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Dioxygen oxidation of a carbonyl ligand to form a chelating peroxycarbonyl ligand: synthesis, structure, and reactions of $\overline{\mathrm{Os(C[O]OO}}\mathrm{)Cl(NO)(PPh_3)_2}$

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Dedicated to Professor Helmut Werner on the occasion of his 70th birthday, in recognition of his many major contributions to inorganic and organometallic chemistry

Abstract

Reaction between the carbonyl, nitrosyl complex, $\mathrm{OsCl(CO)(NO)(PPh_3)_2}$ (**1**) and dioxygen results in combination of CO and O_2, forming a chelating peroxycarbonyl ligand in the yellow complex, $\overline{\mathrm{Os(C[O]OO}}\mathrm{)Cl(NO)(PPh_3)_2}$ (**2**). Confirmation of the unique peroxycarbonyl ligand arrangement in **2** is provided by crystal structure determination. When **2** is heated, as a suspension in heptane under reflux, there is a rearrangement to the regular chelating carbonate ligand in the orange complex, $\overline{\mathrm{Os(OC[O]O}}\mathrm{)Cl(NO)(PPh_3)_2}$ (**3**). The structure of **3** has also been determined by X-ray crystallography. Compound **2** also undergoes the following reactions: with water, releasing CO_2 and forming $\mathrm{Os(OH)_2Cl(NO)(PPh_3)_2}$ (**4**); with HCl releasing CO_2 and forming $\mathrm{Os(OH)Cl_2(NO)(PPh_3)_2}$ (**5**); and with excess triphenylphosphine releasing CO_2 and triphenylphosphine oxide forming $\mathrm{OsCl(NO)(PPh_3)_3}$ (**6**).

Keywords: Peroxycarbonyl complex; Carbonate; Osmium; X-ray crystal structure

1. Introduction

The oxidation with dioxygen of a carbonyl ligand bound in a low oxidation state complex, with the resulting formation of a carbonate ligand, has been reported on several occasions. A good example is the iridium(I) carbonyl complex with the tripodal ligand 1,1,1-tris(diphenylphosphinomethyl)ethane (TDPME), IrCl(CO)(TDPME), which undergoes a reaction with dioxygen to form $\mathrm{IrCl(\kappa^2\text{-}O_2CO)(TDPME)}$ [1]. The iridium(I) carbonyl complex with the ligand *o*-diphenylphosphino-*N*,*N*-dimethylaniline (PN), IrCl(CO)PN also reacts with dioxygen but here CO_2 is formed along with an hydroxy-bridged iridium complex [2]. Related observations are that the dioxygen complexes $\mathrm{Pt(O_2)(PPh_3)_2}$ and $\mathrm{Ir(O_2)(CH_3)(CO)(PR_3)_2}$ (R = *p*-tolyl) with CO form $\mathrm{Pt(\kappa^2\text{-}O_2CO)(PPh_3)_2}$ [3] and $\mathrm{Ir(\kappa^2\text{-}O_2CO)(CH_3)(CO)(PR_3)_2}$ [4], respectively. In the paper describing the formation of $\mathrm{IrCl(\kappa^2\text{-}O_2CO)(TDPME)}$ from IrCl(CO)(TDPME) and O_2 it is suggested that a reasonable intermediate to the chelating carbonate ligand might be a peroxycarbonyl complex (**I**) (see Chart 1). The same peroxycarbonyl binding mode is also drawn as a possible intermediate in [2].

The peroxycarbonyl fragment can also be envisioned as bridging between two metal centres as depicted in **II** in Chart 1 or perhaps with additional carbonyl oxygen coordination as in **IIa** or **IIb**. The binding mode **IIa** has been proposed in the product from reaction between $\mathrm{Pt(O_2)(PPh_3)_2}$ and $\mathrm{[PtCl(CO)(PPh_3)_2]^+}$ but this has not been confirmed by crystal structure determination [5]. The binding mode **II**, spanning an Os–Os bond of the

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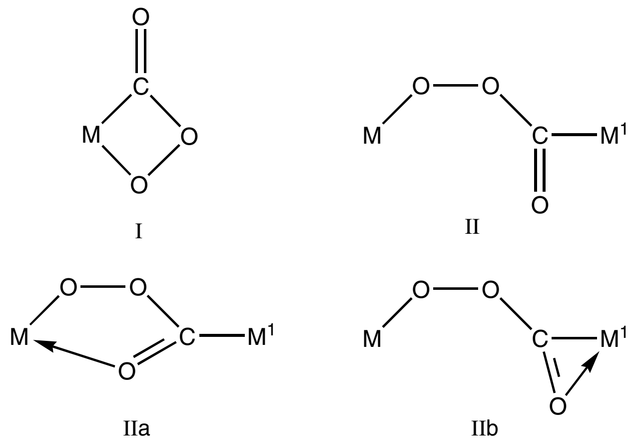
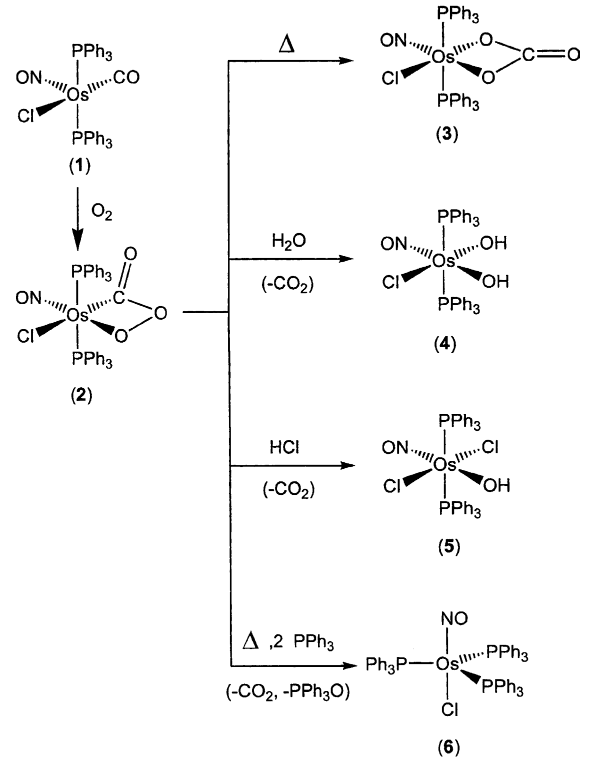


Chart 1. Possible binding modes for the fragment “O$_2$CO” to one and two metals.



Scheme 1. Synthesis and reactions of the peroxycarbonyl complex, Os(C[O]OO)Cl(NO)(PPh$_3$)$_2$ (**2**).

Os$_3$ triangle, has been proposed for the initial dioxygen oxidation product of the anion [(μ-H)Os$_3$(CO)$_{11}$]$^-$ [6].

In this paper, we report: (i) the formation of a stable crystalline peroxycarbonyl complex, Os(C[O]OO)-Cl(NO)(PPh$_3$)$_2$ (**2**) and define the chelating peroxycarbonyl binding mode **I** by crystal structure determination of **2**, (ii) the thermal rearrangement of **2** to the normal chelating carbonate complex, Os(OC[O]O)Cl(NO)-(PPh$_3$)$_2$ (**3**), (iii) the crystal structure of **3**, (iv) reactions of **2**, with water and HCl which result in release of CO$_2$, and the formation of hydroxyl osmium(II) complexes, and (v) the formation of a zero oxidation state complex, OsCl(NO)(PPh$_3$)$_3$, in the presence of triphenylphosphine with formation of triphenylphosphineoxide.

2. Results and discussion

2.1. Reaction of OsCl(CO)(NO)(PPh$_3$)$_2$ with dioxygen and the structure of Os(C[O]OO)Cl(NO)(PPh$_3$)$_2$ (2)

Treatment of a solution of OsCl(CO)(NO)(PPh$_3$)$_2$ in dichloromethane/ethanol with dioxygen at atmospheric pressure results in a rapid colour change from brown to yellow and bright yellow crystals of a 1:1 adduct of OsCl(CO)(NO)(PPh$_3$)$_2$ and O$_2$ are formed (see Scheme 1). We first reported this observation in 1968 and described the yellow product as a carbonate complex [7]. The IR spectrum of the yellow crystals shows ν(NO) at 1780 cm^{-1} and other bands at 1710, 1310, and 1025 cm^{-1} which were associated with the carbonate ligand. However, a later report [3] of the IR spectrum of the related carbonate complex, Pt(κ^2-O$_2$CO)(PPh$_3$)$_2$, gave absorptions for the carbonate ligand at 1685, 1185, 980, and 815 cm^{-1}. These values do not compare favourably with those found for the yellow crystals. Further doubt was cast on the original formulation when it was discovered that the ^{13}C NMR spectrum of the yellow oxidation product revealed a resonance at δ, 169.4 ppm which was a triplet ($J_{\mathrm{CP}} = 6.7$ Hz) suggesting that the “CO$_3$” ligand had a metal-bound carbon atom. Accordingly, the yellow 1:1 adduct of OsCl(CO)(NO)(PPh$_3$)$_2$ and O$_2$ was re-formulated as the peroxycarbonyl complex, Os(C[O]OO)Cl(NO)(PPh$_3$)$_2$ (**2**). Confirmation that **2** did contain the unusual peroxycarbonyl ligand bound as **I** in Chart 1 was sought through a crystal structure determination of **2**. Initially the structure solved well for everything except the electron density in the equatorial plane. The arrangement of the Cl, NO, and peroxycarbonyl ligands appeared to be disordered and made little chemical sense. Eventually, it was appreciated that the structure was disordered by a 180° rotation about the N(1)–Os–O(2) vector with the two orientations present in a ratio of 2:1.

The molecular geometry of **2** is shown in Fig. 1. Crystal data pertaining to this structure and also to the structure of **3** (see below) are presented in Table 1. Selected bond lengths and angles for **2** are collected in Table 2. The overall geometry about osmium is octahedral with the two triphenylphosphine ligands arranged mutually *trans*. One of the peroxy oxygen atoms (O(2)) is *trans* to the nitrosyl ligand. The Os–C(1) distance is short at 1.932(18) Å and is in fact a typical Os–CO distance. The O(2)–O(3) distance of 1.493(11) Å is normal for a peroxide linkage. All other bond lengths and angles are as expected.

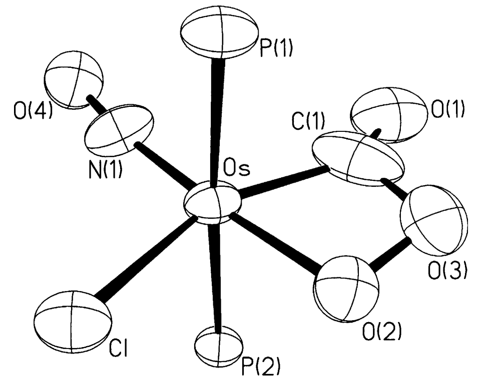


Fig. 1. Molecular geometry of Os(C[O]OO)Cl(NO)$(PPh_3)_2$ (**2**) (phenyl rings omitted from PPh_3 ligands).

Table 1
Crystal data and structure refinement parameters[a]

Compound	**2**	**3**
Empirical formula	$C_{37}H_{30}ClNO_4OsP_2$	$C_{37}H_{30}ClNO_4OsP_2$
Molecular weight	840.21	840.21
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a (Å)	9.966(3)	12.249(1)
b (Å)	9.9980(11)	16.404(1)
c (Å)	17.098(2)	17.752(1)
α (°)	92.880(10)	90.0
β (°)	96.570(15)	111.00(1)
γ (°)	98.610(14)	90.0
V $(Å)^3$	1 669.4(5)	3330.0(4)
Z	2	4
D_{calc} $(g\,cm^{-3})$	1.671	1.676
D_{obs} $(g\,cm^{-3})$	1.67	1.68
$F(000)$	828	1 656
μ (mm^{-1})	4.036	4.047
Crystal size (mm)	0.34 × 0.23 × 0.14	0.19 × 0.17 × 0.16
θ (min–max) (°)	1.20–27.01	1.75–26.96
Reflections collected	7293	7804
Independent reflections	6948, R_{int} 0.019	7000, R_{int} 0.030
T (min, max)	0.421, 0.636	0.522, 0.613
Goodness-of-fit on F^2	1.034	1.042
R, wR_2 (observed data)	0.0392, 0.0983	0.0229, 0.0519

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Following the usual convention that a linear NO ligand be regarded as formally NO^+, complex **2** can be assigned the oxidation state +2. Thus Os(C[O]OO)Cl(NO)$(PPh_3)_2$ (**2**) can be regarded as an octahedral (d^6) complex of osmium(II) and likewise complexes **3**–**5**, discussed below are all octahedral complexes of osmium(II). As depicted in Scheme 1, OsCl(CO)(NO)$(PPh_3)_2$ (**1**) may have a bent NO ligand (formally NO^-) and would therefore be coordinatively unsaturated thus permitting coordination of dioxygen and the overall process forming the peroxycarbonyl complex **2** could be thought of as an inter-ligand combination reaction.

Table 2
Selected bond lengths (Å) and angles (°) for **2**

Os–Cl	2.454(5)
Os–P(1)	2.4370(14)
Os–P(2)	2.4373(13)
Os–O(2)	2.022(5)
Os–N	1.730(6)
Os–C(1)	1.932(18)
O(1)–C(1)	1.170(19)
O(3)–C(1)	1.409(17)
O(2)–O(3)	1.493(11)
C(1)–Os–O(2)	68.8(5)
Os–C(1)–O(1)	138.9(14)
Os–C(1)–O(3)	98.5(9)
O(1)–C(1)–O(3)	122.1(17)
C(1)–O(3)–O(2)	100.7(9)
Os–O(2)–O(3)	91.9(4)
P(1)–Os–P(2)	175.99(6)

We are aware of only one other stable peroxycarbonyl complex of the type exemplified by complex **2**. This is the 1:1 adduct of the carbyne complex, Os(CAr)Cl(CO)$(PPh_3)_2$ (Ar = *p*-dimethylaminophenyl) and O_2, which has IR bands at 1680 and 1058 cm^{-1}, closely comparable with those found for complex **2** [8]. This complex, Os(C[O]OO)Cl(CAr)$(PPh_3)_2$, also releases CO_2 when treated with acids.

2.2. Thermal rearrangement of Os(C[O]OO) Cl(NO) $(PPh_3)_2$ (2) to Os(OC[O]O)Cl(NO)$(PPh_3)_2$ (3) and the crystal structure of Os(OC[O]O) Cl(NO) $(PPh_3)_2$ (3)

If a solution of Os(C[O]OO)Cl(NO)$(PPh_3)_2$ (**2**) in benzene is heated under reflux the only identifiable complex, formed in very low yield, is the dioxygen complex, $Os(O_2)Cl(NO)(PPh_3)_2$. However, if Os(C[O]OO)Cl(NO)$(PPh_3)_2$ (**2**) is *suspended* in heptane and heated under reflux there is formed, in good yield, the orange carbonate complex, Os(OC[O]O) Cl(NO) $(PPh_3)_2$ (**3**) (see Scheme 1). In the IR spectrum of **3** ν(NO) is at 1820, 1775 cm^{-1} (solid state splitting, in CH_2Cl_2 solution, 1800 cm^{-1}), which is higher than the value found for complex **2**. IR bands associated with the chelated carbonate ligand are seen at 1705, 1168, 970, and 790 cm^{-1} which show a close correspondence with those reported for $Pt(\kappa^2\text{-}O_2CO)(PPh_3)_2$ (1685, 1185, 980, and 815 cm^{-1}). As expected, the ^{13}C NMR spectrum reveals a carbon resonance for the carbonate carbon at δ, 160.2 ppm which is a singlet.

Chemically, the carbonate ligand in complex **3** is rather inert and when **3** is heated with dilute HCl no reaction ensues and **3** is recovered unchanged. In contrast, the peroxycarbonyl ligand in complex **2** is much more reactive (see below). For comparison with complex **2**,

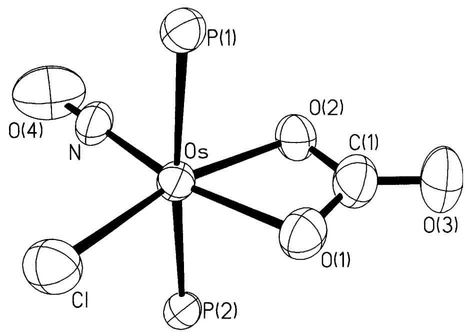


Fig. 2. Molecular geometry of $\overline{\mathrm{Os(OC[O]O}}\mathrm{)Cl(NO)(PPh_3)_2}$ (**3**) (phenyl rings omitted from PPh_3 ligands).

Table 3
Selected bond lengths (Å) and angles (°) for **3**

Os–Cl	2.3630(14)
Os–P(1)	2.4343(12)
Os–P(2)	2.4401(12)
Os–O(1)	2.045(3)
Os–O(2)	2.056(3)
Os–N	1.818(5)
O(1)–C(1)	1.370(6)
O(2)–C(1)	1.351(6)
C(1)–O(3)	1.210(6)
Os–O(1)–C(1)	92.5(3)
Os–O(2)–C(1)	92.6(3)
O(1)–Os–O(2)	65.50(14)
O(1)–C(1)–O(2)	109.3(4)
O(1)–C(1)–O(3)	124.8(6)
O(2)–C(1)–O(3)	125.9(5)
P(1)–Os–P(2)	175.23(4)

the crystal structure of $\overline{\mathrm{Os(OC[O]O}}\mathrm{)Cl(NO)(PPh_3)_2}$ (**3**) was determined.

The molecular geometry of **3** is shown in Fig. 2. Selected bond lengths and angles for **3** are collected in Table 3. The overall geometry about osmium is again octahedral with the two triphenylphosphine ligands arranged mutually *trans*. The carbonate ligand is remarkably symmetrical with Os–O(1) (*trans* to NO) being 2.045(3) Å and Os–O(2) (*trans* to Cl) being 2.056(3) Å. The Os–Cl distance of 2.3630(14) Å is much shorter than that found in **2** (2.454(5) Å) but is close to the mean value for previously determined Os–Cl distances (mean = 2.389 Å, standard deviation = 0.067 [1]). Clearly, carbon has a greater *trans* influence than oxygen.

2.3. Reactions of $\overline{\mathrm{Os(C[O]OO}}\mathrm{)Cl(NO)(PPh_3)_2}$ (2) with water, HCl, and PPh_3

These reactions can be followed in Scheme 1. In marked contrast to the lack of reactivity exhibited by the carbonate complex **3**, the peroxycarbonyl complex, $\overline{\mathrm{Os(C[O]OO}}\mathrm{)Cl(NO)(PPh_3)_2}$, reacts readily with water releasing CO_2 and forming the dihydroxy complex, $\mathrm{Os(OH)_2Cl(NO)(PPh_3)_3}$ (**4**). The ease with which this reaction occurs can be judged from the fact that even solid samples of **2** stored in moist air are converted quantitatively into **4**. The IR spectrum of yellow complex **4** has ν(NO) at 1772 cm^{-1}, slightly lower than ν(NO) for **2** and **3**. There is also an absorption at 3560 cm^{-1} assigned to ν(OH).

Complex **2** reacts with one equivalent of dilute aqueous HCl to form the mono-hydroxy complex, $\mathrm{Os(OH)Cl_2(NO)(PPh_3)_3}$ (**5**). The IR spectrum of yellow **5** has ν(NO) at 1790 cm^{-1}. The comparatively small increase in ν(NO) from the value of 1772 cm^{-1} found for **4**, suggests that the hydroxy group is positioned *trans* to the nitrosyl ligand. Further support for this geometry, with a mutually *trans* arrangement of Cl ligands, is provided by the observation of only one ν(OsCl) band at 313 cm^{-1}.

When a benzene solution of the peroxycarbonyl complex, $\overline{\mathrm{Os(C[O]OO}}\mathrm{)Cl(NO)(PPh_3)_2}$, is heated the solution becomes very dark and the only identifiable complex formed, in very low yield, is $\mathrm{Os(O_2)Cl(NO)(PPh_3)_2}$. However, when three or more equivalents of triphenylphosphine are added to the solution, and with rigorous exclusion of dioxygen, a clean reaction ensues forming CO_2, triphenylphosphineoxide, and the green zero oxidation state complex, $\mathrm{OsCl(NO)(PPh_3)_3}$ (**6**). As expected for a zero oxidation state complex the IR spectrum of **6** has ν(NO) at 1630 cm^{-1} which is ca. 150 cm^{-1} lower than the values found for the osmium(II) nitrosyl complexes described in this paper. Complex **6** undergoes numerous oxidative addition reactions which have been described elsewhere [9]. Two interesting examples are the formation of an osmium methylene complex, $\mathrm{Os(CH_2)Cl(NO)(PPh_3)_2}$ [10], and a carbon disulfide complex, $\mathrm{Os(\eta^2\text{-}CS_2)Cl(NO)(PPh_3)_2}$ [11]. The reactions of complex **6** are, in general, very similar to those of the remarkable four coordinate, planar complex, $\mathrm{OsCl(NO)(P^iPr_3)_2}$ described by Werner et al. [12].

3. Conclusions

A stable intermediate in the oxidation of a carbonyl ligand to a carbonate ligand is confirmed by a crystal structure determination to contain the chelating peroxycarbonyl ligand. This complex, $\overline{\mathrm{Os(C[O]OO}}\mathrm{)Cl(NO)(PPh_3)_2}$ (**2**), is shown to undergo a thermal rearrangement to a carbonate complex, $\overline{\mathrm{Os(OC[O]O}}\mathrm{)Cl(NO)(PPh_3)_2}$ (**3**). The peroxycarbonyl ligand in complex **2** is reactive and protic reagents release CO_2 and form hydroxyl osmium(II) complexes. In the absence of protic reagents CO_2 is still released but the remaining oxygen atom is transferred to a triphenylphosphine li-

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[1] Cambridge Crystallographic Data Base.

gand forming triphenylphosphineoxide. When excess triphenylphosphine is present the zero oxidation state nitrosyl complex, $\mathrm{OsCl(NO)(PPh_3)_3}$, can be isolated.

4. Experimental

4.1. General procedures and instruments

Standard laboratory procedures were followed as have been described previously [13]. The compound $\mathrm{OsCl(CO)(NO)(PPh_3)_2}$ (**1**) [7,14] was prepared according to the literature method.

Infrared spectra (4000–400 $\mathrm{cm^{-1}}$) were recorded as Nujol mulls between KBr plates on a Perkin–Elmer 597 spectrometer. ^{13}C NMR spectra were obtained on a Jeol JNM FX-60 at 25 °C. Resonances are quoted in ppm and ^{13}C NMR spectra were referenced to $\mathrm{CDCl_3}$ (77.00 ppm). Elemental analyses were obtained from the Microanalytical Laboratory, University of Otago.

4.2. Preparation of $\overline{\mathrm{Os(C[O]OO)}}\mathrm{Cl(NO)(PPh_3)_2}$ (2)

$\mathrm{OsCl(CO)(NO)(PPh_3)_2}$ (1.000 g) was dissolved in a mixture of $\mathrm{CH_2Cl_2}$ (100 mL) and ethanol (10 mL). The solution was stirred for 10 min under $\mathrm{O_2}$ (1 atm) during which time the colour changed from brown to yellow. Reduction of the solvent to low volume using a rotary evaporator gave pure **2** as bright yellow crystals (0.810 g, 78%). *Anal.* Calc. for $\mathrm{C_{37}H_{30}ClNO_4OsP_2}$: C, 52.89; H, 3.60; N, 1.67. Found C, 52.92; H, 4.03; N, 1.57%. IR ($\mathrm{cm^{-1}}$): 1780vs ν(NO); 1710s, 1310m, 1025m (peroxycarbonyl); 315s ν(OsCl). ^{13}C NMR ($\mathrm{CDCl_3}$, δ): 126.9 (t′ [13], $^{1,3}J_{\mathrm{CP}} = 54.0$ Hz, i-$\mathrm{C_6H_5}$); 128.4 (t′, $^{2,4}J_{\mathrm{CP}} = 12.0$ Hz, o-$\mathrm{C_6H_5}$); 131.3 (s, p-$\mathrm{C_6H_5}$); 134.7 (t′, $^{3,5}J_{\mathrm{CP}} = 10.0$ Hz, m-$\mathrm{C_6H_5}$); 169.4 (t, $^{2}J_{\mathrm{CP}} = 6.7$ Hz, $C\mathrm{[O]O_2}$).

4.3. Preparation of $\overline{\mathrm{Os(OC[O]O)}}\mathrm{Cl(NO)(PPh_3)_2}$ (3)

$\overline{\mathrm{Os(C[O]OO)}}\mathrm{Cl(NO)(PPh_3)_2}$ (0.500 g) was suspended in distilled n-heptane (30 mL) and the mixture heated under reflux for 10 min. During this time the suspended solid changed colour from yellow to dark brown. After cooling, the resultant solid was filtered, dissolved in a minimum of $\mathrm{CH_2Cl_2}$ and subjected to chromatography on a 10×3 cm Florisil column with $\mathrm{CH_2Cl_2}$ as eluant. The bright orange band was collected and ethanol added. Removal of solvent under reduced pressure yielded orange crystals of the complex. The complex was recrystallised from $\mathrm{CH_2Cl_2}$/EtOH to give pure **3** as orange crystals (0.400 g, 77%). *Anal.* Calc. for $\mathrm{C_{37}H_{30}ClNO_4OsP_2 \cdot 1/3CH_2Cl_2}$: C, 51.63; H, 3.56; N, 1.61. Found: C, 51.93; H, 4.22; N, 1.41%. IR ($\mathrm{cm^{-1}}$): 1820vs, 1775vs ν(NO); 1705s, 1168m, 970m, 790m, 760m (carbonate). ^{13}C NMR ($\mathrm{CDCl_3}$, δ): 125.0 (t′ [13], $^{1,3}J_{\mathrm{CP}} = 54.0$ Hz, i-$\mathrm{C_6H_5}$); 128.5 (t′, $^{2,4}J_{\mathrm{CP}} = 10.0$ Hz, o-$\mathrm{C_6H_5}$); 131.5 (s, p-$\mathrm{C_6H_5}$); 134.4 (t′, $^{3,5}J_{\mathrm{CP}} = 10.0$ Hz, m-$\mathrm{C_6H_5}$); 160.2 (s, $C\mathrm{O_3}$).

4.4. Preparation of $\mathrm{Os(OH)_2Cl(NO)(PPh_3)_2}$ (4)

Solid samples of $\overline{\mathrm{Os(C[O]OO)}}\mathrm{Cl(NO)(PPh_3)_2}$ stored in a moist atmosphere for 1 week were found to be converted quantitatively to $\mathrm{Os(OH)_2Cl(NO)(PPh_3)_2}$ as a yellow solid. This material was recrystallised from $\mathrm{CH_2Cl_2}$/EtOH to give pure **4** as yellow crystals. *Anal.* Calc. for $\mathrm{C_{36}H_{32}ClNO_3OsP_2}$: C, 53.10; H, 3.96; N, 1.72; Cl, 4.35. Found: C, 53.55; H, 4.20; N, 1.65; Cl 4.64%. IR ($\mathrm{cm^{-1}}$): 1772vs ν(NO); 3560w ν(OH); 313, 306 ν(OsCl).

4.5. Preparation of $\mathrm{Os(OH)Cl_2(NO)(PPh_3)_2}$ (5)

$\overline{\mathrm{Os(C[O]OO)}}\mathrm{Cl(NO)(PPh_3)_2}$ (0.400 g, 0.476 mmol) was dissolved in $\mathrm{C_6H_6}$ (30 mL) and dilute aqueous HCl (5 mL of 0.1 M, 0.5 mmol) was added. Sufficient ethanol to make the mixture homogeneous was then added and the solution heated under reflux for 20 min. The volume of the solution was reduced using a rotary evaporator until crystals appeared in the solution. On standing the solution deposited further yellow crystals. These were recrystallised from $\mathrm{CH_2Cl_2}$/EtOH to give pure **5** as bright yellow crystals (0.35 g, 88%). *Anal.* Calc. for $\mathrm{C_{36}H_{31}Cl_2NO_2OsP_2}$: C, 51.92; H, 3.75; N, 1.68; Cl, 8.51. Found: C, 52.17; H, 3.71; N, 1.57; Cl, 8.69%. IR ($\mathrm{cm^{-1}}$): 1790vs ν(NO); 313s ν(OsCl); 628, 619, 607, 490, 444, 416.

4.6. Preparation of $\mathrm{OsCl(NO)(PPh_3)_3}$ (6)

$\overline{\mathrm{Os(C[O]OO)}}\mathrm{Cl(NO)(PPh_3)_2}$ (1.00 g) was suspended in freshly distilled, deoxygenated benzene (15 mL) with triphenylphosphine (1.00 g) and the mixture heated under reflux for 5 min. As the mixture was heated the complex dissolved and the colour changed to dark brown/black. Green crystalline material separated from the reaction mixture as the mixture cooled. Additional material could be obtained by adding freshly distilled n-hexane (50 mL) (1.15 g, 93%) and this material was of sufficient purity for further reactions. For the microanalytical sample, the original reaction mixture (benzene only, no hexane) was cooled in an ice bath and filtered rapidly under nitrogen to give pure **6** as green microcrystals (0.81 g, 65%). *Anal.* Calc. for $\mathrm{C_{54}H_{45}ClNOOsP_3}$: C, 62.21; H, 4.35; N, 1.34; P, 8.91. Found: C, 62.85; H, 4.13; N, 1.45; P, 8.43%. IR ($\mathrm{cm^{-1}}$): 1630vs ν(NO).

4.7. X-ray crystal structure determinations for complexes 2 and 3

Data were collected on an Enraf-Nonius CAD4 diffractometer at 223 and 293 K, respectively, with graphite-monochromated Mo Kα radiation (λ 0.71073

Å) using $\omega/2\theta$ scans. Absorption corrections were applied using empirical ψ scan data [15]. Structures were solved using SHELXS [16] and refined by full-matrix least squares using SHELXL [17]. Hydrogen atoms were included in calculated positions and allowed to ride on their carrier atom. In the crystal structure of **2**, the equatorial ligands are disordered by a 180° rotation about the N(1)–Os–O(2) vector. The arrangement shown in Fig. 1 is present with occupancy 0.67, whereas the alternative orientation (not shown) is present with occupancy of 0.33. Data in Table 2 are for the model with the larger occupancy. Crystal data and refinement details for structures **2** and **3** are given in Table 1.

5. Supplementary material

Crystallographic data (excluding structure factors) for **2** and **3** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. 216909 and 216910. Copies of this information can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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