

Reactions of osmium carbyne complexes $\text{OsCl}_3(\equiv\text{CR})(\text{PPh}_3)_2$ ($\text{R} = \text{CH}=\text{CPh}_2, \text{CH}_2\text{Ar}$) with bromine and hydrogen peroxide

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Supporting Information

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The supplemental file “Os carbyne-SI computation.xyz” contains the computed Cartesian coordinates of all of the molecules reported in this study. The file may be opened as a text file to read the coordinates, or opened directly by a molecular modeling program such as Mercury for visualization and analysis.

1. X-ray crystallographic studies of 10, 11 and 13.

Table S1. Crystal data of **10**, **11** and **13**.

	Complex 10	Complex 11	Complex 13
Empirical formula	C ₃₃ H ₂₈ Br ₃ O ₆ OsP	C _{56.25} H _{51.25} Cl ₄ O _{0.75} OsP ₂	C ₄₈ H ₄₅ Cl ₃ O ₂ OsP ₂
Formula weight	901.45	1133.16	1012.33
Temperature/K	100.01(10)	100.00(10)	173
Crystal system	monoclinic	monoclinic	monoclinic
Space group	P2 ₁ /c	P2 ₁ /n	P2 ₁ /c
a/Å	9.8517(2)	12.91509(14)	10.36250(10)
b/Å	10.3571(2)	17.98521(19)	18.2899(2)
c/Å	29.9335(7)	20.77311(19)	22.6189(3)
α/°	90	90	90
β/°	98.040(2)	91.5799(8)	94.7520(10)
γ/°	90	90	90
Volume/Å ³	3024.25(12)	4823.36(9)	4272.20(8)
Z	4	4	4
ρ _{calc} g/cm ³	1.980	1.560	1.574
μ/mm ⁻¹	13.302	2.972	8.373
F(000)	1720.0	2275.0	2024.0
Crystal size/mm ³	0.1 × 0.07 × 0.05	0.32 × 0.25 × 0.15	0.2 × 0.15 × 0.12
Radiation	CuKα (λ = 1.54184)	MoKα (λ = 0.71073)	CuKα (λ = 1.54178)
2Θ range for data collection/°	9.044 to 133.934	6.756 to 51.994	20.222 to 133.994
Index ranges	-8 ≤ h ≤ 11, -12 ≤ k ≤ 12, -35 ≤ l ≤ 33	-15 ≤ h ≤ 14, -21 ≤ k ≤ 22, -22 ≤ l ≤ 25	-12 ≤ h ≤ 12, -21 ≤ k ≤ 16, -26 ≤ l ≤ 27
Reflections collected	16246	28793	36057
Independent reflections	5363 [R _{int} = 0.0406]	9417 [R _{int} = 0.0197]	7513 [R _{int} = 0.0431]
Data/restraints/parameters	5363/0/353	9417/14/583	7513/10/500
Goodness-of-fit on F ²	1.002	1.000	1.003

2. NMR spectra

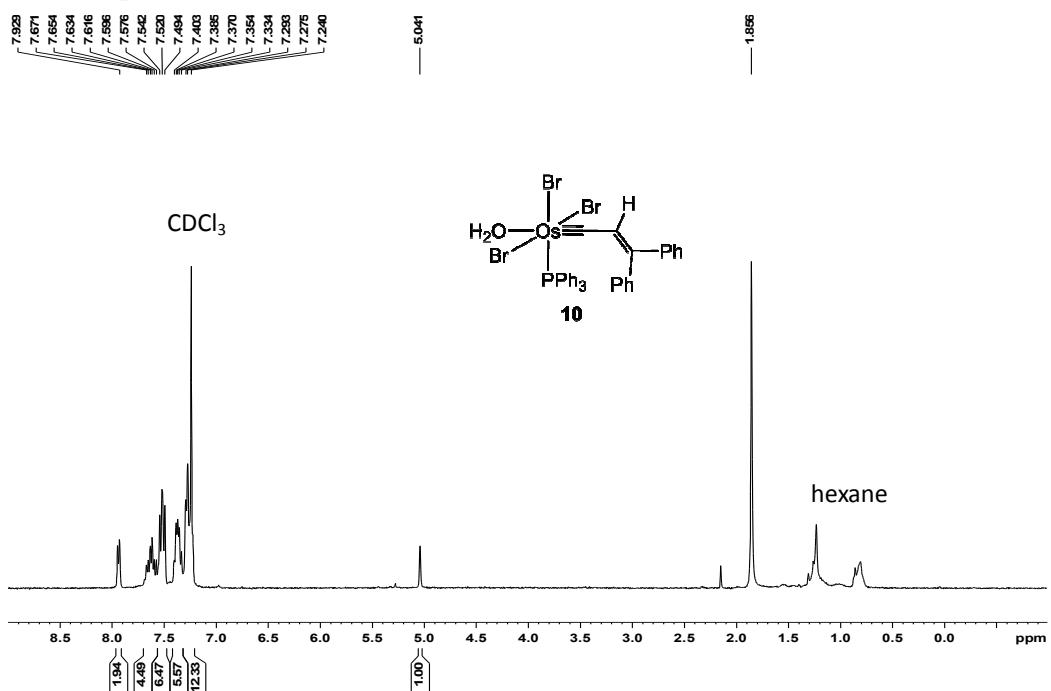


Figure S1. The ^1H NMR spectrum of OsBr₃(≡CCH=CPh₂)(H₂O)(PPh₃) (**10**) in CDCl₃ at 400.1 MHz.

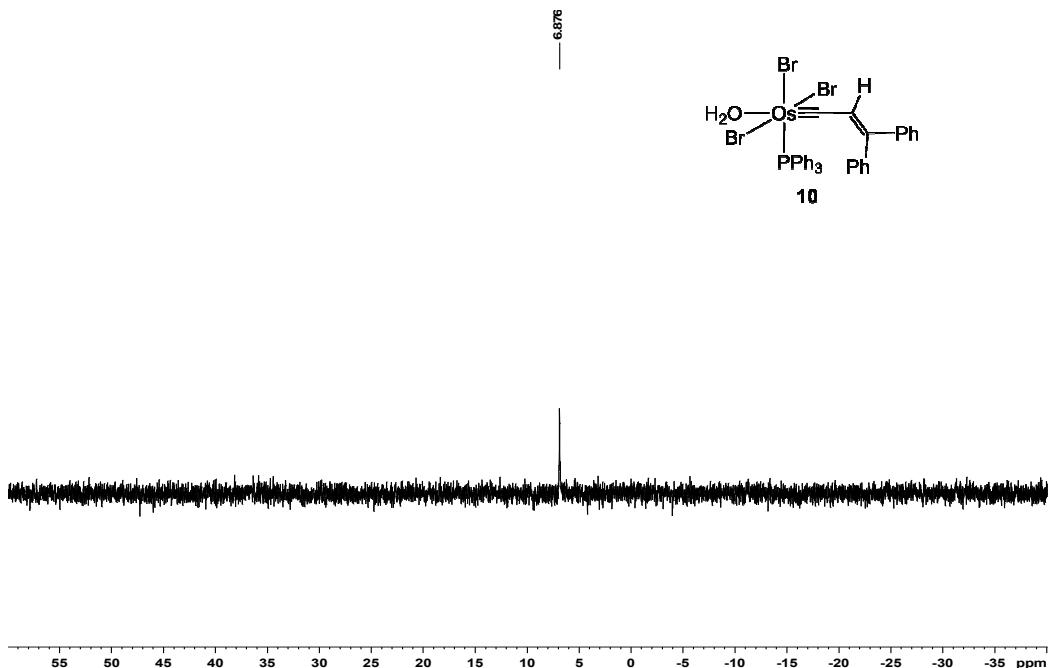


Figure S2. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of OsBr₃(≡CCH=CPh₂)(H₂O)(PPh₃) (**10**) in CDCl₃ at 162.0 MHz.

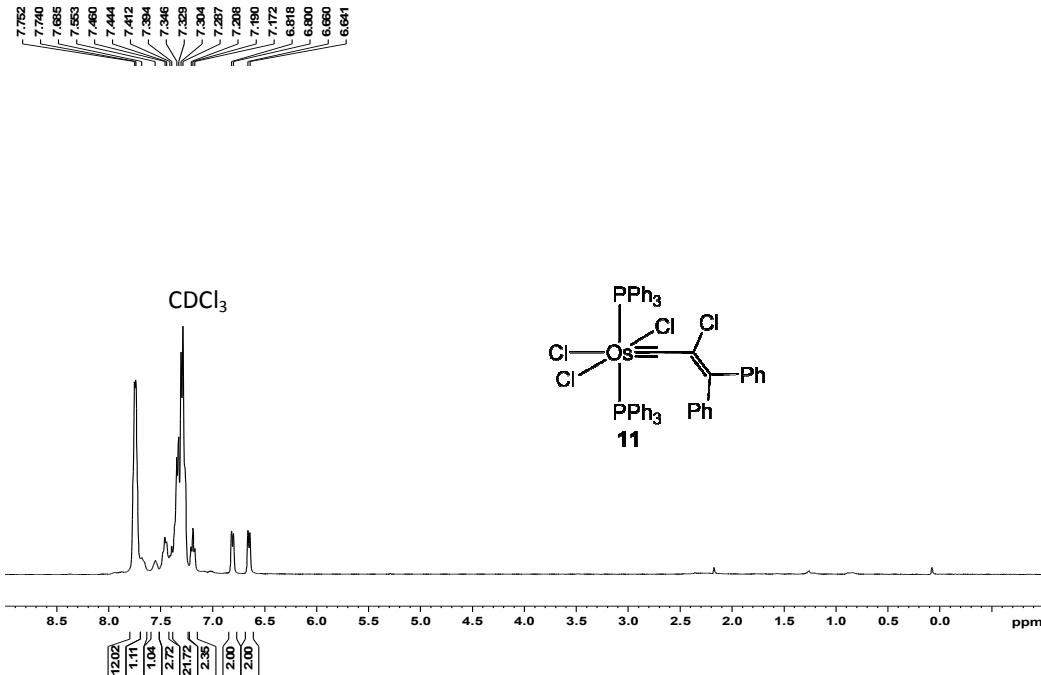


Figure S3. The ^1H NMR spectrum of $\text{OsCl}_3(\equiv\text{CCl}=\text{CPh}_2)(\text{PPh}_3)_2$ (**11**) in CDCl_3 at 400.1 MHz.

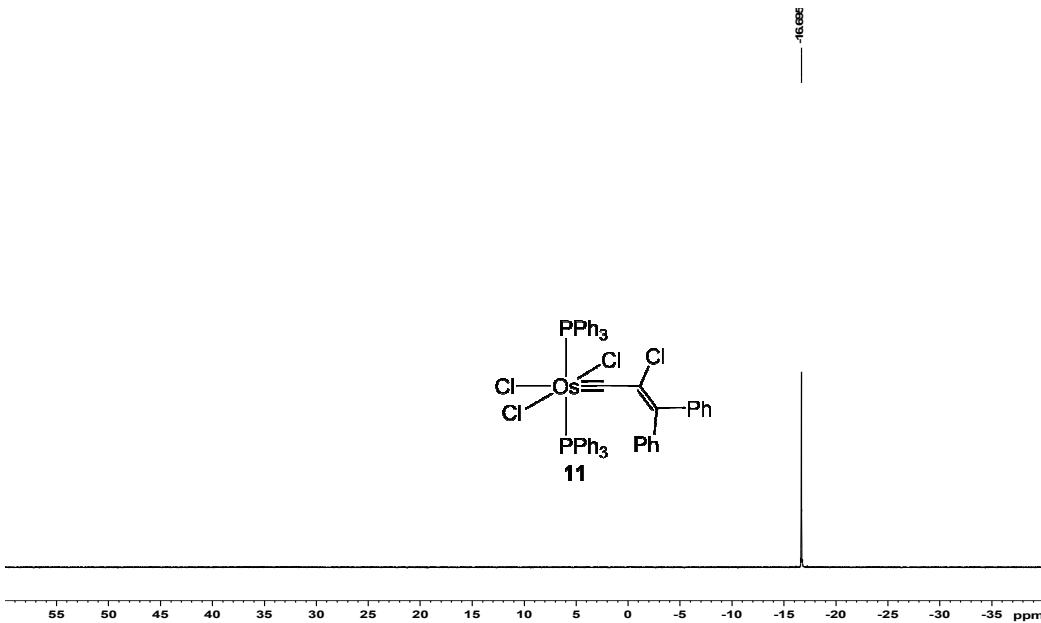


Figure S4. The $^{31}\text{P}\{\text{H}\}$ NMR spectrum of $\text{OsCl}_3(\equiv\text{CCl}=\text{CPh}_2)(\text{PPh}_3)_2$ (**11**) in CDCl_3 at 162.0 MHz.

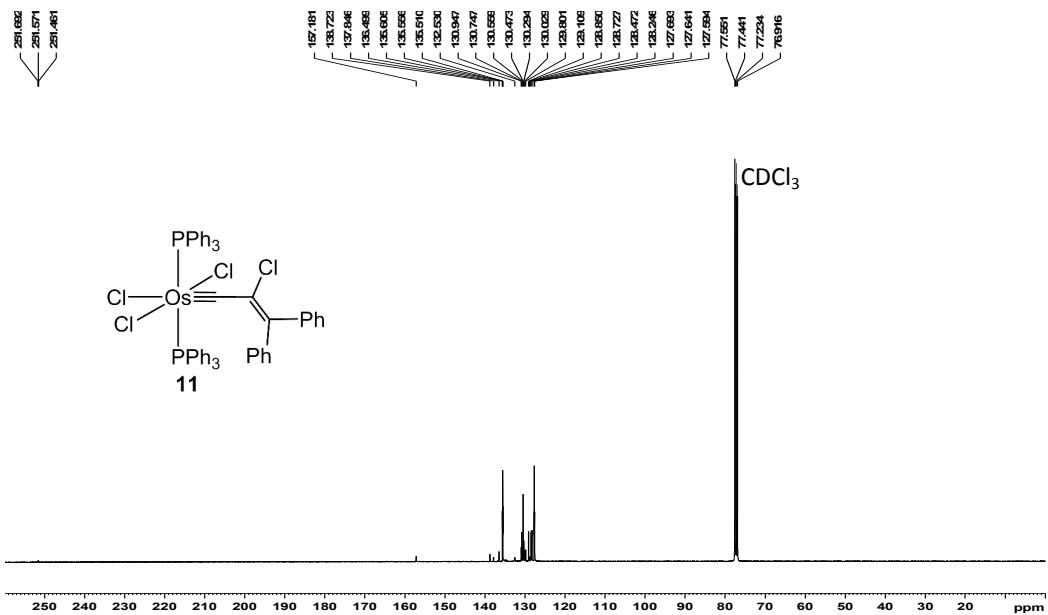


Figure S5. The $^{13}\text{C}\{\text{H}\}$ NMR spectrum of $\text{OsCl}_3(\equiv\text{CCl}=\text{CPh}_2)(\text{PPh}_3)_2$ (**11**) in CDCl_3 at 100.6 MHz.

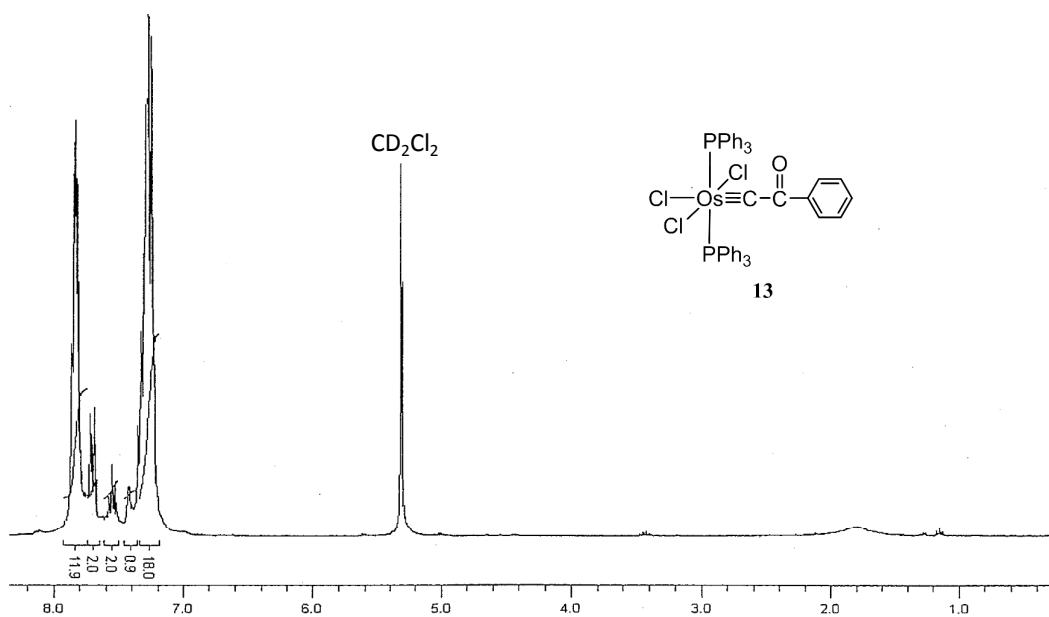


Figure S6. The ^1H NMR spectrum of *mer*- $\text{OsCl}_3(\equiv\text{CC(O)Ph})(\text{PPh}_3)_2$ (**13**) in CD_2Cl_2 at 300.1 MHz.

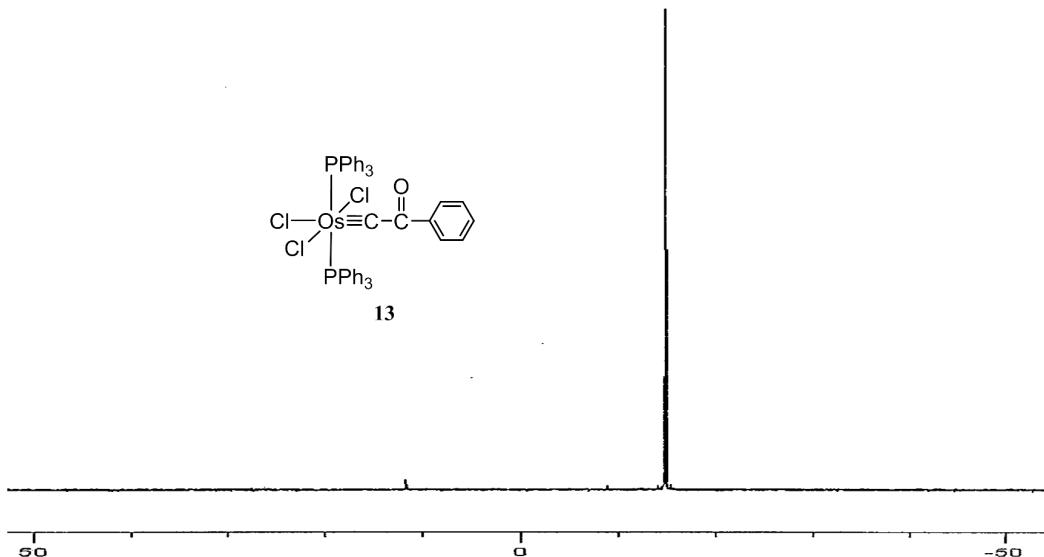


Figure S7. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of *mer*- $\text{OsCl}_3\{\equiv\text{CC}(\text{O})\text{Ph}\}(\text{PPh}_3)_2$ (**13**) in CD_2Cl_2 at 121.5 MHz.

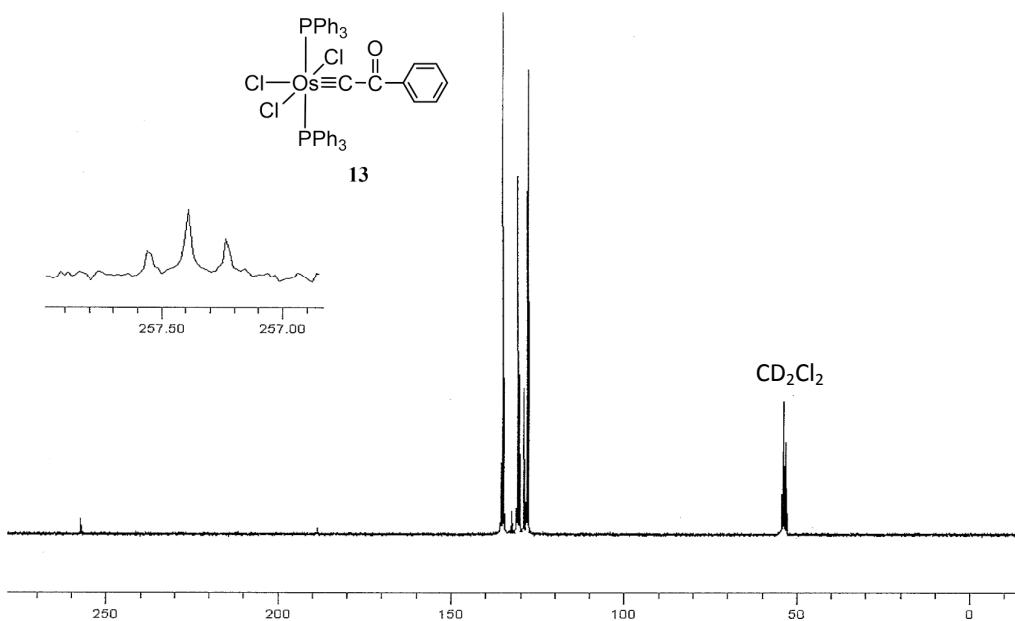


Figure S8. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of *mer*- $\text{OsCl}_3\{\equiv\text{CC}(\text{O})\text{Ph}\}(\text{PPh}_3)_2$ (**13**) in CD_2Cl_2 at 75.5 MHz.

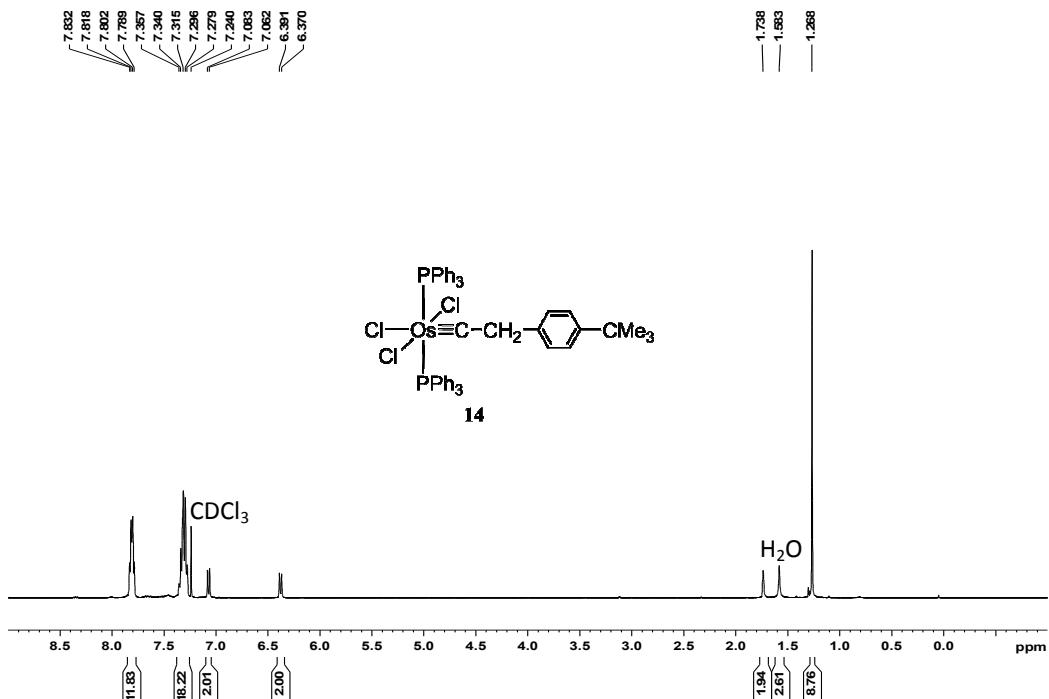


Figure S9. The ^1H NMR spectrum of *mer*- $\text{OsCl}_3(\equiv\text{CCH}_2\text{-C}_6\text{H}_4\text{-}p\text{-CMe}_3)(\text{PPh}_3)_2$ (**14**) in CDCl_3 at 400.1 MHz.

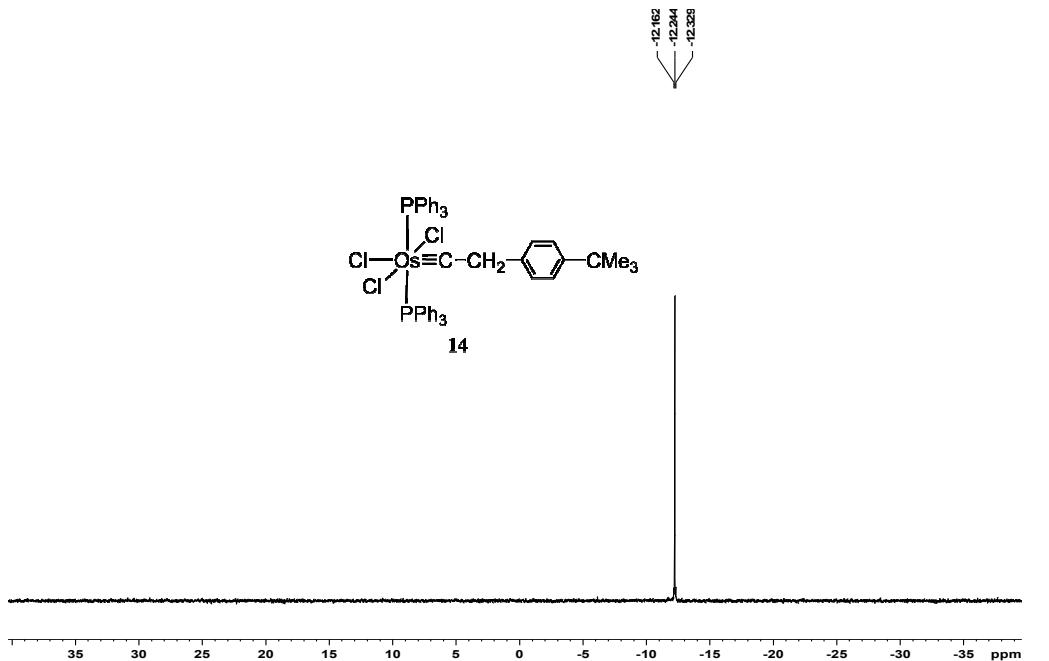


Figure S10. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of *mer*- $\text{OsCl}_3(\equiv\text{CCH}_2\text{-C}_6\text{H}_4\text{-}p\text{-CMe}_3)(\text{PPh}_3)_2$ (**14**) in CDCl_3 at 162.0 MHz.

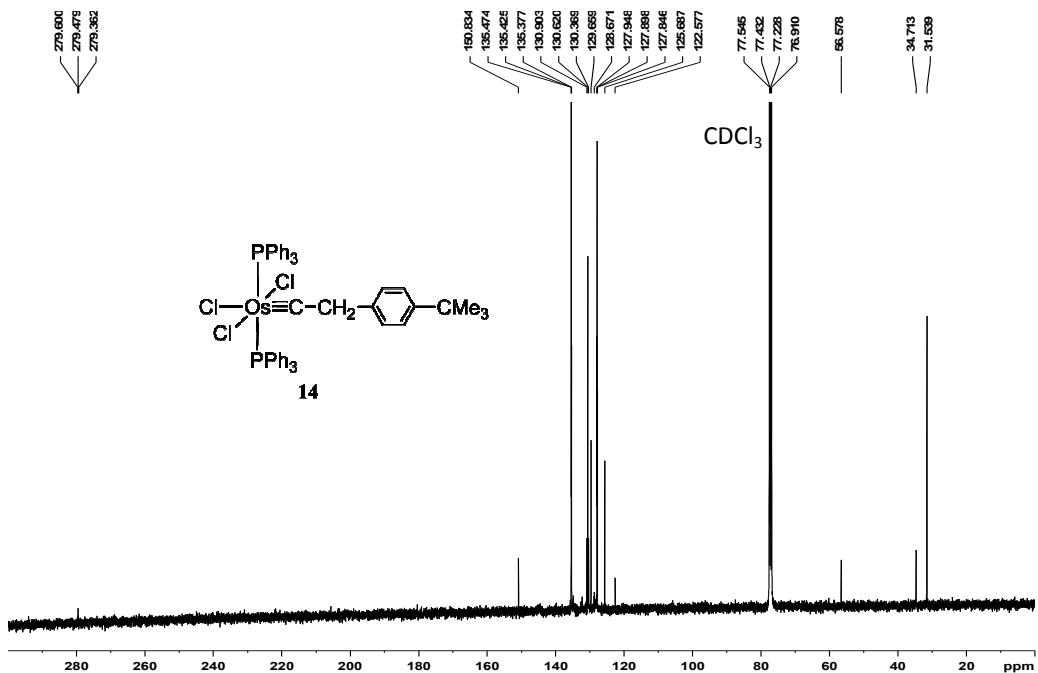


Figure S11. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of *mer*- $\text{OsCl}_3(\equiv\text{CCH}_2\text{-C}_6\text{H}_4\text{-}p\text{-CMe}_3)(\text{PPh}_3)_2$ (**14**) in CDCl_3 at 100.6 MHz.

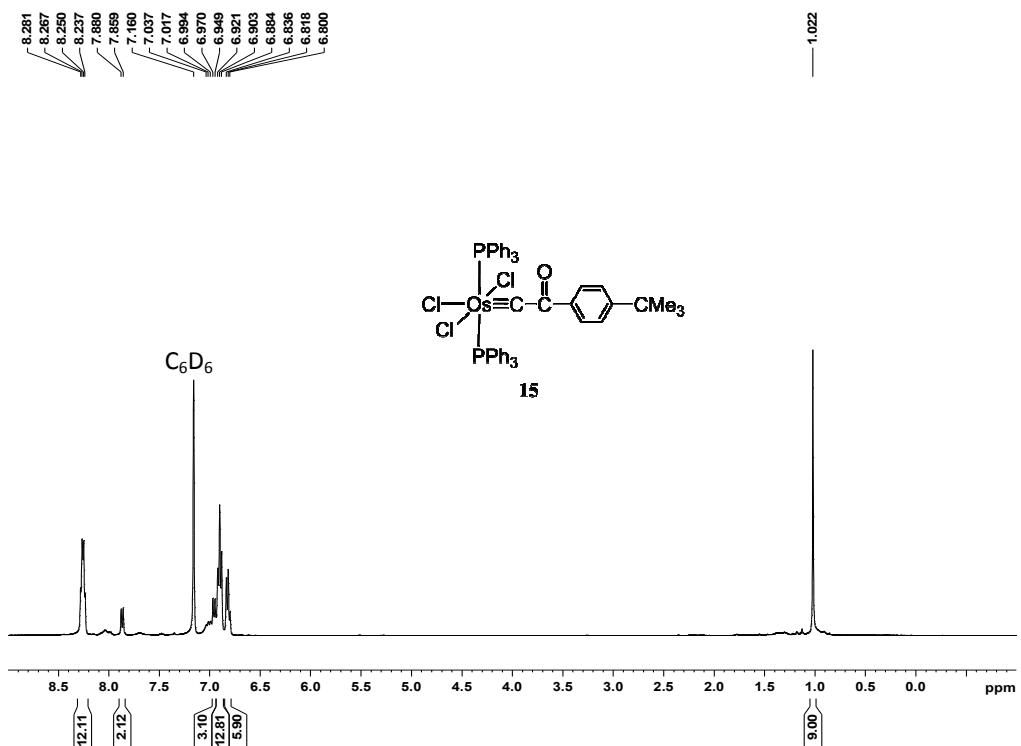


Figure S12. The ^1H NMR spectrum of *mer*- $\text{OsCl}_3\{\equiv\text{CC(O)}\text{-C}_6\text{H}_4\text{-}p\text{-CMe}_3\}(\text{PPh}_3)_2$ (**15**) in C_6D_6 at 400.1 MHz.

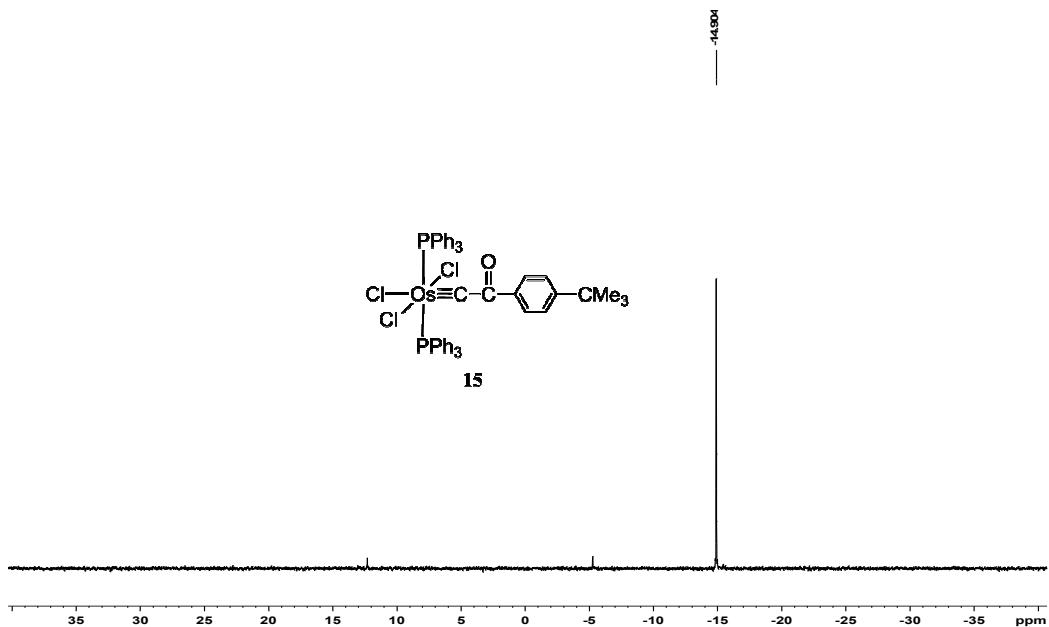


Figure S13. The $^{31}\text{P}\{\text{H}\}$ NMR spectrum of *mer*- $\text{OsCl}_3\{\equiv\text{CC(O)-C}_6\text{H}_4\text{-}p\text{-CMe}_3\}(\text{PPh}_3)_2$ (**15**) in C_6D_6 at 162.0 MHz.

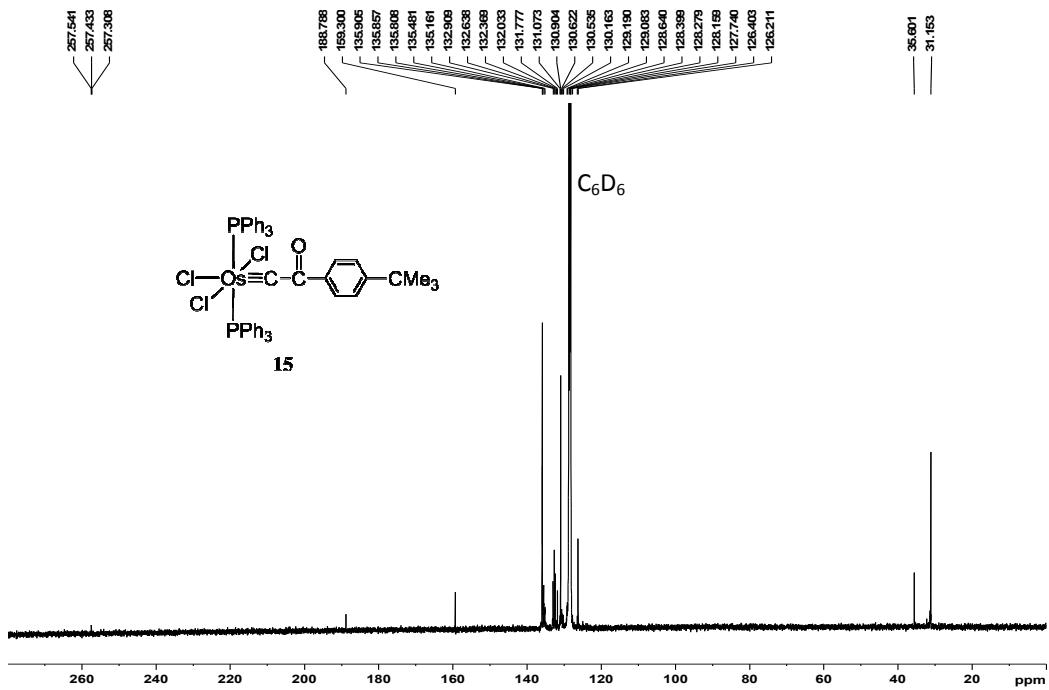


Figure S14. The $^{13}\text{C}\{\text{H}\}$ NMR spectrum of *mer*- $\text{OsCl}_3\{\equiv\text{CC(O)-C}_6\text{H}_4\text{-}p\text{-CMe}_3\}(\text{PPh}_3)_2$ (**15**) in C_6D_6 at 100.6 MHz.