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Double activation of the diphosphinite pincer proligand by a triosmium carbonyl cluster

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Materials and methods

All manipulations on the synthesis of ligand and clusters were conducted under an argon atmosphere using standard Schlenk techniques. The resulting compounds **1** and **2** are air-stable and their purification does not require an inert atmosphere. All the solvents were distilled under an argon atmosphere from the appropriate drying agents. Commercially available reagents were used as received. NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer. ^{1}H and $^{13}C\{^{1}H\}$ NMR chemical shifts are reported in parts per million downfield from tetramethylsilane; the residual signals of deuterated solvents were used as references (7.25 ppm for $CDCl_3$, 5.32 ppm for CD_2Cl_2,). $^{31}P\{^{1}H\}$ NMR spectra-relative to the external 85% H_3PO_4. In $^{13}C\{^{1}H\}$ NMR measurements the signal of CD_2Cl_2 (53.7 ppm) was used as a reference. FTIR spectra were recorded on a Nicolet Magna-IR 750 Fourier spectrometer.

$Os_3(CO)_{12}$ was obtained by carbonylation of OsO_4 at high pressure, from which the labile cluster 1,2-$Os_3(CO)_{10}(MeCN)_2$ was synthesized. The pincer ligand, 1,3-bis(diphenylphosphinito)benzene was obtained by reacting a suspension of 75 mg (0.682 mmol) of resorcinol in 30 ml of toluene with 0.5 ml of triethylamine and 0.25 ml (1.39 mmol) of diphenyl chlorophosphine at 80°C for 8 h. The reaction mixture was filtered, the filtrate was evaporated, resulting in a product in the form of a yellowish oil sensitive to air and moisture. The product was used in the next stage without additional purification.

Synthesis of cluster 1

All amounts of 1,3-bis(diphenylphosphinito)benzene obtained at the previous stage was dissolved in 30 ml of methylene chloride and transferred through a cannula to a solution of 510 mg (0.547 mmol) $Os_3(CO)_{10}(MeCN)_2$ in 100 ml of methylene chloride and stirred for 16 h. The color of the solution gradually changed from yellow to red-orange. The reaction mixture was evaporated to dryness, the rest was chromatographed on a column with silica gel, and the methylene-hexane chloride was washed with a mixture of 1 : 10 (vol.), collected the orange

fraction. After evaporation of the solvent, the product was recrystallized from the methylene chloride–hexane, and 450 mg of cluster **2** was obtained in the form of an orange fine-crystalline powder. Yield 62% based on $Os_3(CO)_{10}(MeCN)_2$.

Synthesis of cluster 2

100 mg (0.075 mmol) of cluster **1** was suspended in 10 ml of toluene and boiled for 40 h. The reaction mixture was evaporated to dryness, the rest was chromatographed on a column with silica gel, and the mixture was washed with methylene chloride–hexane 1 : 2 (vol.), collected the yellow fraction. After evaporation of the solvent, the product was recrystallized from the methylene chloride–hexane and dried *in vacuo* for 2 h at 50 ºC. 61 mg (65%) of cluster **2** was obtained as a yellow fine-crystalline powder.

Cluster **1:** Yield 62%; IR (ν_{CO}) (CH_2Cl_2): 2091s, 2030s, 2009vs, 1976w, 1961w см$^{-1}$. ^{1}H NMR (CD_2Cl_2, 400.13 MHz), δ: 6.753 dd (2H, J_{HH} = 8.01 Hz, J_{PH} = 2.06 Hz), 7.135 br.s (1H). 7.154 t (1H, J_{HH} = 8.01 Hz), 7.48 m (12H), 7.69 m (8H, Ph). ^{31}P{^{1}H} (CD_2Cl_2, 161.98 MHz), δ: 97.08. ^{13}C{^{1}H} (CD_2Cl_2, 100.51 MHz), δ: 115.65d (J_{CP} = 4.5 Hz), 120.55d (J_{CP} = 12.0 Hz), 128.53s, 128.61 s, 130.41 s, 130.49 s, 130.56 s, 131.25 s, 138.62 s, 139.03 s, 151.10 d (J_{CP} = 4.0 Hz), 172.90 s (CO), 182.16 s (CO).

Cluster **2:** Yield 65%, IR (ν_{CO}) (CH_2Cl_2): 2065 s, 2009 vs, 1989 s, 1977 s, 1953 s, 1947 s, 1931 s cm^{-1}. ^{1}H NMR (CD_2Cl_2, 400.13 MHz), δ: -9.331 dd (J_{PH} =18.82 Hz, J_{PH} = 21.89 Hz), 4.925 d (1H, J_{HH} = 8.56 Hz), 6.247 d (1H, J_{HH} = 7.09 Hz), 7.128 t (1H, J_{HH} = 7.95 Hz). ^{31}P{^{1}H} (CD_2Cl_2 161.98 MHz), δ: 103.32, 214.95. ^{13}C{^{1}H} (CD_2Cl_2, 100.51 MHz) δ: 30.98s, 53.46s, 78.79s, 100.87d (J_{PH} =11 Hz), 119.31s (C_6H_3), 127.8 -133.4, 136.6 -139.2 (C_6H_5), 172.33d (J_{PH} = 2 Hz), 177.33d (J_{PH} = 9 Hz), 181.57d (J_{PH} = 6 Hz), 182.63d (J_{PH} = 4 Hz), 189.51d (J_{PH} = 2 Hz), 204.55s, 207.08s (CO). Found (%): C, 35.66; H, 1.81.Calc.for $C_{38}H_{24}O_{10}P_2Os_3$ (%): C, 35.85; H, 1.90%.

NMR spectra

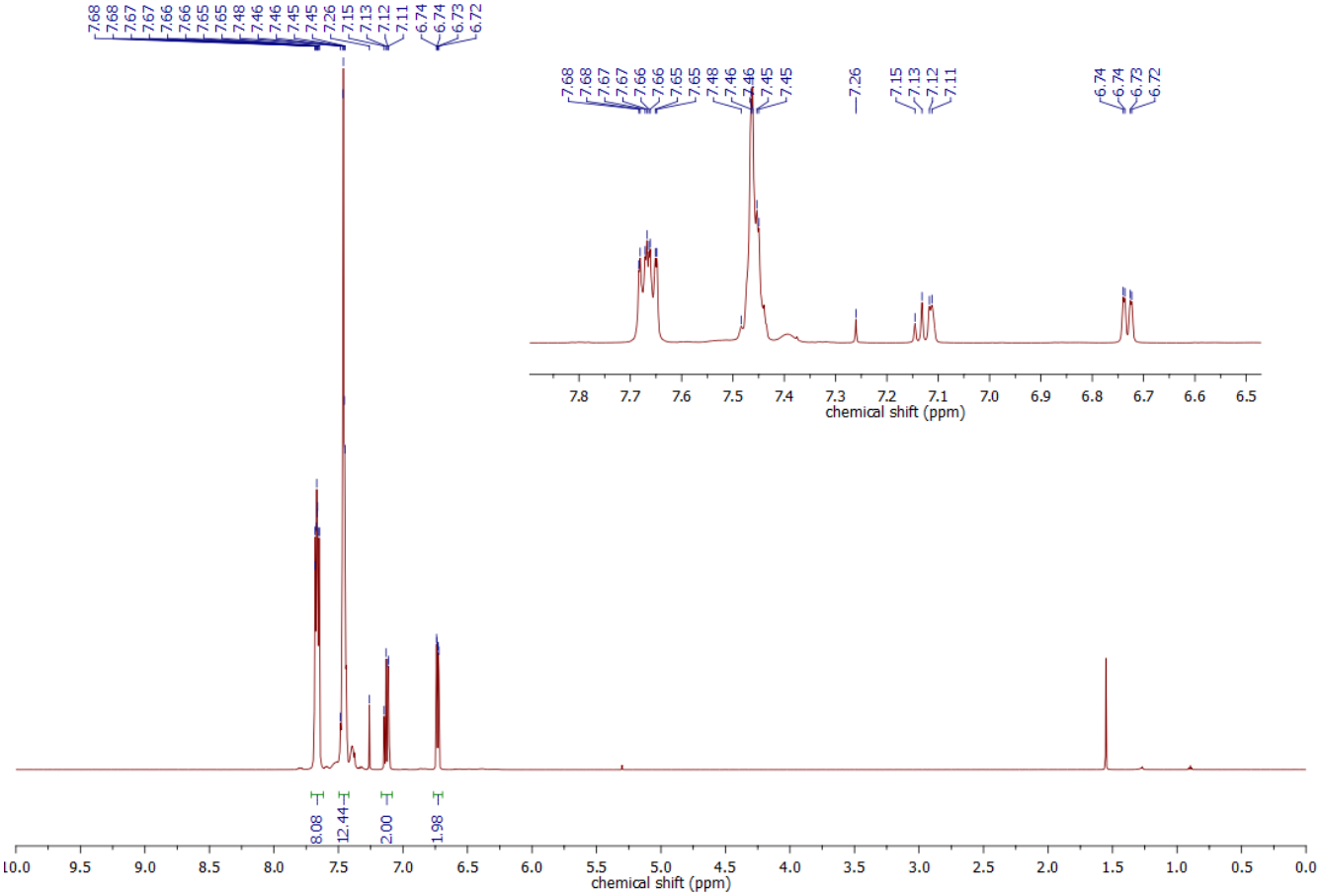

Figure S1 ^{1}H NMR spectrum of **1** (400.1 MHz, $CDCl_3$).

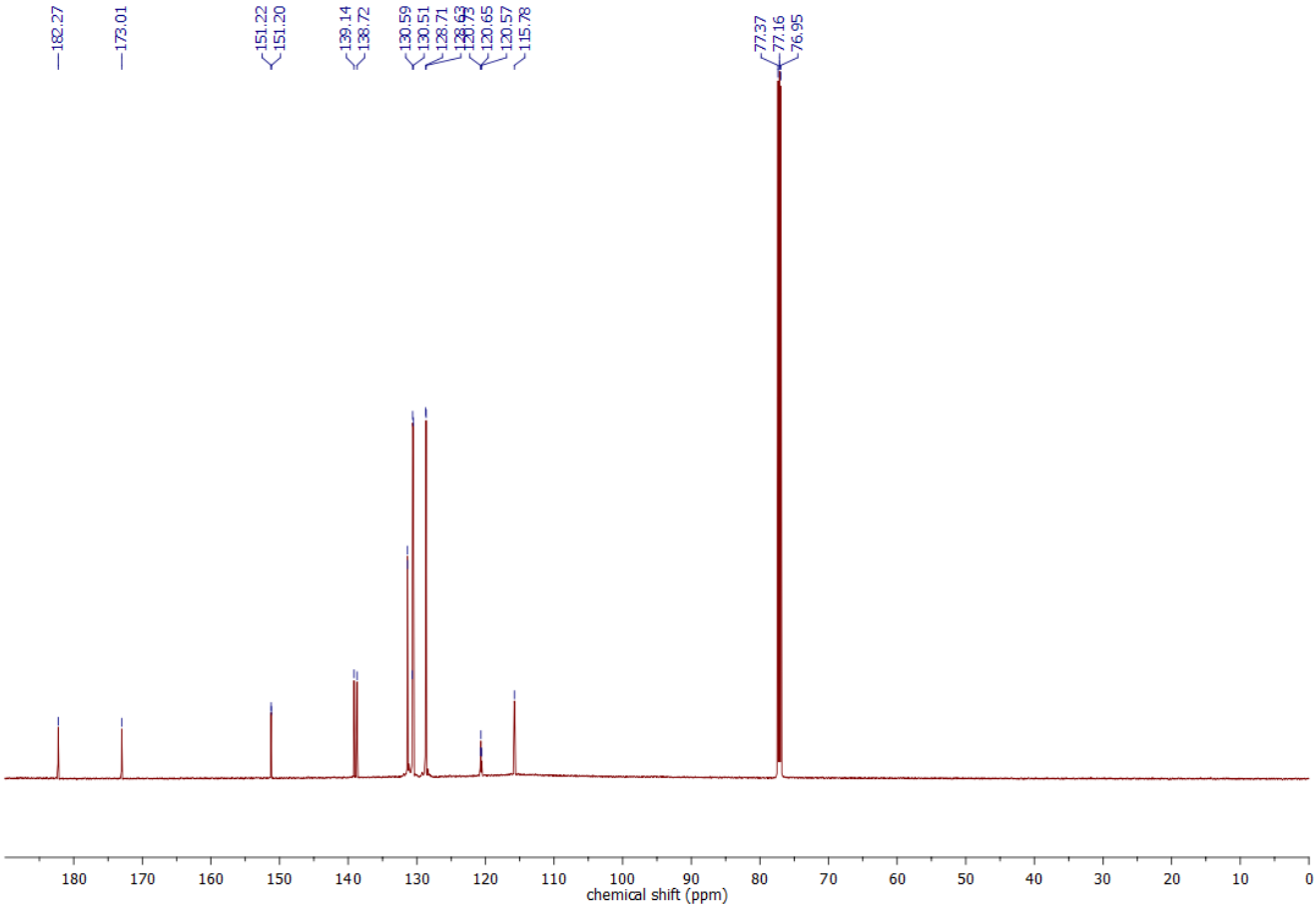

Figure S2 $^{13}C\{^{1}H\}$ NMR spectrum of **1** (162 MHz, $CDCl_3$).

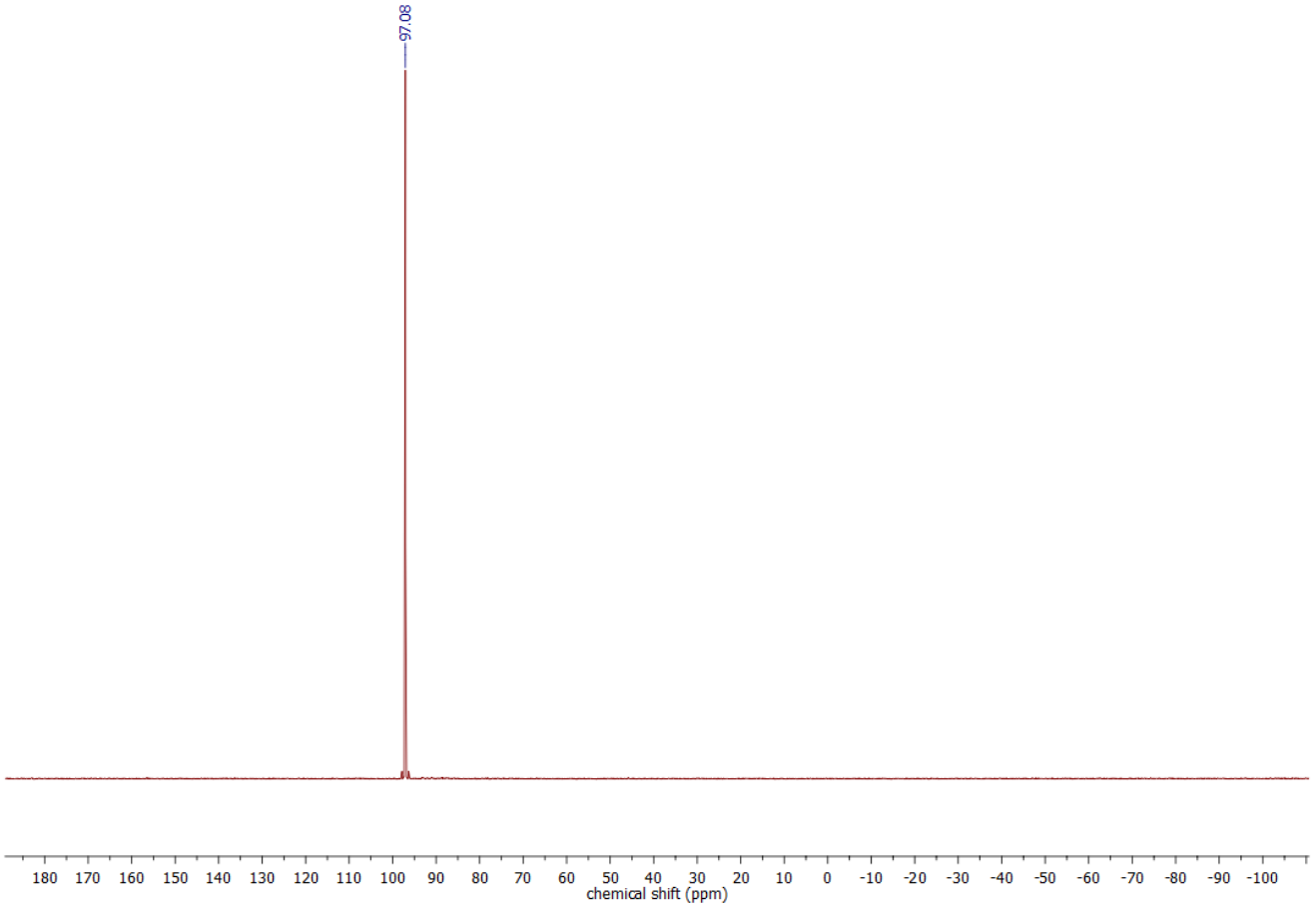

Figure S3 $^{31}P\{^{1}H\}$ NMR spectrum of **1** (100.6 MHz, $CDCl_3$).

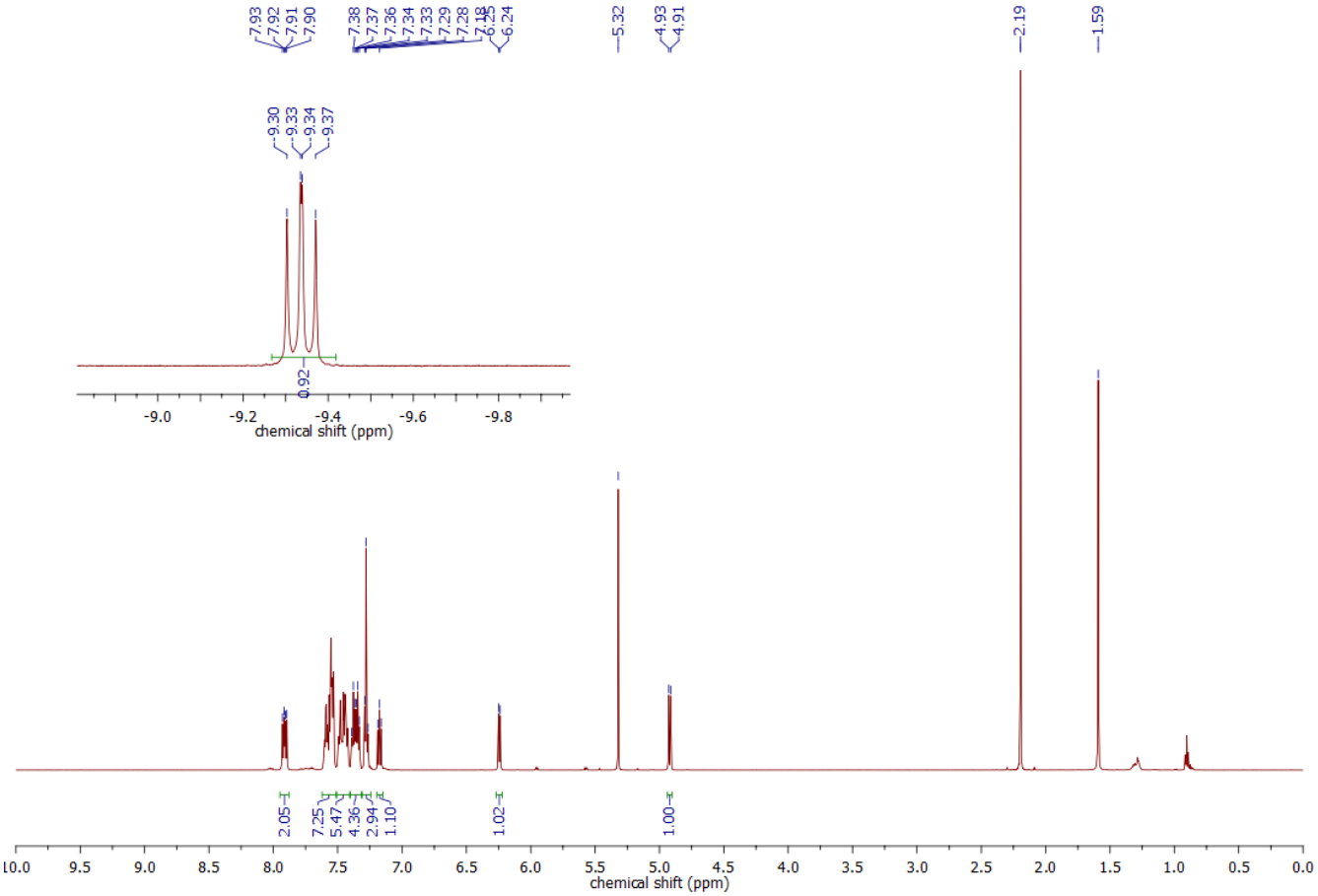

Figure S4 ^{1}H NMR spectrum of **2** (400.1 MHz, CD_2Cl_2).

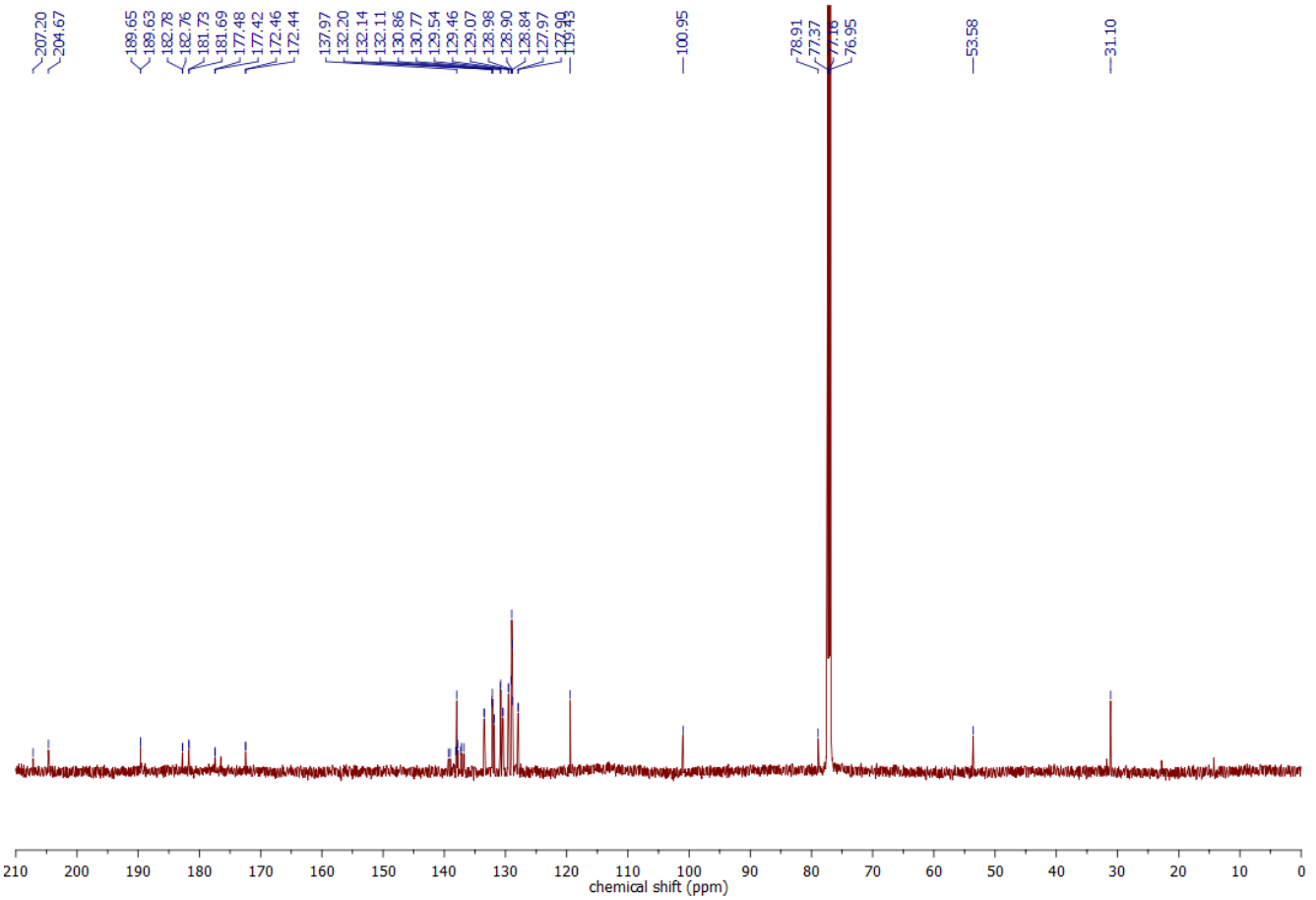

Figure S5 ^{13}C{^{1}H} NMR spectrum of **2** (162 MHz, $CDCl_3$).

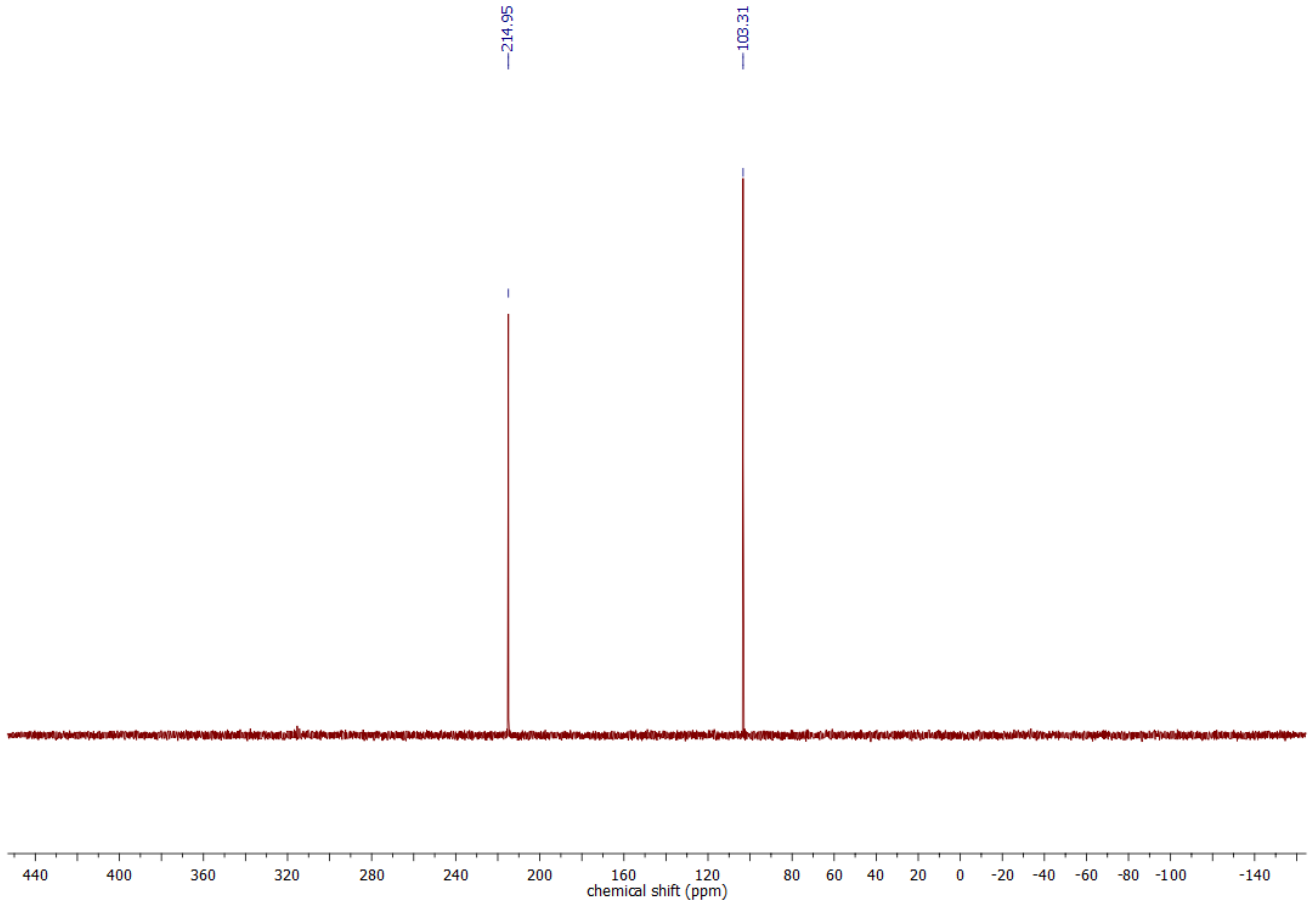

Figure S6 $^{31}P\{^{1}H\}$ NMR spectrum of **2** (100.6 MHz, CD_2Cl_2).

X-ray data

Table S1 Selected bond distances (Å) and angles (deg.)

	Cluster **1**		Cluster **2**
Os(1)-Os(2)	2.9879(5)		2.9573(2)
Os(1)-Os(3)	2.8883(5)		2.8601(2)
Os(2)-Os(3)	2.8941(5)		2.6994(2)
Os(1)-P(1)	2.328(2)		2.4377(9)
Os(1)-P(2)	2.319(2)		2.2765(9)
P(2)-O(12)	1.646(6)		1.638(2)
Os(3)-Os(1)-Os(2)	58.98(1)		55.263(5)
Os(3-Os(2)-Os(1)	58.79(1)		60.539(5)
Os(3)-Os(1)-Os(2)	62.22(1)		64.198(5)
P(1)...P(2)	5.142(2)	Os(3)-P(1)	2.2747(9)
P(1)-O(11)	1.642(6)	Os(1)-O(11)	2.106(2)
P(2)-O(12)	1.646(6)	Os(2)-C(11)	2.182.3
P(1)-O(11)-C(12)	121.4(5)	Os(3)-C(11)	2.294(3)
P(2)-C(12)-O(16)	124.2(5)	Os(2)-H(1M)	1.88(5)
		Os(3)-H(1M)	1.70(5)
		Os(1)-O(11)-C(12)	119.4(2)
		P(2)-O(2)-C(16)	112.9(2)