C–H Activation of 3,3-diphenylcyclopropene in the reaction with Os(CO)$_2$(PPh$_3$)$_3$: 3,3-diphenylcyclopropenyl, 2,2-diphenylcyclopropyl, and 3-phenylindenyl complexes of osmium(II)

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Abstract

Reaction between Os(CO)$_2$(PPh$_3$)$_3$ and 3,3-diphenylcyclopropene under quartz–halogen irradiation leads to C(sp^2)–H bond activation and the formation of the 3,3-diphenylcyclopropenyl complex, OsH[C$_3$H(Ph-2)$_2$](CO)$_2$(PPh$_3$)$_2$ (**1**). When complex **1** is heated there is ring-opening of the cyclopropene ring and rearrangement to the 3-phenylindenyl complex, OsH[C$_9$H$_6$(Ph-3)](CO)$_2$(PPh$_3$)$_2$ (**2**). Compound **1** reacts with HCl forming the 2,2-diphenylcyclopropyl complex, OsCl[C$_3$H$_3$(Ph-2)$_2$](CO)$_2$(PPh$_3$)$_2$ (**3**). Reaction of either **1** or **3** with excess HCl leads to reversible formation of the hydroxycarbene complex, OsCl$_2$[=C(OH)C$_3$H$_3$(Ph-2)$_2$](CO)(PPh$_3$)$_2$ (**4**), through protonation of the acyl group formed by a migratory insertion reaction involving a carbonyl ligand and the σ-bound 2,2-diphenylcyclopropanyl ligand. An X-ray crystal structure determination of **2** is reported.
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Keywords: C–H Activation; Osmium; X-ray crystal structure; 3,3-Diphenylcyclopropenyl; 2,2-Diphenylcyclopropenyl; 3-Phenylindenyl

1. Introduction

The interaction of cyclopropene and substituted cyclopropenes with transition metals is a contemporary area of research that has proved relevant to organometallic, bioinorganic, and organic chemistry. The major product classes formed through these interactions are presented in Chart 1. Two main types of reactivity have been recognised, either η^2-coordination of the intact cyclopropene ligand to form a π-adduct (illustrated by **A** in Chart 1), or ring-opening reactions that can give rise to either vinyl alkylidene species (**B** in Chart 1) or metallacyclobutenes (**C** in Chart 1) [1]. The type of product that forms depends upon the nature of the transition metal, the ancillary ligands, and the sub-

stituents on the cyclopropene. More complex products arising from oxidative cyclisations with two molecules of cyclopropene at a single metal centre have also been reported [2].

The metal–cyclopropene interaction in the η^2-bound cyclopropene complexes ranges from relatively weak (best described as an η^2-olefin complex) to strong as depicted by **A** in Chart 1 which is really a metallabicyclo-[1.1.0]butane. By analogy with complexes of simple alkenes, the weaker interaction would be expected for transition metals in higher oxidation states, where the alkene acts principally as a σ-donor. In this case there would be expected to be minimal change to the length of the C=C bond and the internal angles in the cyclopropene ring. By contrast, the stronger interaction exemplified by the metallabicyclo[1.1.0]butane structure (**A**) is characterised by significant lengthening of the C=C bond and bond angles at these carbon atoms become more consistent with sp^3

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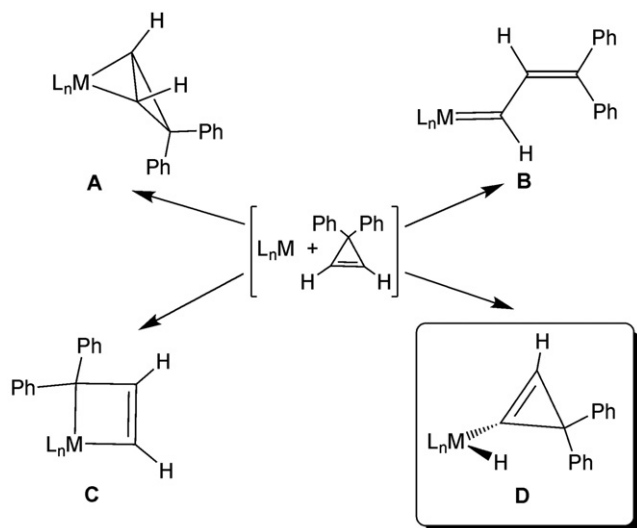*E-mail address:* w.roper@auckland.ac.nz (W.R. Roper).

Chart 1. Different structure types from the interaction of cyclopropenes with low oxidation state metal centres, including a new structure type (**D**) from a C–H activation pathway.

hybridisation. This results in significant relief of ring strain for the three-membered ring.

Cyclopropene complexes have been investigated in nitrogenase reactivity modeling studies, since cyclopropenes have been shown to be potential nitrogenase substrates, being reduced by transition metal complexes to generate cyclopropane and propene [3]. The main focus on nitrogenase model chemistry has focussed on complexes formed with platinum(0) [4–6] with X-ray crystal structures published for three platinum complexes, $[Pt(1,2-Me_2C_3H_2)-(PPh_3)_2]$ [4], $[Pt(3,3-Ph_2C_3H_2)(PPh_3)_2]$ and $[Pt(1,2-Ph_2C_3H_2)(PPh_3)_2]$ [6]. Nickel complexes have also been synthesised [7] and recently the first crystal structure of nickel(0) with a completely substituted cyclopropene, $[Ni(3-Me-3-tert-butyl-1,2-(CO_2Me)_2C_3]$, was reported [8]. Iridium complexes of 3,3-diphenylcyclopropene have also been prepared, with an X-ray crystal structure reported for $[IrCl(CO)(PMe_3)_2(3,3-Ph_2C_3H_2)]$ [9]. As would be expected for complexes of low oxidation state metals, all of these complexes can be described as structural type **A** [5,6,8,9].

Complexes involving Group 6 transition metals are typified by $W(\eta^2-3,3-diphenylcyclopropene)Cl_2(NPh)-[P(OMe)_3]_2$ for which a crystal structure determination also reveals bonding consistent with type **A** coordination [10]. Other examples involving earlier transition metals, which have only been characterised spectroscopically, are $[(Cp)_2Nb(C_3H_4)]$ [11], as well as complexes of η^2-coordinated 1,2-diphenylcyclopropene with titanocene and zirconocene, and η^2-coordinated 4,8-dioxaspiro[2.5]oct-1-ene with titanocene [12].

A special case of an η^2-coordinated cyclopropene is where the cyclopropene is tethered to the metal in the metallabenzvalenes, studied by Haley and co-workers [13]. Crystal structures for several of these iridabenzvalene and

rhodabenzvalene complexes have been reported [14–17]. A related structure has been reported for molybdenum(II), where the cyclopropene is tethered to the metal by a carboxylate group [18].

In contrast to all the above complexes which retained an intact cyclopropene ring, it is also possible to have products resulting from ring-opening forming either vinyl alkylidene complexes (type **B** in Chart 1) or metallacyclobutenes (type **C** in Chart 1). Of the ring-opened structures the vinyl alkylidene complexes of type **B**, particularly ruthenium(II) alkylidene complexes which have found wide application as metathesis catalysts [19], are better known than the metallacyclobutenes. The original ruthenium(II) alkylidene complex reported by Grubbs and co-workers was formed by reaction of either $RuCl_2(PPh_3)_3$ or $RuCl_2(PPh_3)_4$ with 3,3-diphenylcyclopropene [20], the same cyclopropene employed in the current study. 3,3-Diphenylcyclopropene also forms alkylidene complexes with rhenium [21] and tantalum [22]. Ring-opening to give metallacyclobutenes has been observed in reactions between fluorine-substituted cyclopropenes with complexes of platinum(0) [23] and iridium(I) [24]. Metallacyclobutene complexes have also been identified as the rearrangement products of the η^2-1,2-diphenylcyclopropene complexes of titanium and zirconium described above [12], whereas alkylidene complexes of titanium and zirconium have been prepared from titanocene and zirconocene with 3,3-dimethyl-, 3,3-diphenyl- and 3,3-methyl-3-phenylcyclopropene [25].

The diverse reactivity of cyclopropenes upon interaction with low oxidation state complexes prompted us to examine the interaction of 3,3-diphenylcyclopropene with the low oxidation state complexes, $OsCl(NO)(PPh_3)_3$ and $Os(CO)_2(PPh_3)_3$. We have already described that with $OsCl(NO)(PPh_3)_3$ a regular η^2-coordinated complex, $Os(\eta^2-3,3-diphenylcyclopropene)Cl(NO)(PPh_3)_2$, is formed and that this complex upon treatment with HCl ring-opens and rearranges, via a hydride migration, to the σ-diphenylallyl complex, $Os(CH_2CH{=}CPh_2)Cl_2(NO)(PPh_3)_2$ [26]. We now report that the reaction of 3,3-diphenylcyclopropene with $Os(CO)_2(PPh_3)_3$ follows a previously unobserved pathway which involves sp^2 C–H activation and leads to a 3,3-diphenylcyclopropenyl, hydride complex as illustrated by **D** in Chart 1.

Herein, we report (i) the formation of the 3,3-diphenylcyclopropenyl complex, $OsH[C_3H(Ph-2)_2](CO)_2(PPh_3)_2$ (**1**), when solutions of $Os(CO)_2(PPh_3)_3$ and 3,3-diphenylcyclopropene are placed under quartz–halogen irradiation, (ii) the thermal rearrangement of **1** to the 3-phenylindenyl complex, $OsH[C_9H_6(Ph-3)](CO)_2(PPh_3)_2$ (**2**), the structure of which is confirmed by X-ray crystal structure determination, (iii) the reaction of **1** with excess HCl to give the hydroxycarbene complex, $OsCl_2[{=}C(OH)C_3H_3(Ph-2)_2]-(CO)(PPh_3)_2$ (**4**), and (iv) the deprotonation of **4** to give the 2,2-diphenylcyclopropyl complex, $OsCl[C_3H_3(Ph-2)_2]-(CO)_2(PPh_3)_2$ (**3**).

2. Results and discussion

2.1. Reaction between 3,3-diphenylcyclopropene and $Os(CO)_2(PPh_3)_3$ to give the 3,3-diphenylcyclopropenyl complex, $OsH[C_3H(Ph-2)_2](CO)_2(PPh_3)_2$ (1)

As depicted in Scheme 1, reaction between $Os(CO)_2$-$(PPh_3)_3$ and 3,3-diphenylcyclopropene under quartz–halogen tungsten lamp irradiation (pyrex filtered) at room temperature leads to fading of the yellow colour of $Os(CO)_2(PPh_3)_3$ to an almost colourless solution over a period of 15 min. The cyclopropenyl-, hydride-complex, $OsH[C_3H(Ph-2)_2](CO)_2(PPh_3)_2$ (1), can be isolated in moderate yield. The IR spectrum of 1 shows two strong $v(CO)$ bands at 2016 and 1981 cm^{-1} indicating mutually *cis* CO ligands. In the ^{13}C NMR spectrum two signals are seen for the CO ligands at 181.1 ($^2J_{CP} = 7.4$ Hz) and 181.9 ($^2J_{CP} = 7.9$ Hz) ppm, each signal being a triplet through coupling to two equivalent phosphorus nuclei. Consistent with this there is only one singlet resonance in the ^{31}P NMR spectrum for the two equivalent phosphorus ligands and therefore the geometry of 1 is unambiguously defined as drawn in Scheme 1. The ^{1}H NMR spectrum of 1 shows a high-field triplet resonance at −5.78 ($^2J_{HP} = 20.47$ Hz) ppm for the hydride ligand. The hydrogen on the cyclopropenyl ring appears as a singlet at 6.29 ppm. The three cyclopropenyl ring carbon atoms appear at 113.1 (t, $^2J_{CP} = 14.3$ Hz) ppm for the osmium-bound carbon atom, at 121.0 (t, $^2J_{CP} = 5.0$ Hz) ppm for the =CH carbon atom, and at 32.7 ppm for the saturated CPh_2 carbon atom. It can be noted that related complexes containing acyclic vinyl ligands also show coupling of the β-carbon atom to phosphorus [27].
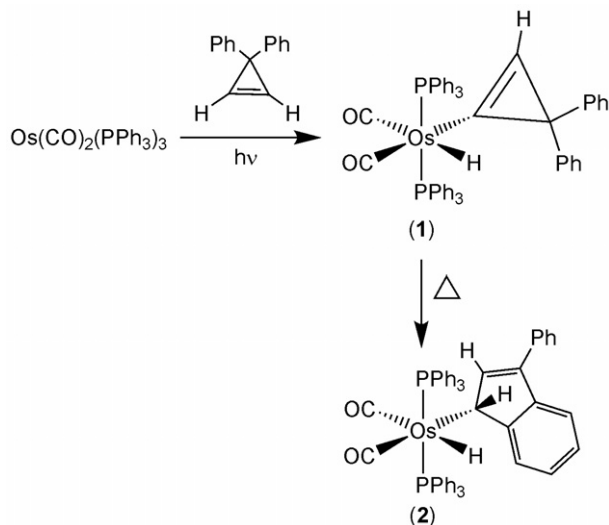
In view of the fact that the zerovalent complex, OsCl-(NO)(PPh_3)_3, forms a regular η^2-complex with 3,3-diphenylcyclopropene [26] and also that both C_2H_4 [28] and maleic anhydride [29] form η^2-adducts with $Os(CO)_2(PPh_3)_3$, it is quite remarkable that 3,3-diphenylcyclopropene undergoes a C–H activation reaction with $Os(CO)_2(PPh_3)_3$. The situation is reminiscent of that existing in the interaction of ethylene with low oxidation state iridium centres where the hydrido-, vinyl-product is sometimes more stable than the η^2-ethylene adduct [30,31]. The only other example of a cyclopropenyl ligand bound to a transition metal through one of the alkene carbon of which we are aware was derived from the reaction of $Pt(C_2H_4)(PPh_3)_2$ with 3-chloromethyl-1,2-dichloro-3-methycyclopropene. The product is claimed to arise through oxidative addition involving one of the chlorines originally at the double bond [6].

2.2. Thermal rearrangement of $OsH[C_3H(Ph-2)_2]$-$(CO)_2(PPh_3)_2$ (1) to the 3-phenylindenyl complex, $OsH[C_9H_6(Ph-3)](CO)_2(PPh_3)_2$ (2) and the crystal structure of 2

$OsH[C_3H(Ph-2)_2](CO)_2(PPh_3)_2$ (1) rearranges slowly in toluene solution at 60 °C over 2.5 h to give another colourless material identified as the 3-phenylindenyl complex, $OsH[C_9H_6(Ph-3)](CO)_2(PPh_3)_2$ (2) in high yield. The IR spectrum of 2 shows two strong $v(CO)$ bands at 2021 and 1958 cm^{-1}, positions similar to that of complex 1 and indicative of a *cis* arrangement of the CO ligands. The transformation of 1 to 2 is most conveniently monitored by observing the ^{31}P NMR spectrum since complex 1 has a singlet resonance while complex 2 shows two doublet resonances at 10.93 ($^2J_{PP} = 249.7$ Hz) ppm and 7.97 ($^2J_{PP} = 249.7$ Hz) ppm. The large phosphorus–phosphorus coupling is indicative of mutually *trans* and inequivalent phosphorus atoms [32,33]. This fixes the geometry of the complex as depicted in Scheme 1 and this was confirmed by an X-ray crystal structure determination (see below). The non-equivalence of the phosphorus atoms arises because of the osmium-bound chiral carbon atom of the 3-phenylindenyl ligand. Note that in complex 1 the osmium-bound carbon atom from the 3,3-diphenylcyclopropenyl ligand is not chiral. The hydride ligand on osmium appears in the ^{1}H NMR spectrum as an apparent triplet at −5.15 ppm. The hydrogen on the osmium-bound carbon atom also has the appearance of an apparent triplet at 4.10 ppm. Similarly, in the ^{13}C NMR spectrum the osmium-bound carbon atom appears at 19.7 ppm as an apparent triplet as do the two CO carbon atoms at 179.8 and 186.0 ppm.

The molecular geometry of complex 2 is shown in Fig. 1, with crystal data collected in Table 1. Selected bond lengths and angles are presented in Table 2. The structure confirms the geometry deduced from spectroscopic data above, i.e., octahedral coordination about osmium with mutually *trans* triphenylphosphine ligands and mutually *cis* CO ligands.
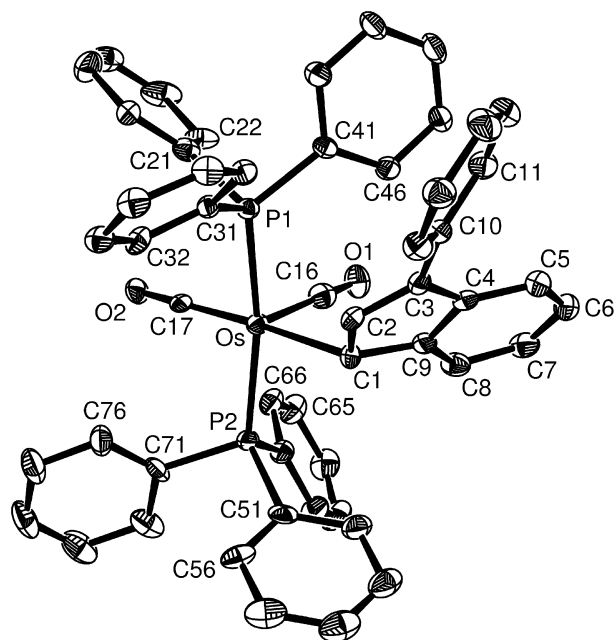

Scheme 1. C–H activation in the reaction of 3,3-diphenylcyclopropene with $Os(CO)_2(PPh_3)_3$ and subsequent rearrangement of the σ-bound 3,3-diphenylcyclopropenyl complex (1) to the σ-bound 3-phenylindenyl complex (2).

Fig. 1. The crystal structure of complex **2** showing the atom labelling and depicting the atoms as 50% probability displacement ellipsoids [47].

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

Compound	$2 \cdot 0.5CH_2Cl_2$
Empirical formula	$C_{53.5}H_{42}ClO_2OsP_2$
Molecular weight	1004.46
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	9.8165(1)
b (Å)	14.1863(2)
c (Å)	17.3840(2)
α (°)	72.637(1)
β (°)	86.346(1)
γ (°)	86.121(1)
V (Å^3)	2302.88(5)
T (K)	85(2)
Z	2
D_{calc} (g cm^{-3})	1.449
$F(000)$	1004
μ (mm^{-1})	2.936
Crystal size (mm)	$0.20 \times 0.08 \times 0.08$
θ (Min–max) (°)	2.21–25.72
Independent reflections ($I > 2\sigma I$)	8667 (R_{int} 0.0512)
T (Min, max)	0.7449, 0.8432
Goodness-of-fit on F^2	1.026
R, wR_2 (observed data)	0.0557, 0.1331
R, wR_2 (all data)	0.0703, 0.1423

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

The hydride ligand was not located. The two Os–P distances are significantly different (Os–P(1), 2.3864(19) and Os–P(2), 2.3767(19) Å) in keeping with the non-equivalence evident from the spectroscopic data discussed above. The presence of the 3-phenylindenyl ligand causes distortion of the geometry at P(1) as the disposition of the phenyl

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

Bond lengths	
Os–C(17)	1.892(8)
Os–C(16)	1.944(9)
Os–C(1)	2.290(7)
Os–P(2)	2.3767(19)
Os–P(1)	2.3864(19)
C(1)–C(9)	1.485(11)
C(1)–C(2)	1.489(11)
C(2)–C(3)	1.363(11)
C(3)–C(4)	1.448(11)
C(4)–C(5)	1.399(11)
C(4)–C(9)	1.421(11)
C(5)–C(6)	1.397(12)
C(6)–C(7)	1.392(12)
C(7)–C(8)	1.395(12)
C(8)–C(9)	1.406(11)

Bond angles	
C(17)–Os–C(16)	92.5(3)
C(17)–Os–C(1)	176.2(3)
C(16)–Os–C(1)	90.9(3)
C(17)–Os–P(2)	87.2(2)
C(16)–Os–P(2)	95.0(2)
C(1)–Os–P(2)	90.9(2)
C(17)–Os–P(1)	90.1(2)
C(16)–Os–P(1)	95.9(2)
C(1)–Os–P(1)	91.2(2)
P(2)–Os–P(1)	168.88(7)
C(31)–P(1)–C(41)	107.3(3)
C(31)–P(1)–C(21)	101.1(4)
C(41)–P(1)–C(21)	96.7(3)
C(31)–P(1)–Os	114.3(2)
C(41)–P(1)–Os	120.4(2)
C(21)–P(1)–Os	114.1(3)
C(61)–P(2)–C(51)	105.5(4)
C(61)–P(2)–C(71)	100.9(4)
C(51)–P(2)–C(71)	100.7(4)
C(61)–P(2)–Os	115.2(3)
C(51)–P(2)–Os	118.3(3)
C(71)–P(2)–Os	113.9(3)
C(9)–C(1)–C(2)	101.9(6)
C(9)–C(1)–Os	118.4(5)
C(2)–C(1)–Os	114.7(5)
C(3)–C(2)–C(1)	112.4(7)
C(2)–C(3)–C(4)	107.7(7)
C(5)–C(4)–C(9)	119.6(7)
C(5)–C(4)–C(3)	132.1(7)
C(9)–C(4)–C(3)	108.3(7)
C(8)–C(9)–C(4)	119.4(7)
C(8)–C(9)–C(1)	131.1(7)
C(4)–C(9)–C(1)	109.5(7)

rings about P(1) adjusts to accommodate the bulk of the 3-phenylindenyl ligand. This is most obvious in that the benzene ring C(41)–C(46) is pushed towards the ring C(21)–C(26) such that the C(41)–P(1)–C(21) angle is reduced to 96.7(3)°. The Os–C(1) distance to the 3-phenylindenyl ligand is 2.290(7) Å. This is an extraordinarily long Os–C distance as can be seen by comparing the Os–CH$_3$ distance (2.209(4) Å) in Os(Me)(SnMe$_2$Cl)(CO)$_2$(PPh$_3$)$_2$, a related molecule which also has mutually *trans* triphenylphosphine molecules and mutually *cis* CO ligands [34].

Undoubtedly the steric bulk of the 3-phenylindenyl ligand contributes to the long Os–C(1) distance.

The facile rearrangement of the 3,3-diphenylcyclopropenyl ligand in complex **1** to the 3-phenylindenyl ligand in complex **2** requires comment. It is well-known that phenyl-substituted cyclopropenes can be induced to rearrange to indenes, the reaction being promoted thermally, by acid or by irradiation [2a]. A specific example is that molten tetraphenylcyclopropene rearranges quantitatively to 1,2,3-triphenylindene [35a] and there are numerous other examples of related rearrangements [35b–35m]. Clearly, the ready isomerisation of the osmium-substituted cyclopropene ring in complex **1** to the osmium-substituted indene in complex **2** is facilitated by the presence of the osmium substituent. It can be noted that the isomerisation of 1,2,3-triphenylcyclopropene to 1,2-diphenylindene has been reported to be catalysed by platinum [36]. It may be relevant that ruthenium complexes [37] and osmium complexes [38] bearing the diphenylvinyl substituted carbyne ligand rearrange to stable complexes bearing a 3-phenylindenylidene ligand. It is conceivable that ring-opening of the cyclopropenyl ligand while bound to osmium in complex **1** could generate a diphenylvinyl substituted carbyne ligand and after rearrangement of this to a 3-phenylindenylidene ligand, hydride return from osmium to the carbene ligand would produce the observed 3-phenylindenyl complex **2**.
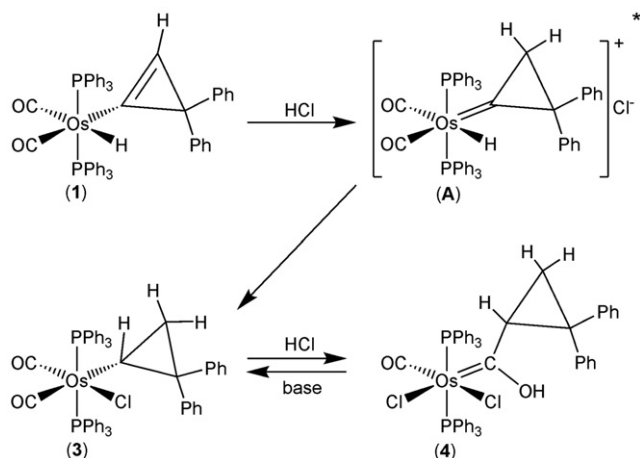
2.3. The reaction of OsH[C₃H(Ph-2)₂](CO)₂(PPh₃)₂ (1) with HCl to give initially the 2,2-diphenylcyclopropyl complex, OsCl[C₃H₃(Ph-2)₂](CO)₂(PPh₃)₂ (3), and further reversible reaction with HCl to give the hydroxycarbene complex, OsCl₂[=C(OH)C₃H₃(Ph-2)₂]-(CO)(PPh₃)₂ (4)

As depicted in Scheme 2, the addition of an excess of HCl to OsH[C₃H(Ph-2)₂](CO)₂(PPh₃)₂ (**1**) produces the hydroxycarbene complex, OsCl₂[=C(OH)C₃H₃(Ph-2)₂]-(CO)(PPh₃)₂ (**4**) which has as the other substituent on the

Scheme 2. Reactions of complex **1** with HCl, complex **A** marked with an asterix is a postulated intermediate.

carbene carbon atom, the saturated 2,2-diphenylcyclopropyl group. A likely intermediate in this transformation is labeled **A** in Scheme 2, i.e., a cationic cyclopropanylidene complex from β-protonation of the cyclopropenyl ligand in complex **1**. The protonation of vinyl ligands to give carbene complexes is an established organometallic reaction [39]. Hydride migration from osmium to the carbene carbon atom driven by chloride coordination gives the 2,2-diphenylcyclopropyl complex, OsCl[C₃H₃(Ph-2)₂]-(CO)₂(PPh₃)₂ (**3**). Again there is ample precedent for this type of transformation [40]. Finally, migration of the 2,2-diphenylcyclopropyl onto an adjacent CO ligand accompanied by protonation at the resulting acyl oxygen atom and further chloride coordination gives the hydroxycarbene complex, OsCl₂[=C(OH)C₃H₃(Ph-2)₂](CO)(PPh₃)₂ (**4**). This final protonation is reversible and a convenient synthesis of OsCl[C₃H₃(Ph-2)₂](CO)₂(PPh₃)₂ (**3**) involves addition of aqueous NaOH to OsCl₂[=C(OH)C₃H₃(Ph-2)₂]-(CO)(PPh₃)₂ (**4**). There is precedent for the formation of an hydroxycarbene complex on osmium by this same process in that treatment of the closely related ethyl derivative, Os(Et)Cl(CO)₂(PPh₃)₂, with HCl gives OsCl₂[=C(OH)Et]-(CO)(PPh₃)₂ [28].

The IR spectrum of complex **3** shows two strong v(CO) bands at 2025 and 1957 cm⁻¹ consistent with the presence of two *cis* CO ligands. In the ³¹P NMR spectrum complex **3** shows two doublet resonances at −9.62 ($^2J_{PP}$ = 308.0 Hz) ppm and −14.02 ($^2J_{PP}$ = 308.0 Hz) ppm. The large phosphorus-phosphorus coupling is indicative of mutually *trans* and inequivalent phosphorus atoms [32,33] so fixing the geometry of the complex as depicted in Scheme 2. Once again the osmium-bound carbon atom of the 2,2-diphenyl-cyclopropyl ligand is chiral, accounting for the non-equivalence of the phosphorus atoms. The two hydrogen atoms of the methylene group in the cyclopropyl ring are also inequivalent for the same reason and as a consequence in the ¹H NMR spectrum of **3** two separate resonances are observed, each a doublet of doublets, at 1.14 ($^2J_{HH}$ = 4.1 Hz; $^3J_{HH}$ = 10.2 Hz) ppm and 1.59 ($^2J_{HH}$ = 4.3 Hz; $^3J_{HH}$ = 9.2 Hz) ppm. The proton on the osmium-bound carbon atom appears as a broad apparent triplet at 1.94 ppm. In the ¹³C NMR spectrum of **3** the three saturated cyclopropyl ring carbon atoms appear at 23.6 (OsCH), 35.8 (CH₂), and 37.5 (CPh₂) ppm while the two CO ligands appear at 174.8 and 178.0 ppm.

The IR spectrum of complex **4** shows only one strong v(CO) band at 1949 cm⁻¹ indicating the presence of one terminal CO ligand. In the ³¹P NMR spectrum complex **4** shows two doublet resonances at −9.87 ($^2J_{PP}$ = 293.1 Hz) ppm and 0.56 ($^2J_{PP}$ = 293.1 Hz) ppm. The large phosphorus–phosphorus coupling is again indicative of mutually *trans* and inequivalent phosphorus atoms [32,33], consistent with the geometry of the complex as depicted in Scheme 2. Once again the carbon atom of the 2,2-diphenyl-cyclopropyl substituent bound to the carbene carbon ligand is chiral, accounting for the non-equivalence of the phosphorus atoms. The ¹H NMR spectrum reveals the

presence of the hydroxycarbene ligand by the singlet resonance at 13.49 ppm attributable to the OH group. This chemical shift is typical of hydroxyl carbene complexes, e.g., Cr[=C(OH)Me](CO)$_5$ has an OH resonance at 12.35 ppm [41]. Another characteristic feature of the hydroxyl carbene ligand in complex **4** is the very low-field, apparent triplet resonance that appears in the ^{13}C NMR spectrum at 269.8 ppm ($^2J_{CP}$ = 6.1 Hz, Os=COH). The three saturated cyclopropyl ring carbon atoms appear at 27.0 (s, CH$_2$), 46.9 (s, CPh$_2$), and 54.7 (s, CH) ppm while the single CO ligand appears at 178.6 ppm.

3. Conclusions

A new pathway for the reaction of 3,3-diphenylcyclopropene with a low-valent metal complex has been demonstrated. The reaction with Os(CO)$_2$(PPh$_3$)$_3$ leads to a C–H activation process producing the 3,3-diphenylcyclopropenyl complex, OsH[C$_3$H(Ph-2)$_2$](CO)$_2$(PPh$_3$)$_2$ (**1**). This complex is thermally unstable and readily rearranges to the 3-phenylindenyl complex, OsH[C$_9$H$_6$(Ph-3)](CO)$_2$(PPh$_3$)$_2$ (**2**). A crystal structure determination of complex **2** reveals a long Os–C distance to the σ-bound 3-phenylindenyl ligand of 2.290(7) Å. Reaction of complex **1** with HCl saturates the 3,3-diphenylcyclopropenyl ligand to the 2,2-diphenylcyclopropyl ligand. Under the acid conditions a migratory insertion reaction ensues leading to the hydroxy carbene complex, OsCl$_2$[=C(OH)C$_3$H$_3$(Ph-2)$_2$](CO)(PPh$_3$)$_2$ (**4**) which has the 2,2-diphenylcyclopropyl group as a carbene substituent. The migratory insertion reaction is reversible and treatment of complex **4** with NaOH produces the dicarbonyl, 2,2-diphenylcyclopropyl complex, OsCl[C$_3$H$_3$(Ph-2)$_2$](CO)$_2$(PPh$_3$)$_2$ (**3**).

4. Experimental

4.1. General procedures and instruments

Standard laboratory procedures were followed as have been described previously [27]. The compounds Os(CO)$_2$(PPh$_3$)$_3$ [42], and 3,3-diphenylcyclopropene [22], were prepared by 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, ^{1}H, ^{13}C and ^{31}P NMR spectra were obtained operating at 400.1 (^{1}H), 100.6 (^{13}C) and 162.0 (^{31}P) MHz, respectively. For the Bruker Avance 300, ^{1}H, ^{13}C, and ^{31}P NMR spectra were obtained operating at 300.13 (^{1}H), 75.48 (^{13}C) MHz, and 121.50 (^{31}P) MHz, respectively. Resonances are quoted in ppm and ^{1}H 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 OsH[C$_3$H(Ph-2)$_2$](CO)$_2$(PPh$_3$)$_2$ (1)

Os(CO)$_2$(PPh$_3$)$_3$ (0.465 g, 0.45 mmol) was dissolved/suspended in deoxygenated benzene (50 mL) contained in a 250 mL Pyrex Schlenk tube and 3,3-diphenylcyclopropene (0.200 mL, 1.15 mmol) was added. The resulting mixture was irradiated with a quartz–halogen tungsten lamp (1000 W) for 15 min with air-cooling of the vessel to ensure the temperature did not rise above 30 °C. During this time all the material dissolved and the colour faded from the bright yellow of Os(CO)$_2$(PPh$_3$)$_3$ to a very pale yellow. This solution was then stirred for 1 h without the lamp at room temperature. The solvent was then removed under vacuum to give a cream-coloured solid. This was purified by chromatography on silica gel, using dichloromethane as eluent. The major colourless band eluted from the column was collected (monitored by thin layer chromatography) and the solvent removed. The resulting solid was washed with hexane to give pure **1** as an almost colourless solid (0.194 g, 45%). m/z 964.22609 (M + H)$^+$; C$_{53}$H$_{42}$O$_2$OsP$_2$ requires 964.22749. Anal. Calc. for C$_{53}$H$_{42}$O$_2$OsP$_2$: C, 66.10; H, 4.40. Found: C, 66.16; H, 4.65%. IR (cm^{-1}): 2016s, 1981s v(CO); 1899 m v(OsH). ^{1}H NMR (CDCl$_3$, δ): −5.78 (t, 1H, OsH, $^2J_{HP}$ = 20.47 Hz), 6.29 (s, 1H, =CH), 6.45, 6.77 (m, 10H, C$_6H_5$ substituents on cyclopropenyl ligand), 7.21–749 (m, 30H, PPh_3). ^{13}C NMR (C$_6$D$_6$, δ): 32.7 (s, quaternary, CPh$_2$), 113.1 (t, quaternary, $^2J_{CP}$ = 14.3 Hz, Os-C), 121.0 (t, $^3J_{CP}$ = 5.0 Hz, =CH), 121.8, 125.5, 127.3, 149.4 (quaternary) (s, aromatic carbons from phenyl substituents on cyclopropenyl ligand), 126.5 (t′ [27], $^{2,4}J_{CP}$ = 9.9 Hz, o-C$_6$H$_5$), 128.5 (s, p-C$_6$H$_5$), 132.8 (m, i-C$_6$H$_5$), 133.0 (t′, $^{3,5}J_{CP}$ = 11.2 Hz, m-C$_6$H$_5$), 181.1 (t, $^2J_{CP}$ = 7.4 Hz, CO), 181.9 (t, $^2J_{CP}$ = 7.9 Hz, CO). ^{31}P NMR (CDCl$_3$, δ): 8.96 (s, PPh_3).

4.3. Preparation of OsH[C$_9$H$_6$(Ph-3)](CO)$_2$(PPh$_3$)$_2$ (2)

OsH[C$_3$H(Ph-2)$_2$](CO)$_2$(PPh$_3$)$_2$ (**1**) (0.300 g, 0.31 mmol) was dissolved/suspended in toluene (40 mL) under nitrogen and the mixture heated to 50–60 °C for 2.5 h. All material dissolved and there was a slight darkening of the solution. The transformation of compound **1** into compound **2** was conveniently monitored by either ^{1}H or ^{31}P NMR spectroscopy. Toluene was removed under vacuum to give an almost colourless solid which was washed with hexane and recrystallised from CH$_2$Cl$_2$/C$_2$H$_5$OH to pure **2** as a colourless crystalline solid (0.250 g, 83%). Anal. Calc. for C$_{53}$H$_{42}$O$_2$OsP$_2$ · 0.5CH$_2$Cl$_2$: C, 63.90; H, 4.31. Found: C, 64.43; H, 4.46%. The presence of the 0.5 equivalent of CH$_2$Cl$_2$ was confirmed by the ^{1}H NMR spectrum and the crystal structure determination. IR (cm^{-1}): 2021s, 1958s v(CO); 1910m v(OsH). ^{1}H NMR (CDCl$_3$, δ): −5.15 (apparent t, 1H, OsH, $^2J_{HP}$ = 20.50 Hz), 4.10 (apparent t, 1H, OsCH, $^3J_{HP}$ = 9.40 Hz), 6.24 (broad s, 1H, Os–CH–

C*H*=), 6.36–7.63, (m, 39H, phenylindenyl protons and P*Ph*₃). ^{13}C NMR (CDCl₃, δ): 19.7 (apparent t, $^2J_{CP}$ = 5.2 Hz, Os–*C*H), 119.1, 121.7, 123.6, 125.3, 127.6–128.2, 129.6, 129.9, 132.7 (quaternary), 133.7–134.9, 137.9 (quaternary), 141.6(quaternary), 157.7 (quaternary) (s, aromatic carbons from phenylindenyl ligand and PPh₃ ligands), 152.0 (s, Os–CH–*C*H=), 179.8 (apparent t, $^2J_{CP}$ = 8.4 Hz, *C*O), 186.0 (apparent t, $^2J_{CP}$ = 6.1 Hz, *C*O). ^{31}P NMR (CDCl₃, δ): 10.93 (d, $^2J_{PP}$ = 249.7 Hz, P*Ph*₃), 7.97 (d, $^2J_{PP}$ = 249.7 Hz P*Ph*₃).

4.4. Preparation of OsCl[C₃H₃(Ph-2)₂](CO)₂(PPh₃)₂ (3)

OsCl₂[=C(OH)C₃H₃(Ph-2)₂](CO)(PPh₃)₂ (**4**) (0.060 g, 0.0058 mmol) was dissolved in dichloromethane (15 mL), aqueous NaOH (5 mL, 0.1 mol L^{-1}) added, and the mixture stirred for 20 min. The organic fraction was removed, washed with water, dried with CaCl₂, and addition of ethanol followed by removal of the dichloromethane under vacuum gave pure **3** as a colourless microcrystalline solid (0.052 g, 90%). Anal. Calc. for C₅₃H₄₃ClO₂OsP₂: C, 63.68; H, 4.34; Cl, 3.55. Found: C, 64.43; H, 4.46; Cl, 4.10%. IR (cm^{-1}): 2025s, 1957s ν(CO). ^{1}H NMR (CDCl₃, δ): 1.14 (dd, 1H, $^2J_{HH}$ = 4.1 Hz, $^3J_{HH}$ = 10.2 Hz, –C*H*₂–), 1.59 (dd, 1H, $^2J_{HH}$ = 4.3 Hz, $^3J_{HH}$ = 9.2 Hz, –C*H*₂–), 1.94 (broad apparent t, 1H, $^3J_{HH}$ = 9.5 Hz, Os–C*H*–), 6.54–7.87 (m, 40H, phenyl substituents and P*Ph*₃). ^{13}C NMR (CDCl₃, δ): 23.6 (apparent t, $^2J_{CP}$ = 9.1 Hz, Os–*C*H), 35.8 (dd, $^3J_{CP}$ = 3.6 Hz, $^3J_{CP}$ = 9.7 Hz, *C*H₂), 37.5 (s (quaternary), *C*Ph₂), 123.5, 125.2, 125.6, 127.3, 127.6, 127.9, 128.0, 128.1, 128.3, 130.2, 130.4, 130.6, 131.6, 131.7, 132.0 (quaternary), 132.1 (quaternary), 132.6 (quaternary), 133.0, 133.2, 133.3 (quaternary), 133.6 (quaternary), 133.7 (quaternary), 133.9 (quaternary), 134.4, 134.5, 134.6, 134.7, 145.0 (quaternary), 151.3 (quaternary), (aromatic carbons from phenyl substituents and PPh₃), 174.8 (apparent t, $^2J_{CP}$ = 6.9 Hz, *C*O), 178.0 (apparent t, $^2J_{CP}$ = 8.1 Hz, *C*O). ^{31}P NMR (CDCl₃, δ): −9.62 (d, $^2J_{PP}$ = 308.0 Hz P*Ph*₃), −14.02 (d, $^2J_{PP}$ = 308.0 Hz P*Ph*₃).

4.5. Preparation of OsCl₂[=C(OH)C₃H₃(Ph-2)₂](CO)(PPh₃)₂ (4)

The 3,3-diphenylcyclopropenyl hydride complex **1** (0.134 g, 0.0139 mmol), was dissolved in dichloromethane (ca. 30 mL). A solution of concd. HCl (12 drops, 32%) in methanol (5 mL) was added and the reaction mixture was stirred at room temperature for 25 min under nitrogen. The solvent was then removed under reduced pressure. The white residue thus obtained was recystallised from dichloromethane/ethanol to give pure **4** as a colourless microcrystalline solid (0.080 g, 56%). Anal. Calc. for C₅₃H₄₄Cl₂O₂OsP₂: C, 61.44; H, 4.28; Cl, 6.84. Found: C, 61.43; H, 4.40; Cl, 6.80%. IR (cm^{-1}): 1949s ν(CO). ^{1}H NMR (CDCl₃, δ): 1.22 (m, 2H, –C*H*₂–), 3.73 (m, 1H, C*H*–CH₂), 6.54–7.78 (m, 40H, phenyl substituents and

P*Ph*₃), 13.49 (s, 1H, O*H*). ^{13}C NMR (CDCl₃, δ): 27.0 (s, *C*H₂), 46.9 (s, *C*Ph₂), 54.7 (s, *C*H–CH₂), 126.4, 126.5, 127.7, 127.8, 127.9, 128.4, 130.0, 130.1, 130.7, 131.2 (quaternary), 131.5 (quaternary), 132.0 (quaternary), 134.4, 134.5, 134.6, 134.7, 139.1 (quaternary), 145.2 (quaternary) (aromatic carbons from phenyl substituents and PPh₃), 178.6 (apparent t, $^2J_{CP}$ = 8.5 Hz, *C*O), 269.8 (apparent t, $^2J_{CP}$ = 6.1 Hz, Os=*C*OH). ^{31}P NMR (CDCl₃, δ): −9.87 (d, $^2J_{PP}$ = 293.1 Hz, P*Ph*₃), 0.56 (d, $^2J_{PP}$ = 293.1 Hz, P*Ph*₃).

4.6. X-ray crystal structure determination for complex 2

X-ray intensity data were recorded on a Siemens SMART diffractometer with a CCD area detector using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 85 K. Data were integrated and corrected for Lorentz and polarisation effects using SAINT [43]. Semi-empirical absorption corrections were applied based on equivalent reflections using SADABS [44]. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using programs SHELXS97 [45] and SHELXL97 [46]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located geometrically and refined using a riding model. The crystals contain 0.5 molecules of dichloromethane of crystallisation. The chlorine atoms of this dichloromethane could be reliably located, but not the methylene group. The diagram was produced using ORTEP3 [47]. Crystal data and refinement details for the structure are given in Table 1.

5. Supplementary material

Crystallographic data (excluding structure factors) for **2** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 612721. 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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