Bu_4NCl and Bu_4NI:

2-$(ICl_2)_2$ (16.8 mg, 0.01 mmol) with Bu_4NCl (13.9 mg, 0.05 mmol), or Bu_4NI (18.5 mg, 0.05 mmol) were reacted for 3 hours in CD_2Cl_2 (0.5 mL) respectively. As shown in Figure S3, other ions such as I^- can also facilitate the transformation to **1**.

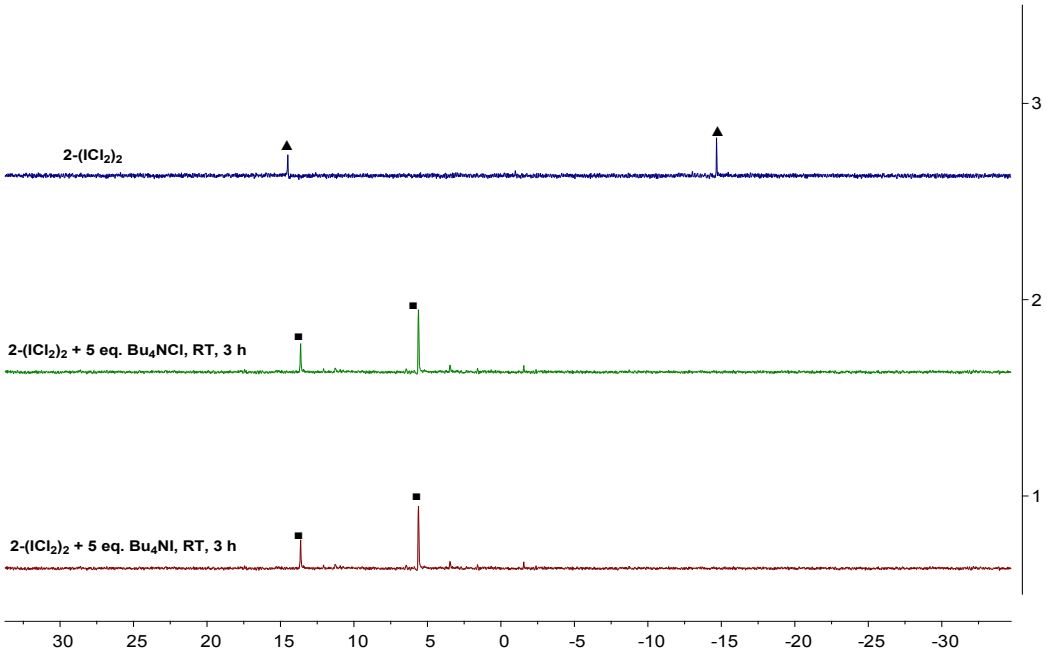


Figure S3. Reactions of complex **2-$(ICl_2)_2$** with Bu_4NCl and Bu_4NI for 3 hours at room temperature respectively. The symbol ▲ and ■ were used to label the characteristic signals of **2-$(ICl_2)_2$** and **1-Cl** respectively.

Reactions of complex 2-$(ICl_2)_2$ with different lewis bases:

2-$(ICl_2)_2$ (16.8 mg, 0.01 mmol) with Bu_4NCl (13.9 mg, 0.05 mmol), NaCl (2.9 mg, 0.05 mmol), or NaSCN (4.0 mg, 0.05 mmol) were reacted for 3 hours in CD_2Cl_2 (0.5 mL) respectively. As shown in Figure S4, other lewis bases such as NaSCN can also facilitate the transformation to **1**. However, NaCl is not feasible due to its poor solubility in CD_2Cl_2.

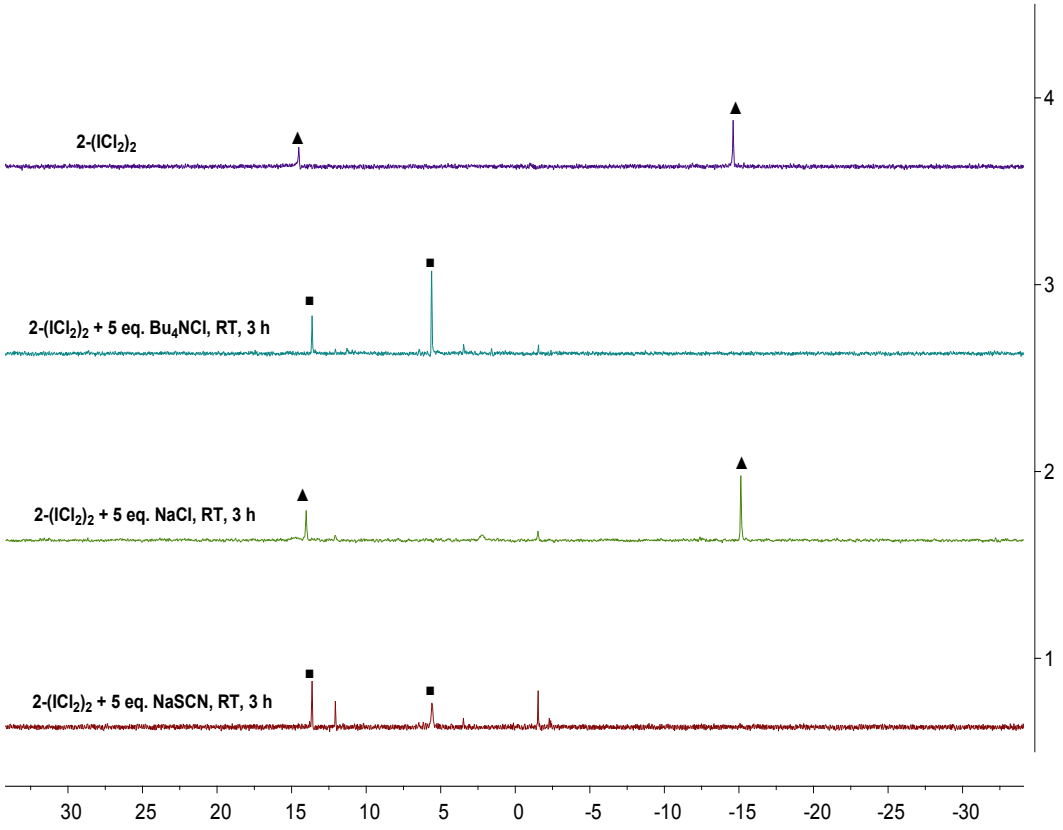


Figure S4. Reactions of complex **2-$(ICl_2)_2$** with different lewis bases. The symbol ▲ and ■ were used to label the characteristic signals of **2-$(ICl_2)_2$** and **1-Cl** respectively.

2. Thermal decomposition test

Table 1. Thermal decomposition data of **2-$(ICl_2)_2$** and **3-$(Br_3)_2$** in solid state[a].

	RT	50 °C	70 °C	100 °C	120 °C	130 °C
2-$(ICl_2)_2$	●[b]	●[c]	■	–	–	–
3-$(Br_3)_2$	●	●	●	●	●	■

Table 2.Thermal decomposition data of **2-$(ICl_2)_2$** and **3-$(Br_3)_2$** in solution[a].

	RT	50 °C
2-$(ICl_2)_2$	■	–
3-$(Br_3)_2$	●	■

[a] All reactions were carried out for 3 hours. [b] ● = Stable. [c] ■ = Partly decomposed.

3. X-ray Crystallographic Analysis

Crystals suitable for x-ray diffraction were grown from dichloromethane (**2-$(ICl_2)_2$**) or chloroform (**3-$(Br_3)_2$**) solutions layered with hexane. Single-crystal X-ray diffraction data were collected on a Rigaku R-AXIS SPIDER IP CCD area detector using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Semi-empirical or multi-scan absorption corrections (SADABS) were applied.[2] All structures were solved by the Patterson function, completed by subsequent difference Fourier map calculations, and refined by full matrix least-squares on F^2 using the SHELXTL program package.[3] All non-hydrogen atoms were refined anisotropically unless otherwise stated. Hydrogen atoms were placed at idealized positions and assumed the riding model. X-ray crystal structures have been deposited in the Cambridge Crystallographic Database under the deposition numbers CCDC 1051920 (**2-$(ICl_2)_2$**) and CCDC 1415345 (**3-$(Br_3)_2$**). The data can be obtained free of charge from the CCDC (www.ccdc.cam.ac.uk/data_request/cif).

Crystal data for 2-$(ICl_2)_2$:

$[C_{63}H_{51}ClIO_2OsP_3]2ICl_2 \cdot 1.5CH_2Cl_2$, M_r = 1808.48, crystal dimension 0.25 × 0.24 × 0.16 mm, Monoclinic, space group $P2_1/c$, a = 12.9311(5) Å, b = 22.2426(7) Å, c = 23.2785(8) Å, α = 90°, β = 102.771(4)°, γ = 90°, V = 6529.8(4) Å^3, Z = 4, T = 143(2) K, $\lambda(Mo_{K\alpha})$ = 0.71073 Å, ρ_{calcd} = 1.840 g·cm^{-3}, $\mu(Mo_{K\alpha})$ = 3.815 mm^{-1}, $F(000)$ = 3492.0, θ_{max} = 25.00°, 27557 reflections, 11489 independent (R_{int} = 0.0286), 809 parameters, R_1 = 0.0518, wR_2 = 0.1074 for all data (R_1 = 0.0419 and wR_2 = 0.1031 for 9876 reflections with I > 2σ(I)). GOF = 1.067. Residual electron density (e. Å^{-3})

max/min: 2.55/−1.39.

Crystal data for 3-$(Br_3)_2$:

$[C_{63}H_{51}Br_2O_2OsP_3]1.75Br_3$ 0.25Br $0.25Br_2 \cdot CH_2Cl_2$, M_r = 1847.31, crystal dimension 0.20 × 0.15 × 0.10 mm, Monoclinic, space group $P\ 2_1/c$, a = 13.0217(3) Å, b = 22.2992(5) Å, c = 23.1406(5) Å, α = 90°, β = 102.857(2), γ = 90°, V = 6551.0(3) $Å^3$, Z = 4, T = 123(2) K, $\lambda(Mo_{K\alpha})$ = 0.71073 Å, ρ_{calcd} = 1.873 $g \cdot cm^{-3}$, $\mu(Mo_{K\alpha})$ = 6.760 mm^{-1}, $F(000)$ = 3552.0, θ_{max} = 25.00°, 28371 reflections, 11541 independent (R_{int} = 0.0581), 808 parameters, R_1 = 0.0937, wR_2 = 0.1669 for all data (R_1 = 0.0670 and wR_2 = 0.1555 for 8788 reflections with I > 2σ(I)). GOF = 1.062. Residual electron density (e. $Å^{-3}$) max/min: 2.08/−1.87.

4. Computational calculations

All the calculations were performed with the Gaussian 09 software package.[4] Input geometry of the complex **2-$(ICl_2)_2$** and **3-$(Br_3)_2$** were taken from the X-ray coordinates. Single point energy calculation and natural bond orbital (NBO)[5] analysis was performed at the B3LYP/6-311++G** level.[6] In the B3LYP calculations, the effective core potentials (ECPs) of Hay and Wadt with a double−ζ valence basis set (LanL2DZ) were used to describe Os, P, I, Cl and Br atom, whereas the standard 6-311++G** basis set was used for C, O, and H.[7] Polarization functions were added for Os (ζ(f) = 0.886), Cl (ζ(d) = 0.514), I (ζ(d) = 0.226), Br (ζ(d) = 0.389) and P (ζ(d) = 0.340).[8]

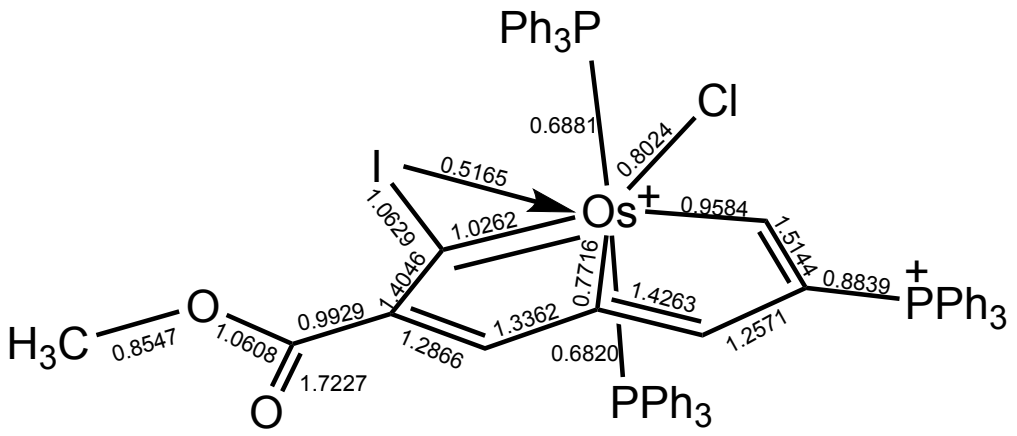


Figure S5. Calculated Wiberg bond indices for the complex **2**.

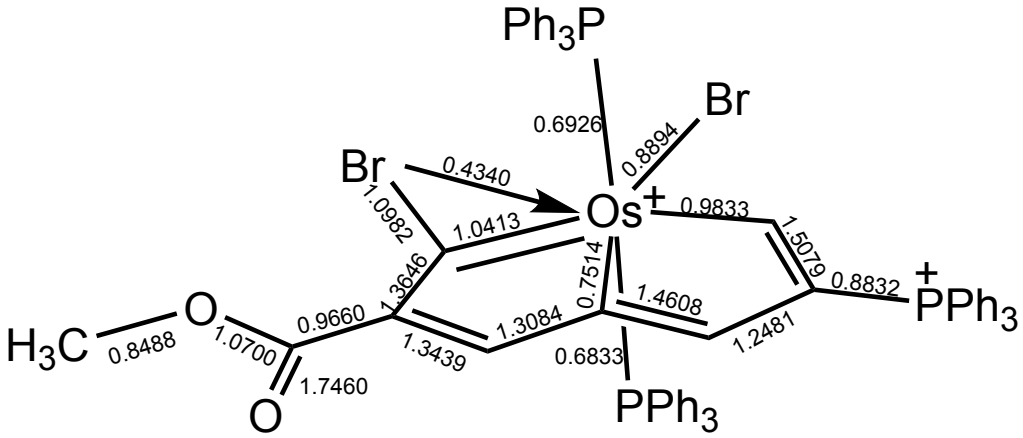


Figure S6. Calculated Wiberg bond indices for the complex **3**.

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