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Synthesis and structure of $Os(\eta^2\text{-3,3-diphenylcyclopropene})Cl(NO)(PPh_3)_2$ and the ring-opening reactions of the π-bound cyclopropene with acids

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Dedicated to Professor Michael Mingos, FRS, in recognition of his contributions to chemistry.

Abstract

Reaction between the zerovalent nitrosyl complex, $OsCl(NO)(PPh_3)_3$ and 3,3-diphenylcyclopropene yields the robust π-adduct, $Os(\eta^2\text{-3,3-diphenylcyclopropene})Cl(NO)(PPh_3)_2$ (**1**), the crystal structure of which reveals the chloride and nitrosyl ligands located mutually *trans* and the Os, the two PPh_3 ligands and the double bond of the cyclopropene, all lying in one plane. Treatment of **1** with the acids HX ($X = Cl$, O_2CCF_3) brings about a ring-opening of the cyclopropene ring (perhaps via an intermediate diphenylvinyl carbene complex) with the organic moiety remaining bound to osmium and with ultimate formation of the σ-diphenylallyl complexes, $Os(CH_2CH{=}CPh_2)Cl_2(NO)(PPh_3)_2$ (**2**) and $Os(CH_2CH{=}CPh_2)Cl(O_2CCF_3)(NO)(PPh_3)_2$ (**3**), respectively. A crystal structure determination for **2** has been obtained.

Keywords: Nitrosyl complex; Osmium; 3,3-Diphenylcyclopropene complex; X-ray crystal structure

1. Introduction

The interaction of cyclopropene and substituted cyclopropenes with transition metals has generated much interest in organic and organometallic chemistry [1]. In addition, transition metal complexes containing η^2-bound cyclopropenes have been studied in bioinorganic chemistry in an endeavour to model nitrogenase reactivity [2].

In organometallic chemistry the reaction between cyclopropene and the metal substrate follows predominantly two pathways [1], either to give η^2-coordination of the intact cyclopropene ligand (favoured at low oxidation state metal centres) as represented by structure **A** in Chart 1, or ring-opening reactions (favoured at higher oxidation state metal centres) that can give rise to various products including vinyl alkylidene species (structure **B** in Chart 1) and metallacyclobutenes (structure **C** in Chart 1). The nature of the product formed depends on the transition metal, the nature and size of accompanying ligands, and the substituents on the cyclopropene. Numerous examples of structure type **A** have been reported and those for the following metals have been characterised by X-ray crystal structure determinations, Mo [3], W [4], Ir [5], Ni [6], and Pt [7]. Further well-characterised examples are provided by the rhoda- and iridabenzvalene compounds described by Haley [8], for which an alternative description of the bonding is as tethered η^2-cyclopropene complexes.

We have previously reported that $OsCl(NO)(PPh_3)_3$ forms stable complexes with tetrafluoroethylene and maleic anhydride viz., $Os(\eta^2\text{-}C_2F_4)Cl(NO)(PPh_3)_2$ and $Os(\eta^2\text{-}$

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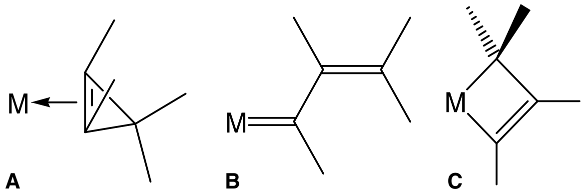


Chart 1. Three typical structure types from the interaction of cyclopropenes with metal centres.

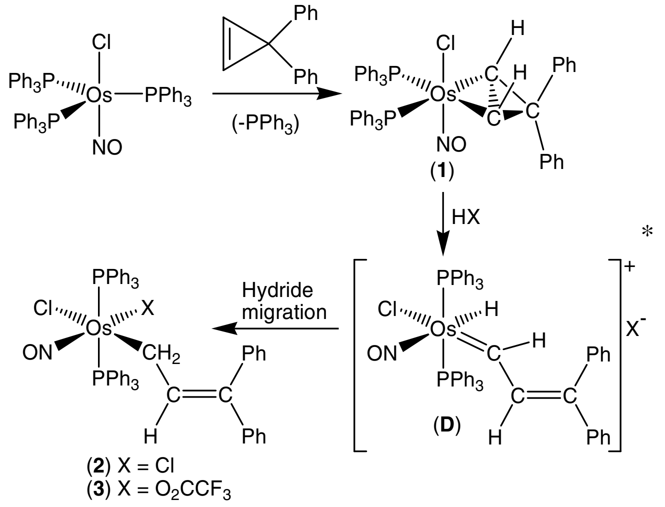
maleic anhydride)Cl(NO)$(PPh_3)_2$, respectively, and in both complexes the triphenylphosphine ligands are located mutually *trans* [9]. In this paper, we investigate the reaction between OsCl(NO)$(PPh_3)_3$ and 3,3-diphenylcyclopropene, and explore the reactivity of the resulting complex towards acids.

We describe herein: (i) the formation and crystal structure of the η^2-cyclopropene complex, Os(η^2-3,3-diphenylcyclopropene)Cl(NO)$(PPh_3)_2$ (**1**); (ii) the reaction of **1** with hydrochloric and trifluoroacetic acids to bring about ring-opening of the cyclopropene and ultimate formation of the σ-diphenylallyl complexes, Os($CH_2CH{=}CPh_2$)Cl_2(NO)$(PPh_3)_2$ (**2**) and Os($CH_2CH{=}CPh_2$)Cl(O_2CCF_3)(NO)$(PPh_3)_2$ (**3**), respectively; and (iii) the crystal structure determination of **2**.

2. Results and discussion

2.1. Reaction between OsCl(NO)$(PPh_3)_3$ and 3,3-diphenylcyclopropene to form the π-complex, Os(η^2-3,3-diphenylcyclopropene)Cl(NO)$(PPh_3)_2$ (1) and the crystal structure of complex 1

Treatment of a dark green solution of OsCl(NO)$(PPh_3)_3$ with 3,3-diphenylcyclopropene brings about an immediate colour change to orange, and bright orange crystals of Os(η^2-3,3-diphenylcyclopropene)Cl(NO)$(PPh_3)_2$ (**1**) can be isolated from the solution (see Scheme 1).



Scheme 1. Synthesis and reactions of Os(η^2-3,3-diphenylcyclopropene)Cl(NO)$(PPh_3)_2$ (**1**) with acids (compound labelled with * is a postulated intermediate).

Complex **1** has a *ν*(NO) band in the IR spectrum at 1768 cm^{-1}, greatly increased from the *ν*(NO) observed for OsCl(NO)$(PPh_3)_3$ at 1630 cm^{-1} but similar to the value observed for Os(η^2-maleic anhydride)Cl(NO)$(PPh_3)_2$ at 1780 cm^{-1} [9]. This observation is consistent with a strong η^2-interaction of the cyclopropene with the metal centre. The ^1H NMR spectrum of **1** shows the two cyclopropene protons as an apparent triplet (not a true triplet because the two carbon atoms to which these protons are bound have a more complex multiplicity, see below) at 4.07 ppm with coupling to the two phosphorus nuclei of 5.1 Hz. The ^{13}C NMR spectrum of **1** shows the two metal-bound carbon atoms as an apparent quintet at 53.5 ppm which we interpret as being part of a second-order spectrum that results because the two olefinic carbon atoms are not exactly equivalent in solution. It is worth noting that the closely related 3,3-diphenylcyclopropene complex of iridium(I), Ir(η^2-3,3-diphenylcyclopropene)Cl(CO)$(PMe_3)_2$, which has the same structure as **1** (see below), has been reported to show exactly the same multiplicity for the olefinic carbon atoms, and the resonance in this case was described as a pseudoquintet at 37.1 ppm [5]. In the ^{31}P NMR spectrum of **1** the phosphorus resonance appears as a singlet at −3.13 ppm. None of the above spectroscopic information unambiguously defines the geometry of **1** and therefore an X-ray crystal structure determination of **1** was undertaken.

The molecular geometry of **1** is depicted in Fig. 1.

Crystal data pertaining to this structure and the other structure reported in this paper are presented in Table 1. Selected bond lengths and angles for **1** are collected in Table 2. The overall geometry about osmium can be described as distorted octahedral with the two triphenylphosphine ligands arranged mutually *cis* (P(1)–Os–P(2),

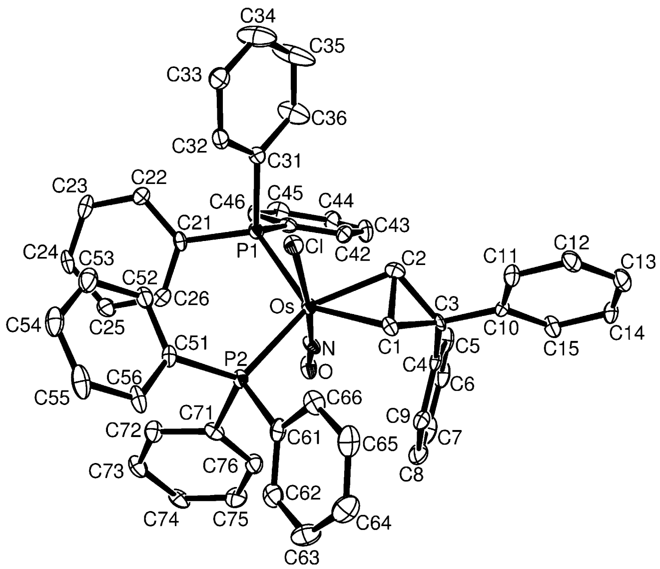


Fig. 1. Molecular geometry of Os(η^2-3,3-diphenylcyclopropene)Cl(NO)$(PPh_3)_2$ (**1**) showing the atom labelling and atoms as 50% probability displacement ellipsoids [22].

Table 1
Data collection and processing parameters for **1** and **2**

Compound	1	2
Formula	$C_{51}H_{42}ClNOOsP_2$	$C_{51}H_{43}Cl_2NOOsP_2$
Molecular weight	972.45	1008.90
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$C2/c$
a (Å)	13.6674(2)	31.6520(5)
b (Å)	11.1122(2)	10.6344(1)
c (Å)	27.9419(1)	26.3414(3)
α (°)	90.0	90.0
β (°)	101.305(1)	106.249(1)
γ (°)	90.0	90.0
V (Å^3)	4161.3(1)	8512.3(2)
T (K)	84	84
Z	4	8
D_{calc} (g cm^{-3})	1.552	1.574
$F(000)$	1944	4032
μ (mm^{-1})	3.245	3.237
Crystal size (mm)	$0.42 \times 0.26 \times 0.20$	$0.202 \times 0.15 \times 0.10$
2θ (minimum–maximum) (°)	1.98–25.50	1.78–25.69
Reflections collected	31 373	23 306
Independent reflections (R_{int})	7752 (0.0512)	8043 (0.0684)
T (minimum–maximum)	0.4297–0.5521	0.5646–0.8249
Goodness-of-fit on F^2	0.991	1.027
R (observed data)	$R_1 = 0.0428$, $wR_2 = 0.0907$	$R_1 = 0.0416$, $wR_2 = 0.0846$
R (all data)	$R_1 = 0.0648$, $wR_2 = 0.0982$	$R_1 = 0.0651$, $wR_2 = 0.0935$

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

111.62(5)°) and the chloride and nitrosyl ligands mutually *trans* (N–Os–Cl, 173.65(19)°). The two olefinic carbon atoms of the cyclopropene occupy the remaining two sites with the very small bite angle of 41.6(2)°. The two Os–C distances are equivalent (Os–C(1), 2.081(6); Os–C(2), 2.095(6) Å) as are the two Os–P distances (Os–P(1), 2.4288(15); Os–P(2), 2.4323(14) Å). The Os–C distances are short when compared with a regular Os–C σ-bond such as that in complex **2** (see below) where the Os–$CH_2CH{=}CPh_2$ distance is 2.196(5) Å. The C(1)–C(2) distance is 1.485(7) Å, indicative of a C–C single bond and reflecting the strong interaction of the cyclopropene with osmium and justifying the depiction of the complex in Scheme 1 as a metallabicyclobutane. The overall structure is closely similar to that reported for the related compound Ir(η^2-3,3-diphenylcyclopropene)Cl(CO)$(PMe_3)_2$ [5] where the C–C distance is 1.445(9) Å. It may be significant that in both structures the cyclopropene ligand is buckled towards the π-acid ligand (CO or NO).

Table 2
Selected bond lengths (Å) and angles (°) for **1**

Bond lengths (Å)	
Os–N	1.749(5)
Os–C(1)	2.081(6)
Os–C(2)	2.095(6)
Os–Cl	2.4228(14)
Os–P(1)	2.4288(15)
Os–P(2)	2.4323(14)
O–N	1.171(6)
C(1)–C(2)	1.485(7)
C(2)–C(3)	1.542(8)
C(1)–C(3)	1.542(7)
C(3)–C(4)	1.502(8)
C(3)–C(10)	1.530(9)
Bond angles (°)	
N–Os–C(1)	105.4(2)
N–Os–C(2)	102.9(2)
C(1)–Os–C(2)	41.6(2)
N–Os–Cl	173.65(19)
C(1)–Os–Cl	80.93(14)
C(2)–Os–Cl	81.88(15)
N–Os–P(1)	87.32(18)
C(1)–Os–P(1)	144.08(14)
C(2)–Os–P(1)	103.23(16)
Cl–Os–P(1)	87.50(5)
N–Os–P(2)	93.80(15)
C(1)–Os–P(2)	101.07(14)
C(2)–Os–P(2)	141.91(16)
Cl–Os–P(2)	84.69(5)
P(1)–Os–P(2)	111.62(5)
C(1)–C(2)–C(3)	61.2(3)
C(2)–C(1)–C(3)	61.2(4)
C(2)–C(3)–C(1)	57.6(3)
C(3)–C(1)–Os	108.7(4)
C(1)–C(2)–Os	68.7(3)
C(3)–C(2)–Os	108.1(3)
C(4)–C(3)–C(10)	116.7(5)
C(4)–C(3)–C(2)	123.2(5)
C(10)–C(3)–C(2)	112.5(5)

*2.2. Reactions of Os(η^2-3,3-diphenylcyclopropene)Cl(NO)$(PPh_3)_2$ (1) with HCl and trifluoroacetic acid to form Os($CH_2CH{=}CPh_2$)Cl_2(NO)$(PPh_3)_2$ (2) and Os($CH_2CH{=}CPh_2$)Cl(O_2CCF_3)(NO)$(PPh_3)_2$ (3), respectively, and the crystal structure of complex **2***

Previous investigations of the protonation of η^2-cyclopropene metal complexes have reported that the organic fragment is lost from the metal and the isolated organic products are the reduced cyclopropanes or derived ring-opened alkenes. Nb(η^2-C_3H_4)Cp_2 for example, with HCl gives only cyclopropane [10]. On the other hand, Leigh et al., have made a detailed study of the reaction between Pt(η^2-3,3-diphenylcyclopropene)$(PPh_3)_2$ and HCl and demonstrated that not only 1,1-diphenylcyclopropane but 3,3-diphenylpropene, 1,2-diphenylpropene, and 1,1-diphenylpropene, are formed as well [1,11]. These organic products are all proposed to arise from a cyclopropyl–platinum intermediate which may rearrange to a σ-allyl platinum complex before final cleavage from platinum.

It is frequently observed that the reaction of acids with low oxidation state osmium complexes containing unsaturated molecules bound as ligands give rise to isolable complexes in which a reduced form of the ligand is retained in the osmium coordination sphere [12]. An example is the η^2-ethylene complex of osmium, Os(η^2-C_2H_4)$(CO)_2(PPh_3)_2$ which reacts with HCl to give the isolable σ-bound ethyl complex Os(C_2H_5)Cl$(CO)_2(PPh_3)_2$ [13]. It might therefore have been expected that treatment of complex **1** with HCl might generate the related σ-bound 2,2-diphenylcyclopropyl complex, "Os($C_3H_3Ph_2$)Cl_2(NO)$(PPh_3)_2$". In fact, as shown in Scheme 1 treatment of **1** with either HCl or trifluoroacetic acid generates, in high yield, the stable, yellow, σ-bound diphenylallyl complexes $Os(CH_2CH{=}CPh_2)Cl_2(NO)(PPh_3)_2$ (**2**) or $Os(CH_2CH{=}CPh_2)Cl(O_2CCF_3)(NO)(PPh_3)_2$ (**3**), respectively. This surprising result can be rationalized if it is supposed that initial protonation at the osmium (oxidation) brings about a ring-opening of the cyclopropene ring to form an intermediate diphenylvinyl carbene complex, the proposed intermediate **D** in Scheme 1. This is reasonable since ruthenium(II) and osmium(II) substrates have been shown to react with 3,3-diphenylcyclopropene to form ring-opened diphenylvinyl carbene complexes [4]. Since there is an adjacent hydride ligand in this intermediate, migratory insertion (hydride to carbene) would be expected to follow rapidly and coordination of either chloride or trifluoracetate would give the observed products. An alternative possibility is that protonation of **1** occurs to give first a σ-2,2-diphenylcyclopropyl complex which might then rearrange to the observed σ-bound diphenylallyl complex [11].

The IR spectra of **2** and **3** show ν(NO) at 1825 and 1832 cm^{-1}, respectively, both values increased from the value observed for **1** (1768 cm^{-1}). The ^{1}H NMR spectrum of **2** shows a doublet of triplets resonance at 4.10 ppm ($^3J_{HP} = 4.1$ Hz, $^3J_{HH} = 8.4$ Hz) for the osmium-bound CH_2 group, and a triplet resonance at 6.22 ppm ($^3J_{HH} = 8.5$ Hz) for the –CH= group of the diphenylallyl ligand. Corresponding signals for **3** occur at 4.30 ppm ($^3J_{HP} = 3.9$ Hz, $^3J_{HH} = 7.9$ Hz), and 6.18 ppm ($^3J_{HH} = 8.1$ Hz). The ^{13}C NMR spectrum of **2** shows a broad signal at 13.1 ppm for the osmium-bound CH_2 group, and a singlet at 139.4 ppm for the –CH= group of the diphenylallyl ligand. Corresponding signals for **3** occur at 5.5 and 138.9 ppm. For both compounds there are virtual triplets in the carbon resonances of the triphenylphosphine ligands indicating a mutually *trans* arrangement of these ligands and the ^{31}P NMR spectra show singlets at −11.96 ppm for **2** and −6.48 ppm for **3**.

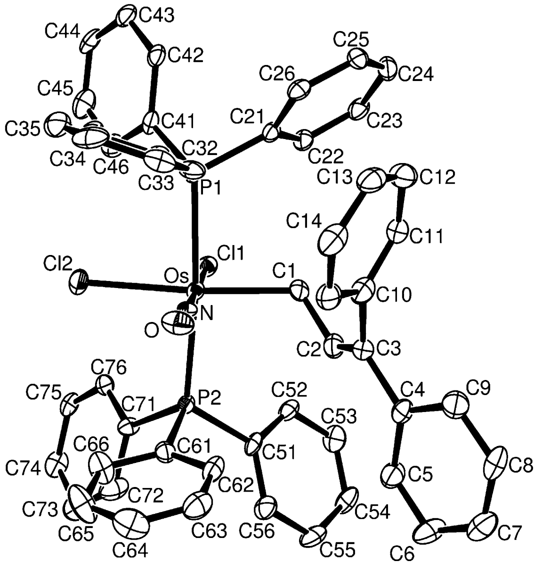


Fig. 2. Molecular geometry of $Os(CH_2CH{=}CPh_2)Cl_2(NO)(PPh_3)_2$ (**2**) showing the atom labelling and atoms as 50% probability displacement ellipsoids [22].

Table 3
Selected bond lengths (Å) and angles (°) for **2**

Bond lengths (Å)	
Os–N	1.763(6)
Os–C(1)	2.196(5)
Os–Cl(1)	2.3887(14)
Os–P(1)	2.4501(14)
Os–P(2)	2.4524(14)
Os–Cl(2)	2.4984(14)
O–N	1.127(6)
C(1)–C(2)	1.475(8)
C(2)–C(3)	1.349(8)
C(3)–C(10)	1.495(8)
C(3)–C(4)	1.509(8)
Bond angles (°)	
N–Os–C(1)	92.5(2)
N–Os–Cl(1)	179.25(15)
C(1)–Os–Cl(1)	87.12(14)
N–Os–P(1)	91.68(15)
C(1)–Os–P(1)	89.78(15)
Cl(1)–Os–P(1)	87.68(5)
N–Os–P(2)	89.96(15)
C(1)–Os–P(2)	95.57(15)
Cl(1)–Os–P(2)	90.71(5)
P(1)–Os–P(2)	174.33(5)
N–Os–Cl(2)	89.65(15)
C(1)–Os–Cl(2)	175.42(15)
Cl(1)–Os–Cl(2)	90.71(5)
P(1)–Os–Cl(2)	86.10(5)
P(2)–Os–Cl(2)	88.49(5)
O–N–Os	175.6(5)
C(2)–C(1)–Os	119.3(4)
C(3)–C(2)–C(1)	126.9(5)
C(2)–C(3)–C(10)	122.2(5)
C(2)–C(3)–C(4)	122.2(5)
C(10)–C(3)–C(4)	115.5(5)

The molecular structure of **2** is depicted in Fig. 2. Selected bond lengths and angles for **2** are collected in Table 3.

The overall geometry about osmium can be described as octahedral with the two triphenylphosphine ligands arranged mutually *trans* and the two chloride ligands mutually *cis*. The Os–Cl distance *trans* to the diphenylallyl ligand is 2.4984(14) Å, while the corresponding distance *trans* to the nitrosyl ligand is 2.3887(14) Å. This reflects the strong structural *trans* influence of the diphenylallyl ligand relative to the nitrosyl group. The Os–C distance is 2.196(5) Å, typical for an Os–C single bond and can be compared with the Os–Methyl distance in $Os(Me)(SnMe_2Cl)(CO)_2(PPh_3)_2$ which is 2.209(4) Å [14]. The C–C distances within the diphenylallyl group are C(1)–C(2), 1.475(8) Å, appropriate for a single bond and C(2)–C(3), 1.349(8) Å, appropriate for a double bond.

3. Conclusions

It has been demonstrated that the 3,3-diphenylcyclopropene complex, Os(η^2-3,3-diphenylcyclopropene)Cl(NO)-

$(PPh_3)_2$ (**1**) has a strong π-interaction with the C═C double bond and the overall geometry has the chloride and nitrosyl ligands located mutually *trans* and the Os, the two PPh_3 ligands and the double bond of the cyclopropene, all lying in one plane. Treatment of this compound with acids (HCl and CF_3CO_2H) brings about a ring-opening of the cyclopropene ring with ultimate formation in high yield of the stable σ-diphenylallyl complexes, $Os(CH_2CH{=}CPh_2)Cl_2(NO)(PPh_3)_2$ (**2**) and $Os(CH_2CH{=}CPh_2)Cl(O_2CCF_3)(NO)(PPh_3)_2$ (**3**), respectively. The structures of **2** and **3** are established by spectroscopic data and a crystal structure determination of **2**.

4. Experimental

4.1. General procedures and instruments

Standard laboratory procedures were followed as have been described previously [15]. The compounds $OsCl(NO)(PPh_3)_3$ (and its precursor $Os(peroxycarbonyl)Cl(NO)(PPh_3)_2$) [16] and 3,3-diphenylcyclopropene [17] were prepared according to the literature methods.

Infrared spectra (4000–400 cm^{-1}) were recorded as Nujol mulls between KBr plates on a Perkin–Elmer Paragon 1000 spectrometer. NMR spectra were obtained on either a Bruker DRX 400 or a Bruker Avance 300 at 25 °C. For the Bruker DRX 400, ^1H, ^{13}C, and ^{31}P NMR spectra were obtained operating at 400.1 (^1H), 100.6 (^{13}C), and 162.0 (^{31}P) MHz, respectively. For the Bruker Avance 300, ^1H, ^{13}C, and ^{31}P NMR spectra were obtained operating at 300.13 (^1H), 75.48 (^{13}C), and 121.50 (^{31}P) MHz, respectively. Resonances are quoted in ppm and ^1H NMR spectra referenced to either tetramethylsilane (0.00 ppm) or the proteo-impurity in the solvent (7.25 ppm for $CHCl_3$). ^{13}C NMR spectra were referenced to $CDCl_3$ (77.00 ppm), and ^{31}P NMR spectra to 85% orthophosphoric acid (0.00 ppm) as an external standard. Elemental analyses were obtained from the Microanalytical Laboratory, University of Otago.

4.2. Preparation of *Os(η^2-3,3-diphenylcyclopropene)Cl(NO)(PPh$_3$)$_2$* (*1*)

$Os(peroxycarbonyl)Cl(NO)(PPh_3)_2$ (see Ref. [16]) (0.569 g) and PPh_3 (0.564 g) were placed in freshly distilled benzene (35 mL) contained in a Schlenk tube. The mixture was then deoxygenated by several "freeze–pump–thaw" cycles, and then heated under reflux under a nitrogen atmosphere for 5 min. After cooling to room temperature, 3,3-diphenylcyclopropene (260 μL) was added via syringe to the dark green reaction mixture (now containing $OsCl(NO)(PPh_3)_3$), immediately turning the colour of the solution orange. After 10 min the benzene was removed in vacuo, leaving a dark orange oil. Dry hexane was added to this oil and the mixture was stirred for several hours, causing precipitation of a pale orange powder. Recrystallisation of this powder from CH_2Cl_2/EtOH yielded pure **1** as vivid orange microcrystals (0.329 g, 50%). *Anal.* Calc. for $C_{51}H_{42}ClNOOsP_2$: C, 62.99; H, 4.35; N, 1.44. Found: C, 62.89; H, 4.50; N, 1.50%. IR (cm^{-1}): 1768 *ν*(NO). ^1H NMR ($CDCl_3$, *δ*): 4.07 (apparent t, 2H, $^3J_{HP} = 5.1$ Hz, *H*C═C*H*), 7.01–7.88 (m, 40H, P*Ph*$_3$ and C_3H_2*Ph*$_2$). ^{13}C NMR ($CDCl_3$, *δ*): 53.5 (apparent quintet, $^2J_{CP} =$ ca.18 Hz, H*C*═*C*H), 69.2 (s, *C*Ph$_2$), 126.3, 127.4, 132.2, 147.1, 151.9 (s, C*Ph*$_2$), 127.9, 130.0, 132.7, 134.4 (s/m, P*Ph*$_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, *δ*): −3.13 (s, *P*Ph$_3$).

4.3. Preparation of *Os(CH$_2$CH═CPh$_2$)Cl$_2$(NO)(PPh$_3$)$_2$* (*2*)

Os(η^2-3,3-diphenylcyclopropene)Cl(NO)$(PPh_3)_2$ (**1**) (0.256 g) was dissolved in a solvent mixture of dry dichloromethane (30 mL) and ethanol (3 mL). HCl (36%, 30 μL) was added via syringe to this stirred orange solution and after 15 min the dichloromethane was removed under reduced pressure. Pale orange microcrystals of pure **2** were collected (0.218 g, 81%). These micro crystals retained a $\frac{1}{4}$ mole equivalent of CH_2Cl_2 as evidenced by the NMR spectrum and the elemental analysis. However, the single crystal grown slowly by layering ethanol over a CH_2Cl_2 solution of **2** was unsolvated. *Anal.* Calc. for $C_{51}H_{43}Cl_2NOOsP_2 \cdot 1/4CH_2Cl_2$: C, 59.70; H, 4.22; N, 1.36. Found: C, 59.91; H, 4.33; N, 1.58%. IR (cm^{-1}): 1825 *ν*(NO). ^1H NMR ($CDCl_3$, *δ*): 4.10 (dt, 2H, $^3J_{HP} = 4.1$ Hz, $^3J_{HH} = 8.4$ Hz, C*H*$_2$), 6.22 (t, 1H, $^3J_{HH} = 8.5$ Hz, C*H*═), 6.53–7.94 (m, 40H, P*Ph*$_3$ and C_3H_2*Ph*$_2$). ^{13}C NMR ($CDCl_3$, *δ*): 13.1 (broad s, *C*H$_2$), 126.9, 127.7, 130.8, 135.7, 139.9, 142.9 (s, C*Ph*$_2$), 128.1 (t′ [15], $^{2,4}J_{CP} = 10.2$ Hz, *o*-P*Ph*$_3$), 129.4 (t′, $^{1,3}J_{CP} = 52.6$ Hz, *i*-P*Ph*$_3$), 130.5 (s, *p*-P*Ph*$_3$), 134.5 (t′, $^{3,5}J_{CP} = 9.8$ Hz, *m*-P*Ph*$_3$), 139.4 (s, ═*C*H). $^{31}P\{^1H\}$ NMR ($CDCl_3$, *δ*): −11.96 (s, *P*Ph$_3$).

4.4. Preparation of *Os(CH$_2$CH═CPh$_2$)Cl(O$_2$CCF$_3$)(NO)(PPh$_3$)$_2$* (*3*)

Os(η^2-3,3-diphenylcyclopropene)Cl(NO)$(PPh_3)_2$ (**1**) (0.182 g) was dissolved in a solvent mixture of dichloromethane (25 mL) and ethanol (2.5 mL). CF_3COOH (16 μL) was added via syringe to this stirred orange solution and after 15 min the dichloromethane was removed under reduced pressure. Yellow microcrystals of pure **3** were collected (0.157 g, 77%). *Anal.* Calc. for $C_{53}H_{43}ClF_3NO_3OsP_2$: C, 58.59; H, 3.99; N, 1.29. Found: C, 58.70; H, 4.08; N, 1.30%. IR (cm^{-1}): 1832 *ν*(NO), 1676 *ν*(CO). ^1H NMR ($CDCl_3$, *δ*): 4.30 (dt, 2H, $^3J_{HP} = 3.9$ Hz, $^3J_{HH} = 7.9$ Hz, C*H*$_2$), 6.18 (t, 1H, $^3J_{HH} = 8.1$ Hz, C*H*═), 6.86–7.74 (m, 40H, P*Ph*$_3$ and C_3H_2*Ph*$_2$). ^{13}C NMR ($CDCl_3$, *δ*): 5.5 (broad s, *C*H$_2$), 114.7 (q, $^1J_{CF} = 291.4$ Hz, *C*F$_3$), 127.2, 127.8, 136.6, 137.9, 140.2, 143.3 (s, C*Ph*$_2$), 128.4 (t′, $^{2,4}J_{CP} = 9.8$ Hz, *o*-P*Ph*$_3$), 129.4 (t′, $^{1,3}J_{CP} = 53.0$ Hz, *i*-P*Ph*$_3$), 130.8 (s, *p*-P*Ph*$_3$), 134.4 (t′, $^{3,5}J_{CP} = 9.8$ Hz, *m*-P*Ph*$_3$), 138.9 (s, ═*C*H), 160.8 (q, $^2J_{CF} = 36.8$ Hz, O$_2$*C*CF$_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, *δ*): −6.48 (s, *P*Ph$_3$).

4.5. X-ray crystal structure determinations for complexes **1** and **2**

X-ray intensities were recorded on a Siemens SMART diffractometer with a CCD area detector using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 84 K. Data were integrated and corrected for Lorentz and polarisation effects using SAINT [18]. Semi-empirical absorption corrections were applied based on equivalent reflections using SADABS [19]. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using programs SHELXS-97 [20] and SHELXL-97 [21]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located geometrically and refined using a riding model. Diagrams were produced using ORTEP-3 [22]. Crystals of compounds **1** and **2** contain no solvent molecules of crystallization. There are no hydrogen bonds. Crystal data and refinement details for both structures are given in Table 1.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos. CCDC 283171 and 283172 for **1** and **2**. 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 www: http://www.ccdc.cam.ac.uk).

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