

Products from the photoreaction of $(\text{Me}_3\text{P})(\text{OC})_4\text{OsW}(\text{CO})_5$ with CCl_4 ; synthesis and isomerization of $\text{Os}(\text{CO})_3(\text{PMe}_3)\text{Cl}_2$

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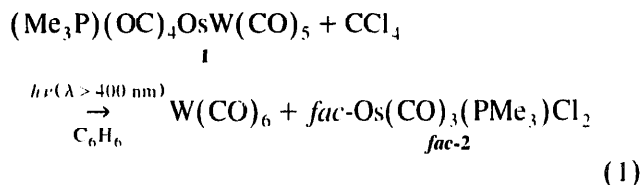
Abstract

This paper reports the characterization of the *fac*- $\text{Os}(\text{CO})_3(\text{PMe}_3)\text{Cl}_2$ (**fac-2**) product that is formed when $(\text{Me}_3\text{P})(\text{OC})_4\text{OsW}(\text{CO})_5$ (**1**; a complex with a dative Os–W bond) is irradiated ($\lambda > 400$ nm) in the presence of CCl_4 . In an attempt to independently synthesize **fac-2**, $\text{Os}_3(\text{CO})_9(\text{PMe}_3)_3$ was allowed to react with Cl_2 . The product, however, was *mer-cis*- $\text{Os}(\text{CO})_3(\text{PMe}_3)\text{Cl}_2$ (**mer-cis-2**). The *mer-cis* isomer is converted to the *fac* isomer (**fac-2**) by stirring under nitrogen in THF for nine days. The stereochemistry of each compound was confirmed by infrared and NMR spectroscopy and by X-ray crystallography. The $[\text{Os}(\text{CO})_2(\text{PMe}_3)(\text{Cl})(\mu\text{-Cl})]_2$ compound (**3**) was also formed as a minor product in the conversion of *mer-cis*- $\text{Os}(\text{CO})_3(\text{PMe}_3)\text{Cl}_2$ to *fac*- $\text{Os}(\text{CO})_3(\text{PMe}_3)\text{Cl}_2$. Irradiation ($\lambda > 400$ nm) of $\text{Os}(\text{CO})_4(\text{PMe}_3)$ in benzene in the presence of CCl_4 gave a product tentatively identified as *fac*- $\text{Os}(\text{CO})_3(\text{PMe}_3)(\text{CCl}_3)\text{Cl}$ (**4**), which results from the oxidative-addition of CCl_4 to $\text{Os}(\text{CO})_3(\text{PMe}_3)$. © 1997 Elsevier Science S.A.

Keywords: Photochemistry; Isomerization; Oxidative-addition of CCl_4 ; *Mer-cis*- to *fac*-isomerization

1. Introduction

We recently reported that irradiation of $(\text{Me}_3\text{P})(\text{OC})_4\text{OsW}(\text{CO})_5$ (**1**) led to heterolytic cleavage of the Os–W dative bond [1]. Among the key experiments to test for homolytic cleavage were metal radical trapping experiments, all of which proved negative. The metal radical traps employed were benzyl chloride, TMIO (1,1,3,3-tetramethylisindoline-2-oxyl) [2,3], and carbon tetrachloride. Although no products indicative of metal radicals were detected, a photochemical reaction did take place when **1** was irradiated ($\lambda > 400$ nm) in the presence of CCl_4 in C_6H_6 :



In this paper, we report the synthesis and characterization of the Os-containing product formed in Eq. (1), namely *fac*- $\text{Os}(\text{CO})_3(\text{PMe}_3)\text{Cl}_2$ (**fac-2**). During the investigation, we discovered a synthesis of the *mer-cis*- $\text{Os}(\text{CO})_3(\text{PMe}_3)\text{Cl}_2$ isomer (**mer-cis-2**) and the conditions for its transformation to the *fac* isomer. The *fac*- $\text{Os}(\text{CO})_3(\text{PMe}_3)(\text{CCl}_3)\text{Cl}$ molecule (**4**) was also synthesized and its transformation to $\text{Os}(\text{CO})_3(\text{PMe}_3)\text{Cl}_2$ was investigated. The X-ray structures of *fac*- $\text{Os}(\text{CO})_3(\text{PMe}_3)\text{Cl}_2$ and *mer-cis*- $\text{Os}(\text{CO})_3(\text{PMe}_3)\text{Cl}_2$ are also reported. Finally, the synthesis of $[\text{Os}(\text{CO})_2(\text{PMe}_3)(\text{Cl})(\mu\text{-Cl})]_2$ (**3**) is described.

2. Results and discussion

2.1. Synthesis of *mer-cis*- $\text{Os}(\text{CO})_3(\text{PMe}_3)\text{Cl}_2$ (**mer-cis-2**) and *fac*- $\text{Os}(\text{CO})_3(\text{PMe}_3)\text{Cl}_2$ (**fac-2**)

The Os-containing product formed in Eq. (1) has IR $\nu(\text{CO})$ bands at 2125, 2050, and 2004 cm^{-1} . These bands were tentatively assigned to $\text{Os}(\text{CO})_3(\text{PMe}_3)\text{Cl}_2$ by comparison to the spectra of the related complexes

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Table 1
Selected IR and NMR data

Compound	^1H NMR (ppm) ^a	$^{31}\text{P}\{^1\text{H}\}$ NMR, ppm ^a	$^{13}\text{C}\{^1\text{H}\}$ NMR (ppm) ^b	IR $\nu(\text{CO})$ bands (cm^{-1})
<i>mer-cis</i> -Os(CO) ₃ (PMe ₃)Cl ₂	1.93 (d, CH ₃ , ² J _{P-H} = 11.6 Hz)	-36.10 (s, PMe ₃)	18.12 (d, CH ₃ , ¹ J _{P-C} = 42.3 Hz), 167.23 (d, CO, 1C, ² J _{P-C} = 6.9 Hz), 172.42 (d, CO, 2C, ² J _{P-C} = 7.6 Hz)	2145 (vw), 2066 (s), 2019 (m) ^c , 2064 (s), 2010 (m) ^d
<i>fac</i> -Os(CO) ₃ (PMe ₃)Cl ₂	1.77 (d, CH ₃ , ² J _{P-H} = 11.5 Hz)	-31.78 (s, PMe ₃)	12.60 (d, CH ₃ , ¹ J _{P-C} = 40.4 Hz), 167.22 (d, CO, 2C, ² J _{P-C} = 9.2 Hz), 167.96 (d, CO, 1C, ² J _{P-C} = 107.6 Hz)	2127 (m), 2054 (s), 2012 (m) ^c , 2125 (m), 2050 (s), 2004 (s) ^d
[Os(CO) ₂ (PMe ₃)X(μ-Cl)] ₂	1.76 (d, CH ₃ , ² J _{P-H} = 11.8 Hz), 1.80 (d, CH ₃ , ² J _{P-H} = 11.4 Hz)	-30.74 (s, PMe ₃), -30.35 (s, PMe ₃)	15.5 (d, CH ₃ , ¹ J _{P-C} = 43.1 Hz), 170.5 (d, CO, 4C, ² J _{P-C} = 10.0 Hz), 170.9 (d, br, CO, 11C, ² J _{P-C} = 11.0 Hz), 171.9 (d, br, CO, 12C, ² J _{P-C} = 5.8 Hz)	2047 (s), 1971 (s) ^c
Os ₃ (CO) ₉ (PMe ₃) ₃	1.81 (d, CH ₃ , ² J _{P-H} = 10.2 Hz)	-58.20 (s, PMe ₃)	23.19 (d, CH ₃ , ¹ J _{P-C} = 37.2 Hz), 183.6 (s, CO, 3C), 196.7 (s, CO, 6C)	1977 (sh,m), 1965 (vs,br), 1920 (s) ^c
Os ₃ (CO) ₉ (PPh ₃)Cl ₂				2123 (w), 2048 (s), 2017 (w), 1978 (s) ^c
Os(CO) ₃ (PEt ₃)Cl ₂				2144 (w), 2070 (vs), 2023 (s) ^f
OPMe ₃	0.97 (d, CH ₃ , ² J _{P-H} = 1.6 Hz)	-60.53 (s, PMe ₃)		
H ₂ O	1.38 (d, CH ₃ , ² J _{P-H} = 13.2 Hz) 2.21 (s, H ₂ O)			

^a In CD₃CN at 35°C.

^b In CH₂Cl₂/CD₂Cl₂ (3/1) at -40°C.

^c In CH₂Cl₂ at room temperature (i.e., samples were removed from the reaction solution. CD₃CN removed and the remaining solid dissolved in CH₂Cl₂).

^d In C₆H₆ at room temperature.

^e From Ref. [4,5], in *n*-ujol.

^f From Ref. [6], in cyclohexane.

Table 2

Crystal data and structure refinement for *mer-cis*-Os(CO)₃(PMe₃)Cl₂ (*mer-cis-2*) and *fac*-Os(CO)₃(PMe₃)Cl₂ (*fac-2*)

	<i>mer-cis-2</i>	<i>fac-2</i>
Formula	C ₆ H ₉ Cl ₂ O ₃ OsP	C ₆ H ₉ Cl ₂ O ₃ OsP
FW	421.22	421.22
Temp (°C)	21	21
Wavelength (Å)	0.71069	0.71069
Cryst system	Monoclinic	Monoclinic
Space group ^a	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	6.4377(7)	6.4691(4)
<i>b</i> (Å)	15.3782(13)	13.2890(11)
<i>c</i> (Å)	12.3148(10)	27.915(2)
β (deg)	100.744(8)	95.261(6)
<i>V</i> (Å ³)	1197.8(2)	2389.7(3)
<i>Z</i>	4	8
2 θ range of unit cell (deg)	35.0–45.0	32.2–42.1
<i>D</i> (calc.) (g cm ⁻³)	2.336	2.342
μ (Mo, K α) (cm ⁻¹)	112.15	112.43
Cryst size (mm)	0.16 × 0.21 × 0.27	0.11 × 0.18 × 0.32
Transmission coeff.	0.176–0.271	0.0857–0.376
Scan range (2 θ) (deg)	3.6–47.0	3.6–50.0
Scan width (ω) (deg)	0.70 + 0.35 tan <i>q</i>	0.70 + 0.35 tan <i>q</i>
Scan width (ω) (deg)	0.70 + 0.35 tan <i>q</i>	0.70 + 0.35 tan <i>q</i>
Scan rate (ω) (deg min ⁻¹)	0.573–3.296	0.573–3.296
No. of unique reflns.	1759	4176
No. of obs. reflns.	1583	3559
No. of parameters	147	242
No. of restraints	9	0
<i>R</i> ^b	0.016	0.024
<i>R</i> _w ^c	0.021	0.034
Instrument instability factor (k)	0.00005	0.0002
Extinction parameter (<i>r</i> ⁻¹)	0.411(14)	0.57(3)
Largest shift/esd in final 1s cycle	0.05	0.12
Largest positive/negative residual electron density in final diff map (e Å ⁻³)	0.44(9)/–0.51(9)	0.82(15)/–1.07(15)
Goodness-of-fit ^d	1.6	1.6
<i>F</i> (000)	775.78	1540.15

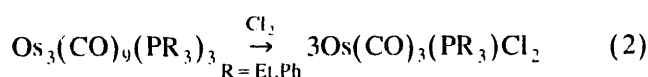
^aA non-standard orientation of *P*2₁/*c*. General equivalent positions are *x, y, z*; 1/2 – *x, 1/2 – y, 1/2 – z*; 1/2 + *x, 1/2 + y, 1/2 + z*.

^b $R = \sum ||F_o| - |F_c|| / \sum |F_o|$.

^c $R_w = (\sum_w (|F_o| - |F_c|)^2 / \sum_w (|F_o|)^2)^{1/2}$.

^dGoodness-of-fit = $(\sum_w (|F_o| \pm |F_c|)^2 / (\text{degrees of freedom}))^{1/2}$.

Os(CO)₃(PPh₃)Cl₂ [4,5] and Os(CO)₃(PEt₃)Cl₂ [6] (Table 1). (The stereochemistry of the Os(CO)₃(PR₃)Cl₂ (R = Ph, Et) products was not addressed, and moreover the number and intensities of the CO-stretching bands reported in the IR spectrum of Os(CO)₃(PPh₃)Cl₂ suggested the presence of more than one isomer [4,5].) In order to identify definitively Os(CO)₃(PMe₃)Cl₂ and its stereochemistry, it was decided to prepare the molecule by an alternate route. The Os(CO)₃(PPh₃)Cl₂ [4,5] and Os(CO)₃(PEt₃)Cl₂ [6] complexes had been previously prepared by the reaction of Os₃(CO)₉(PR₃)₃ with Cl₂ (Eq. (2)), and thus the reaction of Os₃(CO)₉(PMe₃)₃ with Cl₂ appeared a viable pathway to Os(CO)₃(PMe₃)Cl₂.



The reaction of Os₃(CO)₉(PMe₃)₃ in toluene with an excess of Cl₂ at 0°C was instantaneous; the clear orange solution changed to yellow and a white precipitate formed. The precipitate was recrystallized from THF–hexanes. An IR spectrum of this product indicated that it was not the same as the product from the reaction given in Eq. (1). An X-ray structure determination revealed it to be *mer-cis*-Os(CO)₃(PMe₃)Cl₂ (*mer-cis-2*) (Fig. 1; Tables 2–4). A complete discussion of this structure is presented in the Supplementary Material.

The similarities in the infrared spectrum of *mer-cis-2* to the product in Eq. (1) suggested that the product in Eq. (1) may be a stereoisomer of *mer-cis-2*. Literature precedents suggested a *fac* configuration: for example, Ru(CO)₃(OPPh₃)Br₂ has the *fac* configuration [7], and the *fac* geometry was also suggested for the Os(CO)₃(PPh₃)H₂ complex [8]. To investigate the

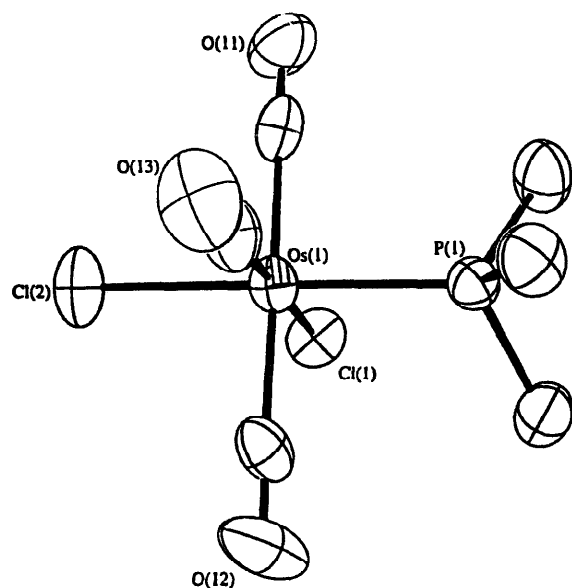


Fig. 1. Molecular structure of the *mer-cis*-Os(CO)₃(PMe₃)Cl₂ (*mer-cis-2*) complex showing the atom-numbering scheme.

stereoisomerization reactions of *mer-cis-2*, a THF solution of *mer-cis-2* was stirred at room temperature in the dark under N₂ for nine days (Eq. (3)). After this time, an infrared spectrum of the solution showed only new $\nu(\text{CO})$ bands at 2127 (s), 2054 (vs), 2011 (s), and 1982 (m) cm⁻¹. Column chromatography of the reaction mixture afforded two products, and the major product was recrystallized from C₆H₁₄-C₆H₅CH₃ to afford colorless needles. A crystal structure determination of this product revealed it to be *fac-2* (Table 2).

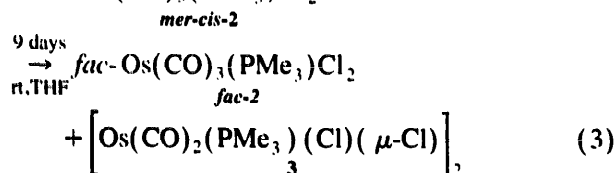


Table 3
Selected bond lengths (Å) of *mer-cis*-Os(CO)₃(PMe₃)Cl₂ (*mer-cis-2*)

Os(1)–P(1)	2.341(1)	Os(1)–C(11)	1.978(6)
Os(1)–Cl(1)	2.427(1)	Os(1)–C(12)	1.957(6)
Os(1)–Cl(2)	2.457(1)	Os(1)–C(13)	1.856(5)

Table 4
Selected bond angles (deg) of *mer-cis*-Os(CO)₃(PMe₃)Cl₂ (*mer-cis-2*)

P(1)–Os(1)–Cl(1)	87.36(4)	Cl(1)–Os(1)–C(12)	89.5(1)
P(1)–Os(1)–C(12)	90.5(1)	Cl(1)–Os(1)–Cl(2)	87.37(5)
P(1)–Os(1)–C(13)	94.0(2)	Cl(1)–Os(1)–C(13)	178.4(2)
P(1)–Os(1)–C(11)	91.0(1)	Cl(1)–Os(1)–C(11)	87.6(1)
P(1)–Os(1)–Cl(2)	174.61(4)	Cl(2)–Os(1)–C(12)	90.6(1)
C(11)–Os(1)–C(12)	176.6(2)	Cl(2)–Os(1)–C(13)	91.3(2)
C(11)–Os(1)–C(13)	91.5(2)	Cl(2)–Os(1)–C(11)	87.7(1)
C(12)–Os(1)–C(13)	91.5(2)		

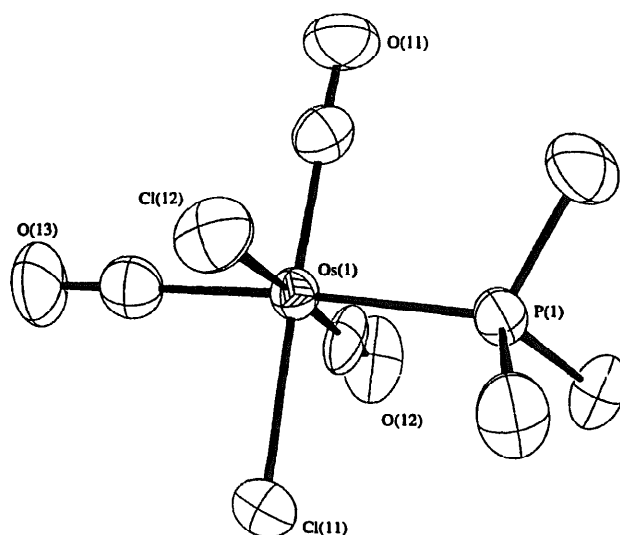


Fig. 2. Molecular structure of the *fac*-Os(CO)₃(PMe₃)Cl₂ (*fac-2*) complex showing the atom labeling scheme.

The structure of *fac-2* is shown in Fig. 2 and selected bond lengths and bond angles are listed in Tables 5 and 6, respectively. The asymmetric unit cell contains two crystallographically distinct molecules, and the osmium atom has octahedral coordination. A complete discussion of this structure is presented in the Supplementary Material.

2.2. The spectroscopic properties of *fac*-Os(CO)₃(PMe₃)Cl₂ (*fac-2*)

The IR spectrum in the CO region of *fac-2* (Table 1) is identical to that observed for the product obtained by irradiation of **1** in C₆H₆ in the presence of CCl₄ (Eq. (1)), and it is consistent with the retention of a *fac* geometry in solution. The pattern and intensity of the $\nu(\text{CO})$ bands is analogous to that of *fac*-Ru(CO)₃(C₅H₅N)Cl₂ [9]. In nujol, the infrared spectrum of *fac-2* exhibits two bands at 318(s) and 296(s) cm⁻¹, assigned to $\nu(\text{Os–Cl})$ by analogy to Os(CO)₂(PPh₃)₂Cl₂ ($\nu(\text{Os–Cl})$: 306(m) and 284(m) cm⁻¹) [5], Os(CO)₃(PEt₃)Cl₂ ($\nu(\text{Os–Cl})$: 312(s) and 289(s) cm⁻¹) [6,9] and to those in *mer-cis-2* (see below). That both bands are intense is consistent with the Cl ligands being mutually *cis*, as in the *fac* arrangement.

The ¹³C{¹H} NMR spectrum of *fac-2* in CD₂Cl₂-CH₂Cl₂ at -40°C is consistent with the solid-state structure. It showed two doublets in the carbonyl region at 167.2 ppm (2C, ²J_{P-C} = 9.2 Hz) and 168.0 ppm (1C, ²J_{P-C} = 107.6 Hz) (Table 1). The chemical shift of the resonance at 167.2 ppm of relative intensity 2 is identical to that of the resonance of the CO ligand *trans* to a Cl atom and *cis* to a PMe₃ group in *mer-cis-2*. Both resonances have a small two-bond carbon-phosphorus

Table 5
Selected bond lengths (Å) of *fac*-Os(CO)₃(PMe₃)Cl₂ (*fac-2*)

Molecule 1		Molecule 2	
Os(1)–Cl(11)	2.422(2)	Os(2)–Cl(21)	2.418(2)
Os(1)–Cl(12)	2.426(1)	Os(2)–Cl(22)	2.426(2)
Os(1)–P(1)	2.399(1)	Os(2)–P(2)	2.402(2)
Os(1)–C(11)	1.890(7)	Os(2)–C(21)	1.882(7)
Os(1)–C(12)	1.912(6)	Os(2)–C(22)	1.889(6)
Os(1)–C(13)	1.959(7)	Os(2)–C(23)	1.959(7)

Table 6
Selected bond angles (deg) of *fac*-Os(CO)₃(PMe₃)Cl₂ (*fac-2*)

Molecule 1		Molecule 2	
Cl(11)–Os(1)–Cl(12)	90.24(6)	Cl(21)–Os(2)–Cl(22)	89.77(6)
Cl(11)–Os(1)–P(1)	86.56(5)	Cl(21)–Os(2)–P(2)	87.79(6)
Cl(11)–Os(1)–C(12)	88.6(2)	Cl(21)–Os(2)–C(22)	87.4(2)
Cl(12)–Os(1)–P(1)	87.01(6)	Cl(22)–Os(2)–P(2)	85.18(6)
Cl(12)–Os(1)–C(13)	86.4(2)	Cl(22)–Os(2)–C(23)	89.9(2)
P(1)–Os(1)–C(11)	91.6(2)	P(2)–Os(2)–C(21)	92.8(2)
P(1)–Os(1)–C(12)	93.0(2)	P(2)–Os(2)–C(22)	92.5(2)
C(11)–Os(1)–C(12)	90.8(3)	C(21)–Os(2)–C(22)	94.4(3)
C(11)–Os(1)–C(13)	93.8(3)	C(21)–Os(2)–C(23)	91.4(3)
C(12)–Os(1)–C(13)	93.5(3)	C(22)–Os(2)–C(23)	92.2(3)
Cl(11)–Os(1)–C(11)	178.1(2)	Cl(21)–Os(2)–C(21)	178.1(2)
Cl(11)–Os(1)–C(13)	88.1(2)	Cl(21)–Os(2)–C(23)	87.9(2)
Cl(12)–Os(1)–C(11)	90.4(2)	Cl(22)–Os(2)–C(21)	88.5(2)
Cl(12)–Os(1)–C(12)	178.8(2)	Cl(22)–Os(2)–C(22)	176.4(2)
P(1)–Os(1)–C(13)	171.5(2)	P(2)–Os(2)–C(23)	173.5(2)

coupling characteristic of a *cis* coupling in octahedral complexes.² The resonance of the *fac* isomer at 168.0 ppm of relative intensity 1 exhibits a large two-bond carbon–phosphorus coupling (²J_{P–C} = 107.6 Hz) characteristic of a *trans* coupling.³

2.3. The spectroscopic properties of *mer-cis*-Os(CO)₃(PMe₃)Cl₂ (*mer-cis-2*)

The CO-stretching region in the IR spectrum of *mer-cis-2* in CH₂Cl₂ showed three bands at 2145(vw), 2066(s), and 2019(m) cm⁻¹. These bands positions are similar to those reported for Os(CO)₃(PEt₃)Cl₂ in cyclohexane (2144(w), 2070(vs), and 2023(s) cm⁻¹) [6]. The very weak band at the highest frequency is attributed to the symmetric stretch [15] of the two *trans*

CO ligands, for which the dipole moment change is expected to be small. Bands at 310(m) and 279(s) cm⁻¹ (nujol) are assigned to ν(Os–Cl) vibrations by analogy to the literature [5,6].⁴

The ¹³C{¹H} NMR spectrum of the complex in CD₂Cl₂–CH₂Cl₂ at –40°C showed two doublets at 167.2 ppm (1C, ²J_{P–C} = 6.9 Hz) and 172.4 ppm (2C, ²J_{P–C} = 7.6 Hz) in the carbonyl region. Both of these resonances exhibited a small, two-bond, carbon–phosphorus coupling typical of a CO ligand *cis* to a phosphine ligand.² This result indicates that both carbonyl ligands are *cis* to the PMe₃ ligand, in agreement with the solid-state structure.

2.4. Preparation of [Os(CO)₂(PMe₃)(Cl)(μ-Cl)]₂ (**3**)

In the preparation of *fac-2* from *mer-cis-2* described above, a minor product also formed (Eq. (3)). This product was separated from *fac-2* by column chromatography and recrystallized from C₆H₅CH₃–CH₂Cl₂ to give small, white, star-shaped crystals. Repeated attempts to obtain a crystal of this complex that was suitable for X-ray crystallography were unsuccessful, but spectroscopic analysis suggests the compound is [Os(CO)₂(PMe₃)(Cl)(μ-Cl)]₂ (**3**). The ν(CO) region of the material in CH₂Cl₂ showed two strong bands at 2050(s) and 1983(s) cm⁻¹. These frequencies are very similar to the spectrum reported for [Os(CO)₂(PPh₃)(Cl)(μ-Cl)]₂ (2051(s) and 1981(s) cm⁻¹ [6]). The infrared spectrum of **3** in nujol also had bands at 314(m), 273(m), and 242(m) cm⁻¹, which are assigned to ν(Os–Cl) vibrations by analogy to [Os(CO)₂(PPh₃)(Cl)(μ-Cl)]₂ (ν(Os–Cl): 321(s), 280(s), and 242(m) cm⁻¹).⁵

The mass spectrum (EI) of **3** exhibits a peak envelope with a maximum at 753 m/z, assigned to [Os₂(CO)₄(PMe₃)₂Cl₃]⁺. Compound **3** started to decompose at 257°C, which is much higher than the melting points of *mer-cis-2*, *fac-2* (119°C, dec), and Os(CO)₃(PPh₃)Cl₂ (90°C), and it is similar to [Os(CO)₂(PPh₃)Cl₂]₂ (290°C) [6].

Carbon monoxide inhibited the conversion of **2** to **3** (see Supplementary Material), and furthermore, the process is reversible: CO reacts with **3** to give *fac-2* as the sole observable product. This reactivity supports the

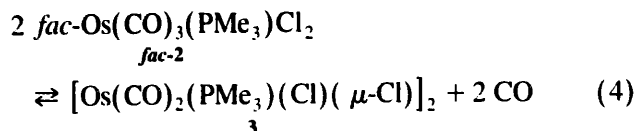
² Some examples of two-bond carbon–phosphorus NMR couplings in similar systems are: Os₃(CO)₁₅(PMe₃) δ 181.6 (d, CO, 4C, ²J_{P–C} = 4.1 Hz) [10]; Os₃(CO)₁₀(PEt₃)₂ δ 197.1 (d, CO, 2C, ²J_{P–C} ≈ 7 Hz), δ 196.2 (d, CO, 2C, ²J_{P–C} ≈ 7 Hz) [11].

³ For comparison, the two-bond carbon–phosphorus couplings are 71.1 Hz with the PMe₃ ligand *trans* to a CO ligand and 13.2 and 8.9 Hz with PMe₃ *cis* to a CO ligand in the ¹³C{¹H} NMR spectrum of (Me₃P)(OC)₃Os₂(CO)₅ (**1**) with the PMe₃ ligand *cis* to the Os–W bond and *trans* to a CO ligand [12–14].

⁴ For the *mer-trans*-isomer, the symmetric A₁ (Os–Cl) stretch in the IR spectrum would be expected to be weak or of negligible intensity. The nujol IR spectral results are therefore also consistent with a *mer-cis*-arrangement of the ligands.

⁵ The assignment of these bands is based on that for the [Ru(CO)₃(Cl)(μ-Cl)]₂ compound, which has three ν(Ru–Cl) bands at 331, 290, and 260 cm⁻¹, assigned to one terminal and two bridged Ru–Cl stretches, respectively [9,16–18].

proposed identity of the dimeric species and it also suggests that *fac-2* and **3** are in equilibrium (Eq. (4)).



Similar equilibria have been established for $[\text{Ru}(\text{CO})_3\text{Cl}_2]_2/\text{Ru}(\text{CO})_4\text{Cl}_2$ [9], and $[\text{Ru}(\text{CO})(\text{PMe}_2\text{Ph})_2(\text{Cl})(\mu\text{-Cl})]_2/\text{all-cis-Ru}(\text{CO})_2(\text{PMe}_2\text{Ph})_2\text{Cl}_2$ [18].

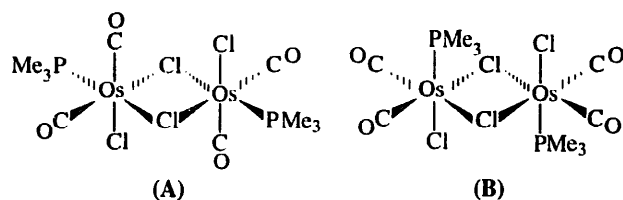
2.5. Proposed structure of $[\text{Os}(\text{CO})_2(\text{PMe}_3)(\text{Cl})(\mu\text{-Cl})]_2$ (**3**)

The ^1H NMR spectrum of **3** in CD_3CN at 35°C (Table 1) shows two sets of doublets at 1.76 ppm ($^2J_{\text{P-H}} = 11.7$ Hz) and 1.80 ppm ($^2J_{\text{P-H}} = 11.7$ Hz) in the ratio 3:1, respectively, consistent with the presence of two isomers in solution.⁶ The corresponding $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows two singlets at -30.73 and -30.37 ppm also in the ratio 3:1, respectively. Repeated recrystallizations and preparations of the dimeric compound did not alter the IR or NMR spectra of the mixture, suggesting the additional peaks are not due to impurities.

The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3** in $\text{CH}_2\text{Cl}_2\text{-CD}_2\text{Cl}_2$ at -40°C was unfortunately of poor quality but showed three sets of doublets in the carbonyl region at δ 170.5 ($^2J_{\text{P-C}} = 10.0$ Hz), 170.9 ($^2J_{\text{P-C}} = 11.0$ Hz) and 171.9 ppm ($^2J_{\text{P-C}} = 5.8$ Hz) in the ratio 4:11:12, respectively. The latter two resonances are assigned to the major isomer, with the peak at δ 170.5 ppm being attributed to the minor isomer and the second peak of the minor isomer being accidentally degenerate with a resonance from the major isomer. There was no evidence in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum that would suggest an isomer with a CO ligand *trans* to a PMe_3 group.

The two most likely structural arrangements of **3** that maintain the $\text{Os}_2(\text{Cl})_2(\mu\text{-Cl})_2$ core (analogous to $[\text{M}(\text{CO})_3(\text{Cl})(\mu\text{-Cl})]_2$ ($\text{M} = \text{Ru}$ [16,19], Os [20]) and are consistent with all the prior spectroscopic data and electronic discussions [7] are shown in Scheme 1.⁷

Both structures would give rise to two slightly different $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR environments for the PMe_3 ligand, yet in the IR spectrum the different $\nu(\text{CO})$



Scheme 1. (A) Proposed structural isomers of $[\text{Os}(\text{CO})_2(\text{PMe}_3)(\text{Cl})(\mu\text{-Cl})]_2$ (**3**).

bands for the two isomers would probably not be discernible in polar solvents such as CH_2Cl_2 . At present, it is not known whether the dimeric species is formed from a five coordinate unsaturated, fluxional species interacting with a saturated six coordinate species or from two five coordinate species, although the former pathway is mechanistically more likely.

2.6. Conversion of *mer-cis-2* to *fac-2* to **3**

The conversion of *mer-cis-2* to *fac-2* and then to **3** in CD_3CN at 35°C was also studied by $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectroscopy. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra and the resonance assignments are shown in Fig. 3.⁸ After 4 h, three new $^{31}\text{P}\{^1\text{H}\}$ NMR resonances were observed that were assigned to *fac-2* and the two isomeric forms of **3** (Fig. 3). After 18 h, the major product was *fac-2* with traces of **3**. After 47 h, the $^{31}\text{P}\{^1\text{H}\}$ NMR resonance of *mer-cis-2* was not detectable and the resonance of *fac-2* was drastically reduced; the major signals present were those of **3**. Finally, after 283 h, the only detectable resonances were those of **3**. An infrared spectrum of the $\nu(\text{CO})$ region showed only two bands attributed to the two isomers of **3** (Table 1). Control experiments with PMe_3 , OPMe_3 , H_2O , and **4** demonstrated that these species were not present.

It was previously reported that in CH_3CN the *all-trans-Ru*($\text{CO})_2(\text{PMe}_2\text{Ph})_2\text{Cl}_2$ species forms $\text{Ru}(\text{CO})(\text{PMe}_2\text{Ph})_2(\text{NCMe})\text{Cl}_2$ exclusively in the *cis*-arrangement [18]. In the present study, there was no ^1H , $^{31}\text{P}\{^1\text{H}\}$ NMR or IR spectroscopic evidence to suggest the presence of $\text{Os}(\text{CO})_2(\text{PMe}_3)(\text{NCCD}_3)\text{Cl}_2$. Although not definitive evidence, the fact that $\text{Os}(\text{CO})_2(\text{PMe}_3)(\text{NCCD}_3)\text{Cl}_2$ was not observed suggests that the isomerization of *mer-cis-2* to *fac-2* goes by way of a nondissociative pathway, such as a trigonal twist mechanism. Trigonal twist mechanisms have been implicated in the isomerization of a number of related complexes, as for example in $\text{Cr}(\text{CO})_2(\text{CY})(\text{P}(\text{OMe})_3)_3$ ($\text{Y} = \text{S}, \text{Se}$) [21] and $\text{Ru}(\text{CO})(\text{H})_2(\text{PPh}_3)_3$ [22].

⁶ The structure of $[\text{Os}(\text{CO})_2(\text{PMe}_3)(\text{Cl})(\mu\text{-Cl})]_2$ (**3**) is probably similar to that of $[\text{Ru}(\text{CO})_3(\text{PPh}_3)(\text{Cl})(\mu\text{-Cl})]_2$ [16,17] which is based upon $[\text{Ru}(\text{CO})_3(\text{Cl})(\mu\text{-Cl})]_2$ [19]. However, both ruthenium compounds exist as only one isomer in solution [9,16], whereas NMR spectroscopy indicates there are two isomers of **3** present in solution.

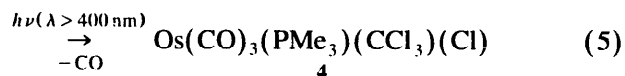
⁷ Other isomers of $[\text{Os}(\text{CO})_2(\text{PMe}_3)(\text{Cl})(\mu\text{-Cl})]_2$ (**3**) with C_2 , C_2v , and C_s point group symmetry were considered less likely based on the number of IR $\nu(\text{CO})$ and $\nu(\text{Os-Cl})$ bands predicted from group theory.

⁸ The assignments were confirmed by comparison with the spectra of authentic compounds under the same conditions.

2.7. Tentative identification of *fac*-Os(CO)₃(PMe₃)(CCl₃)Cl (**4**)

Irradiation ($\lambda > 400$ nm) of Os(CO)₄(PMe₃) in C₆H₆ in the presence of CCl₄ or stirring a solution of Os(CO)₄(PMe₃) in C₆H₆ in the presence of CCl₄ at room temperature in the absence of light for 18 h gave a product with three $\nu(\text{CO})$ bands in the IR spectrum at 2118(m), 2054(s), and 2010(s) cm⁻¹ and a doublet in the ¹H NMR spectrum at δ 0.92 (²J_{P-H} = 10.4 Hz) in C₆H₆. The frequencies and intensities of these bands are similar to those of *fac*-**2** in C₆H₆ (See Table S11, Supplementary Material). The IR spectrum of **4** also resembles that of Fe(CO)₃(PPh₃)(C₃F₇)(I): 2103(w), 2051(s), and 2035(m) in C₂Cl₄ [23]. It is proposed therefore that the product of the reaction is *fac*-Os(CO)₃(PMe₃)(CCl₃)Cl (**4**) (Eq. (5)). (Also, note that

Os(CO)₄(PMe₃) irradiated in the presence of C₆H₅CH₂Cl yielded Os(CO)₃(PMe₃)(C₆H₅CH₂)(Cl) [1].)



Due to its instability, repeated attempts to isolate **4** for complete characterization were unsuccessful.^{9,10,11}

An alternative possibility is that the initial photoproduct in Eq. (5) is Os(CO)₂(PMe₃)(CCl₂)Cl₂.¹² Such a complex, however, would exhibit only two $\nu(\text{CO})$ bands in the solution IR spectrum, and would not readily convert to *fac*-**2**. Likewise, a dimeric species such as **3**, if present, would also be expected to show two $\nu(\text{CO})$ bands. Other possibilities are [Os(CO)₄(PMe₃)(X)]⁺[Cl]⁻ (X = CCl₃, Cl).¹³ Given that Os(CO)₃(PMe₃)(CH₃)Cl has IR $\nu(\text{CO})$ bands at 2097(s), 2027(s), and 1982(s) cm⁻¹ [28], these data would seem to further support the idea that the identity of the photoproduct is Os(CO)₃(PMe₃)(CCl₃)Cl.

A ¹³C{¹H} NMR spectrum of Os(CO)₄(PMe₃) in C₆D₆ at room temperature in the presence of an excess

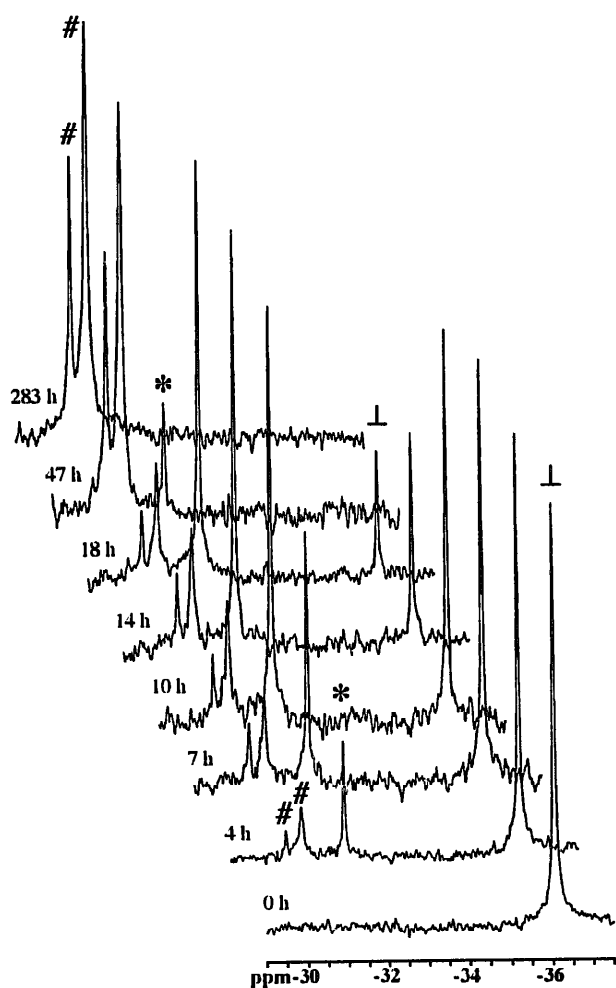


Fig. 3. The ³¹P{¹H} NMR spectra of *mer-cis*-Os(CO)₃(PMe₃)Cl₂ (*mer-cis*-**2**) in CD₃CN showing the conversion to *fac*-Os(CO)₃(PMe₃)Cl₂ (*fac*-**2**) and [Os(CO)₂(PMe₃)(μ-Cl)Cl]₂ (**3**) at 35°C over the time period 0–283 h. The peak marked with ⊥ is assigned to the *mer* form; the peak marked with * is assigned to the *fac* isomer; the signals marked with # are attributed to the two isomers of **3**.

⁹ Such reactivity is not unexpected. The [M(CCl₃)(Cl)(CO)(PPh₃)₃] (M = Ru, Os) complexes were proposed as intermediates in the formation of M(Cl)₂(=CCl₂)(CO)(PPh₃)₂, but both molecules resisted all attempts at isolation [24–26]. The instability of these CCl₃ species was attributed to spontaneous chloride loss or a rearrangement [26]. When a solution of the putative *fac*-Os(CO)₃(PMe₃)(CCl₃)Cl was left standing for 2 days in the dark at room temperature, it converted to *fac*-**2**, as demonstrated by IR spectroscopy^{10,11}.

¹⁰ A control experiment showed that when Os(CO)₄(PMe₃) was irradiated ($\lambda > 400$ nm) in C₆H₆ for 3 h, no other species were observed except the starting material. This result suggests that Os(CO)₃(PMe₃)(H)(C₆H₅) (which might then lead to Os(CO)₃(PMe₃)(Cl)(C₆H₅) in the presence of CCl₄) is not an intermediate in the reaction, and it also indicates that Os(CO)₃(PMe₃)(η²-C₆H₆) was probably not produced.

¹¹ Irradiation ($\lambda > 400$ nm) of Os(CO)₄(PMe₃) in C₆H₆ in the presence of an excess of CH₂Cl₂ (10 drops) for 2 h showed no reaction by ¹H NMR and IR spectroscopy. The ¹H NMR spectra of Os₃(CO)₉(PMe₃)₃, *mer-cis*-**2**, and *fac*-**2** in C₆H₆ indicate that none of these complexes are initially formed on irradiation of Os(CO)₄(PMe₃) in C₆H₆ in the presence of CCl₄. Both the IR and ¹H NMR spectrum of the initial photoproduct do, however, suggest that it is similar in structure to *fac*-**2** (also see Supplementary Material).

¹² Note that Fe(CO)₃(CCl₂)Cl₂ is proposed as the product in the photochemical reaction of Fe(CO)₅ with CCl₄ [27], and, furthermore, Os(CO)(PPh₃)₂(CCl₂)Cl₂ is also well characterized [25].

¹³ These compounds would be analogous to [Os(CO)₄(PMe₃)(CH₃)]⁺[I]⁻, which has $\nu(\text{CO})$ bands at 2158(s), 2098(s), and 2071(vs) cm⁻¹ in CH₂Cl₂ [28] (the compound [Os(CO)₄(PMe₃)(Br)]⁺Br⁻ has C–O stretching bands at 2182(m), 2128(s), 2107(vs), and 2080(s) cm⁻¹ in CH₂Cl₂ (H. Nagra, R.K. Pomeroy, unpublished results)). The CCl₃ and Cl ligands are more electron withdrawing than the CH₃ group and therefore the $\nu(\text{CO})$ frequencies would be expected to be much higher than those for the methyl derivative, which is not observed.

of CCl_4 was run before and after irradiation ($\lambda > 400$ nm) for 3 h. The NMR spectrum showed that the carbonyl resonance (189.6 ppm) due to $\text{Os}(\text{CO})_4(\text{PMe}_3)$ had been replaced by three major resonances at δ 169.3 (CO, ${}^2J_{\text{P-C}} = 100.6$ Hz), 170.2 (CO, ${}^2J_{\text{P-C}} = 7.6$ Hz), 170.8 (CO, ${}^2J_{\text{P-C}} = 7.8$ Hz). Unfortunately, the poor signal-to-noise ratio prohibited a meaningful integration of the peak areas of the signals. The spectrum is, however, consistent with a *fac* configuration and the chemical shifts of the resonances are similar to those observed for **3**, *mer-cis-2*, and *fac-2*.

3. Experimental

3.1. General methods

All manipulations were performed under nitrogen or argon by using standard Schlenk, drybox, or vacuum line techniques, unless stated otherwise. Toluene and hexanes were distilled from potassium; 1,4-dimethylbenzene was distilled from sodium; dichloromethane was distilled from CaH_2 ; propan-2-ol was refluxed with CaO and distilled and then further refluxed with CaH_2 and distilled again. Trimethylphosphine and $\text{Os}_3(\text{CO})_{12}$ were used as purchased. Carbon-13 CO (99.5 at.% ${}^{13}\text{C}$ and 10.1 at.% ${}^{18}\text{O}$) was used in the labeling of complexes with ${}^{13}\text{CO}$. Samples to be examined with ${}^1\text{H}$ NMR spectroscopy before and after photolysis were contained in NMR tubes fitted with a J. Young valve.

All NMR data were recorded at the specified temperatures on a Bruker AMX 400 instrument at an operating frequency of 400.13, 161.98, and 100.61 MHz for ${}^1\text{H}$, ${}^{31}\text{P}$, and ${}^{13}\text{C}$ nuclei, respectively. The chemical shifts for ${}^{31}\text{P}$ NMR are referenced to external 85% H_3PO_4 . Mass spectra (MS) were obtained with a Hewlett-Packard Model 5985 mass spectrometer. Spectra were determined in the EI (70 eV), CI (isobutane) or FAB mode (FAB, *m*-nitrobenzyl alcohol, xenon). For molecules of molecular mass above 1000 m/z the MS were obtained on a Kratos-MS-50 instrument (University of British Columbia, regional facility). The pattern of the envelope of ions for the parent ion or the species of highest mass matched the computer simulated pattern for all complexes considered. Microanalyses were performed by the Simon Fraser University Microanalytical Laboratory.

3.2. Synthesis of $\text{Os}_3(\text{CO})_9(\text{PMe}_3)_3$

The preparation of $\text{Os}_3(\text{CO})_9(\text{PMe}_3)_3$ has been previously reported [29] but it was made as a side product in the synthesis of $\text{Os}_3(\text{CO})_{12-n}(\text{PMe}_3)_n$ ($n = 1, 2$) and the yield was 11%. An alternative method that produces the trisubstituted cluster as the only cluster species is described herein. This method is analogous to the prepara-

tion of $\text{Os}_3(\text{CO})_9(\text{PPh}_3)_3$ [4,5] and $\text{Os}_3(\text{CO})_9(\text{PEt}_3)_3$ [6] and it produced similar products to those reported by Bellachioma et al. [28] and Martin et al. [30]. A slurry of $\text{Os}_3(\text{CO})_{12}$ (0.700 g, 0.772 mmol) in 1,4-dimethylbenzene (10 ml) was prepared in a Pyrex Carius tube, to which was added PMe_3 (0.30 ml, 2.9 mmol) and additional 1,4-dimethylbenzene (10 ml). The reaction vessel was sealed under N_2 and heated at 130°C with stirring for 6 h to give a clear, deep-orange solution. The solvent and excess PMe_3 were removed under vacuum. The products of the reaction were: $\text{Os}_3(\text{CO})_9(\text{PMe}_3)_3$, $\text{Os}(\text{CO})_4\text{PMe}_3$ and $\text{Os}(\text{CO})_3(\text{PMe}_3)_2$, as identified by IR spectroscopy [4–6,29–31]. The complex $\text{Os}(\text{CO})_4\text{PMe}_3$ (0.150 g) was obtained by sublimation (9.8×10^{-3} mm Hg) at 20 – 40°C to a probe cooled by cold water or it could also be separated by column chromatography (silica gel, 20×1 cm, $\text{C}_6\text{H}_{14}-\text{CH}_2\text{Cl}_2$). The mononuclear product $\text{Os}(\text{CO})_3(\text{PMe}_3)_2$ could be abstracted by sublimation (9.8×10^{-3} mm Hg) at 70 – 90°C to a probe at -78°C . Attempted chromatography on a silica gel column (silica gel, 20×1 cm, $\text{C}_6\text{H}_{14}-\text{CH}_2\text{Cl}_2$) was unsuccessful. (It is known that $\text{Os}(\text{CO})_3(\text{PMe}_3)_2$, reacts with O_2 to produce $\text{Os}(\text{CO})_2[\text{O}(\text{CO})\text{O}](\text{PMe}_3)_2$ [31]. The crude $\text{Os}_3(\text{CO})_9(\text{PMe}_3)_3$ was purified by recrystallization from $\text{C}_6\text{H}_{14}-\text{C}_6\text{H}_5\text{CH}_3$. In this way $\text{Os}_3(\text{CO})_9(\text{PMe}_3)_3$ (0.25 g, 31% yield) was obtained as orange air-stable crystals. For the ${}^{13}\text{C}\{^1\text{H}\}$ NMR experiments ${}^{13}\text{CO}$ -labeled $\text{Os}_3(\text{CO})_9(\text{PMe}_3)_3$ was prepared in an identical manner to the unlabeled cluster except ${}^{13}\text{CO}$ -labeled $\text{Os}_3(\text{CO})_{12}$ was employed [32] (typically 46–49% ${}^{13}\text{C}$ -enriched.¹⁴ For $\text{Os}_3(\text{CO})_9(\text{PMe}_3)_3$: IR (C_6H_{14}), $\nu(\text{CO})$: 1988(m,sh), 1975(s), 1932(m), 1920(m,sh) cm^{-1} ; (CH_2Cl_2), $\nu(\text{CO})$: 1977(sh,m), 1965(vs,br), 1920(s) cm^{-1} ; ${}^1\text{H}$ NMR (CD_2Cl_2 , -40°C): δ 1.78 (d, PMe_3 , ${}^2J_{\text{P-H}} = 10.0$ Hz); ${}^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , -40°C): δ -58.62 (s, PMe_3); ${}^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$, 1/3, -40°C): δ 23.2 (d, PMe_3 , ${}^1J_{\text{P-C}} = 37.2$ Hz), 183.6 (s, 3C, CO), 196.7 (s, 6C, CO); ¹⁵ MS (EI, m/z): 1052 (M^+); Anal. Calc. for $\text{C}_{18}\text{H}_{27}\text{O}_9\text{Os}_3\text{P}_3$: C, 20.57; H, 2.59. Found: C, 20.72; H, 2.61.

3.3. Synthesis of *mer-cis-Os(CO)₃(PMe₃)Cl₂* (*mer-cis-2*)

To $\text{Os}_3(\text{CO})_9(\text{PMe}_3)_3$ (0.090 g, 0.086 mmol) in $\text{C}_6\text{H}_5\text{CH}_3$ (15 ml) was added 4 ml of a saturated solution of Cl_2 in $\text{C}_6\text{H}_5\text{CH}_3$ at 0°C . The solution

¹⁴ The mass spectra (MS) were simulated with a computer program written by Dr. W.K. Leong in which the MS of ${}^{13}\text{C}$ -labeled species are simulated using a modified version of a program which prompts for the identity and numbers of each element using the 'dummy' elements C* and O* for ${}^{13}\text{C}$ and ${}^{18}\text{O}$, respectively.

¹⁵ At higher temperatures the carbonyl signals broaden due to carbon-13 carbonyl ligand exchange analogous to that previously observed for $\text{Os}_3(\text{CO})_9[\text{P}(\text{OMe})_3]_3$ [33].

instantly went opaque red–orange and then rapidly (≈ 10 s) altered to a pale yellow solution (presumably due to the excess Cl_2) along with a fine white precipitate. The mixture was stirred further for 10 min with no apparent change, the solvent was reduced to a minimum by evacuation and C_6H_{14} (10 ml) was added to the mixture to complete the precipitation. An IR spectrum in CH_2Cl_2 ($\nu(\text{CO})$ region) of the supernatant indicated the presence of *fac-2* and trace amounts of **3** in the solution. The supernatant was removed and the remaining white solid washed several times with C_6H_{14} . The crude white solid was recrystallized from $\text{THF}-\text{C}_6\text{H}_{14}$ to afford colorless crystals of *mer-cis-2* (0.095 g, 88% yield). The ^{13}C -labeled *mer-cis-2* was prepared in an identical manner from ^{13}C -labeled $\text{Os}_3(\text{CO})_9(\text{PMe}_3)_3$. For *mer-cis-2*: IR (CH_2Cl_2), $\nu(\text{CO})$: 2145(vw), 2066(s), 2019(m) cm^{-1} ; (C_6H_6), $\nu(\text{CO})$: 2064(s), 2010(m) cm^{-1} ; (nujol), $\nu(\text{Os}-\text{Cl})$: 310(m), 279(s) cm^{-1} ; ^1H NMR (CD_2Cl_2 , rt): δ 1.96 (d, CH_3 , $^2J_{\text{P}-\text{H}} = 11.0$ Hz); $^{31}\text{P}\{^1\text{H}\}$ (CD_2Cl_2 , rt): δ -38.42 (s, PMe_3); $^{13}\text{C}\{^1\text{H}\}$ ($\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$ 1/3, -40°C): δ 18.1 (d, CH_3 , $^1J_{\text{P}-\text{C}} = 42.3$ Hz), 167.2 (d, 1C, CO, $^2J_{\text{P}-\text{C}} = 6.9$ Hz), 172.4 (d, 2C, CO, $^2J_{\text{P}-\text{C}} = 7.6$ Hz); MS (EI, m/z): 422 (M^+); mp: at 119°C the colorless crystals became opaque and there was no further change to 200°C ; Anal. Calc. for $\text{C}_6\text{H}_9\text{Cl}_2\text{O}_3\text{OsP}$: C, 17.11; H, 2.15. Found: C, 17.14; H, 2.09.

3.4. Synthesis of *fac-Os(CO)₃(PMe₃)Cl₂* (*fac-2*)

A solution of *mer-cis-2* (0.140 g, 0.332 mmol) in THF (15 ml) was allowed to stir at room temperature in the dark under N_2 for 9 days. After this time the IR $\nu(\text{CO})$ bands due to *mer-cis-2* were no longer present in the solution and had been replaced by the IR $\nu(\text{CO})$ bands of *fac-2*, and much weaker bands due to **3** (see below). The solution was evaporated to dryness under vacuum. The remaining white solid was chromatographed on a silica gel column (1 \times 20 cm); the *fac-2* was eluted with $\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$ (4/1) and **3** (0.010 g, 8%) with CH_2Cl_2 . The crude, white solid of *fac-2* (0.095 g, 68%) was recrystallized from $\text{C}_6\text{H}_{14}-\text{C}_6\text{H}_5\text{CH}_3$ to afford colorless crystals. The ^{13}C -labeled *fac-2* was prepared in an identical manner from ^{13}C -labeled *mer-cis-2*. For *fac-2*: IR (C_6H_{14}), $\nu(\text{CO})$: 2126(m), 2048(m), 2005(m) cm^{-1} ; (CH_2Cl_2), $\nu(\text{CO})$: 2127(m), 2054(s), 2012(m) cm^{-1} ; (CH_3CN), $\nu(\text{CO})$: 2128(m), 2054(s), 2012(s) cm^{-1} ; (C_6H_6), $\nu(\text{CO})$: 2126(m), 2050(s), 2004(s) cm^{-1} ; (nujol), $\nu(\text{Os}-\text{Cl})$: 318(s), 296(s) cm^{-1} ; ^1H NMR (CD_2Cl_2 , rt): δ 1.81 (d, CH_3 , $^2J_{\text{P}-\text{H}} = 11.2$ Hz); $^{31}\text{P}\{^1\text{H}\}$ (CD_2Cl_2 , rt): δ -33.59 (s, PMe_3); $^{13}\text{C}\{^1\text{H}\}$ ($\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$ 1/3, -40°C): δ 12.6 (d, CH_3 , $^1J_{\text{P}-\text{C}} = 40.4$ Hz), 167.2 (d, 2C, CO, $^2J_{\text{P}-\text{C}} = 9.2$ Hz), 168.0 (d, 1C, CO, $^2J_{\text{P}-\text{C}} = 107.6$ Hz); MS (EI, m/z): 422 (M^+), (Cl, m/z): 387 ($\text{M}-\text{Cl}$) $^+$; mp: at 119°C the colorless crystals became

opaque and there was no further change to 200°C ; Anal. Calc. for $\text{C}_6\text{H}_9\text{Cl}_2\text{O}_3\text{OsP}$: C, 17.11; H, 2.15. Found: C, 17.30; H, 2.16.

3.5. Synthesis of $[\text{Os}(\text{CO})_2(\text{PMe}_3)(\text{Cl})(\mu\text{-Cl})_2]$ (**3**)

A solution of *mer-cis-2* (0.020 g, 0.048 mmol) in $\text{C}_6\text{H}_5\text{CH}_3-\text{CH}_3\text{CN}$ (15 ml, 2/1 v/v, respectively) was stirred in the dark at 50°C for 18 h. After this period, the IR $\nu(\text{CO})$ bands for *mer-cis-2* were no longer present in the solution and the sole product, as suggested by the IR $\nu(\text{CO})$ bands present, was **3**. The solution was evaporated to dryness on the vacuum line and the white solid recrystallized from $\text{C}_6\text{H}_5\text{CH}_3-\text{CH}_2\text{Cl}_2$ to afford small white star-shaped crystals of **3** (0.010 g, 54% yield). Repeated attempts to grow crystals suitable for crystallographic analysis were unsuccessful. The ^{13}C -labeled **3** was prepared from ^{13}C -labeled *mer-cis-2*. For **3**: IR (CH_2Cl_2), $\nu(\text{CO})$: 2050(s), 1983(s) cm^{-1} ; (CH_3CN), $\nu(\text{CO})$: 2047(s), 1971(s) cm^{-1} ; (nujol), $\nu(\text{Os}-\text{Cl})$: 314(m), 273(m), 242(m) cm^{-1} ; ^1H NMR (CD_3CN , 35°C): δ 1.76 (d, CH_3 , $^2J_{\text{P}-\text{H}} = 11.7$ Hz), 1.80 (d, CH_3 , $^2J_{\text{P}-\text{H}} = 11.7$ Hz); relative intensities 3:1, respectively; $^{31}\text{P}\{^1\text{H}\}$ (CD_3CN , 35°C): δ -30.73 (s, PMe_3), -30.37 (s, PMe_3); relative ratios 3:1, respectively; $^{13}\text{C}\{^1\text{H}\}$ ($\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$ 1/3, -40°C): δ 15.5 (d, PMe_3 , $^1J_{\text{P}-\text{C}} = 43.1$ Hz), 170.5 (d, 4C, CO, $^2J_{\text{P}-\text{C}} = 10.0$ Hz), 170.9 (d, br, 11C, CO, $^2J_{\text{P}-\text{C}} = 11.0$ Hz), 171.9 (d, br, 12C, CO, $^2J_{\text{P}-\text{C}} = 5.8$ Hz); MS (EI, m/z): 753 (M^+-Cl); mp: 257°C dec.; Anal. Calc. for $\text{C}_{10}\text{H}_{18}\text{Cl}_4\text{O}_4\text{Os}_2\text{P}_2$: C, 15.27; H, 2.31. Found: C, 15.75; H, 2.38.

3.6. Preparation of *fac-Os(CO)₃(PMe₃)(CCl₃)Cl* (**4**)

Typically 5×10^{-3} – 1.0×10^{-2} g of $\text{Os}(\text{CO})_4(\text{PMe}_3)$ were placed in a vial, in the drybox, in minimal light and to this was added C_6H_6 (0.5 ml) and, depending on the experiment, an excess (10 drops) of CCl_4 . This mixture was then filtered and transferred to a 5 mm NMR tube fitted with a J. Young valve. The room temperature sample was maintained in the absence of light and a ^1H NMR spectrum obtained of the sample with a presaturation pulse program on a Bruker AMX 400 spectrometer. The air-cooled sample was then photolyzed (200W medium pressure mercury arc lamp, water and air cooled) through a CS 3-74 filter ($\lambda > 400$ nm) for 2–3 h.¹¹ The ^1H NMR spectrum was reacquired. Immediately following this procedure an IR spectrum of the sample was obtained in C_6H_6 .

3.7. X-ray structure determinations

Intensity data were collected at room temperature on an Enraf Nonius diffractometer by using graphite-monochromated Mo K α radiation, in bisecting geometry.

Background measurements for each scan were made by extending the scan width by 25% on each side of the peak. The final unit cell was determined from 25 well-centered high-angle reflections chosen to be as widely scattered in reciprocal space as possible. Crystal orientation was checked by monitoring three orientation standards after every 200 reflections. Two intensity standards were measured at intervals of 60 min of exposure time.

The final least-squares refinement included coordinates and anisotropic thermal parameters for all non-H atoms. An extinction parameter was refined for both structures. Counterweights were employed in the weighting schemes. Complex scattering factors for neutral atoms [34] were used in the calculation of structure factors. The NRCVAX Crystal Structure System suite of programs [35] was used in data reduction, structural solution and initial refinement. The program suite CRYSTALS [36] was employed in the latter stages, including placement of the H atoms. All computations were carried out on a MicroVAX-II computer.

3.8. Molecular structure of *mer-cis-Os(CO)₃(PMe₃)Cl₂* (*mer-cis-2*)

X-ray quality crystals of *mer-cis-2* proved difficult to grow as the complex has a tendency to form crystals that are of the appropriate size in only two dimensions (i.e., platelike). This problem was overcome by dissolving *mer-cis-2* in a minimum amount of THF in an NMR tube and layering C₆H₁₄ on top of the THF and placing the NMR tube within a Schlenk tube filled with N₂ in the freezer (at ~ -40°C). A colorless block cut from a large needle was used for intensity measurements. The two intensity standards showed random variations corresponding to scale changes of ±2%. A Gaussian correction was applied [37]. The H atoms were located directly from a difference map. The H atoms were given a common isotropic temperature factor, and their coordinates refined, with the C–H distances restrained to their mean. The largest residual peak in the final difference map was 0.44(9) eÅ⁻³, located 1.10 Å from the Os atom.

3.9. Molecular structure of *fac-Os(CO)₃(PMe₃)Cl₂* (*fac-2*)

X-ray quality crystals of *fac-2* also proved difficult to grow for the same reasons as the *mer* isomer. This problem was overcome by dissolving the compound in a minimum amount of C₆H₅CH₃ in an NMR tube and placing the NMR tube within a Schlenk flask charged with C₆H₁₄. The vessel and the contents were frozen and evacuated and allowed to warm slowly to room temperature, allowed to stand for a day at room temperature before placing the Schlenk tube in the freezer

(~ -40°C) to afford suitable crystals. A colorless block cut from a large needle was used for intensity measurements. The two intensity standards showed steady decay corresponding to scale changes of about 14%. An empirical absorption correction [38] was employed, together with a θ -dependent correction for a sphere of 150 μm diameter. There were two crystallographically distinct molecules in the asymmetric unit. The H atoms were placed in calculated positions and linked to the C atoms that they were attached to; each group of H's were given a common isotropic thermal parameter. The largest residual peak in the final difference map was 0.82(15) eÅ⁻³, located 0.91 Å from Os(2).

4. Supplementary material

Two pages of discussion relating to bond lengths and bond angles of *mer-cis-2* and *fac-2*. Eleven tables showing the atomic coordinates, bond lengths, bond angles, anisotropic thermal parameters and close intermolecular contacts for *mer-cis-2* and *fac-2*, and the experimental details of the products of the photolysis of Os(CO)₄PMe₃ in the presence of CCl₄. One figure showing the infrared spectroscopic changes for the reaction of *fac-2* / **3** under CO.

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