

## Exchange of boryl ligand substituents in $\text{Os}[\text{B}(\text{OEt})_2]\text{Cl}(\text{CO})(\text{PPh}_3)_2$

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### Abstract

Reaction between  $\text{Os}[\text{B}(\text{OEt})_2]\text{Cl}(\text{CO})(\text{PPh}_3)_2$  and 1,2-ethanediol in the presence of  $\text{Me}_3\text{SiCl}$  (1 equivalent) leads to the tethered boryl complex,  $\text{Os}[\text{B}(\text{OEt})(\text{OC}_2\text{H}_4\text{OH})]\text{Cl}(\text{CO})(\text{PPh}_3)_2$  (**1**), in which one ethoxy substituent on the boryl ligand is exchanged with one hydroxy group of the 1,2-ethanediol leaving the other OH group available to coordinate to osmium, so giving a six coordinate complex. This formulation is confirmed by crystal structure determination. The same reactants, but with 2 equivalents of  $\text{Me}_3\text{SiCl}$ , lead to the yellow, coordinatively unsaturated complex,  $\text{Os}(\text{BOC}_2\text{H}_4\text{O})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  (**2**). Complex (**2**) adds CO to give  $\text{Os}(\text{BOC}_2\text{H}_4\text{O})\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$  (**3**). Crystal structure determinations of **2** and **3** reveal a very marked difference in the Os–B distances found in the five coordinate complex **2** (2.043(4) Å) and the six coordinate complex **3** (2.179(7) Å). In a reaction similar to that used for forming **2** but with 1,3-propanediol replacing 1,2-ethanediol, the product is  $\text{Os}(\text{BOC}_3\text{H}_6\text{O})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  (**4**). The crystal structure for **4** is also reported.

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**Keywords:** Boryl complex; Boron; Osmium; X-ray crystal structure

### 1. Introduction

Transition metal-boryl complexes,  $\text{L}_n\text{M}-\text{BR}_2$ , have been widely studied in the past decade both because of their fundamental interest and because of their role as important intermediates in the metal-catalyzed syntheses of boron-functionalised organics. These developments have been extensively reviewed [1]. An interesting class of reactions, which some metal-boryl complexes undergo, is substitution of the boryl substituents without interference with the M–B bond. Such reactions have been observed for chloro-boryl ligands [2–5]. In organoboron chemistry, borate esters,  $\text{B}(\text{OR})_3$ , readily undergo exchange reactions with other alcohols. Interestingly, this exchange process has not been reported for  $\text{L}_n\text{M}-\text{B}(\text{OR})_2$  complexes and indeed, we have recently

described that  $\text{Os}[\text{B}(\text{OEt})_2]\text{Cl}(\text{CO})(\text{PPh}_3)_2$  can be re-crystallised unchanged from methanol and is not hydrolysed by moist solvents [3]. The availability of this simple and thoroughly characterised bis(ethoxy)boryl complex, led us to explore conditions under which exchange processes might occur. In this paper we report: (i) that exchange of the ethoxy groups in  $\text{Os}[\text{B}(\text{OEt})_2]\text{Cl}(\text{CO})(\text{PPh}_3)_2$  with 1,2-ethanediol or 1,3-propanediol takes place in the presence of  $\text{Me}_3\text{SiCl}$  to give the cyclic boryl complexes,  $\text{Os}(\text{BOC}_2\text{H}_4\text{O})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  (**2**) or  $\text{Os}(\text{BOC}_3\text{H}_6\text{O})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  (**4**), respectively, (ii) that in the case of 1,2-ethanediol it is possible to isolate and structurally characterise an intermediate in which only one ethoxy group is replaced,  $\text{Os}[\text{B}(\text{OEt})(\text{OC}_2\text{H}_4\text{OH})]\text{Cl}(\text{CO})(\text{PPh}_3)_2$  (**1**), (iii) a structural comparison between the coordinatively unsaturated boryl complex  $\text{Os}(\text{BOC}_2\text{H}_4\text{O})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  (**2**) and the corresponding coordinatively saturated boryl complex  $\text{Os}(\text{BOC}_2\text{H}_4\text{O})\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$  (**3**), and (iv) a crystal structure determination of  $\text{Os}(\text{BOC}_3\text{H}_6\text{O})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  (**4**).

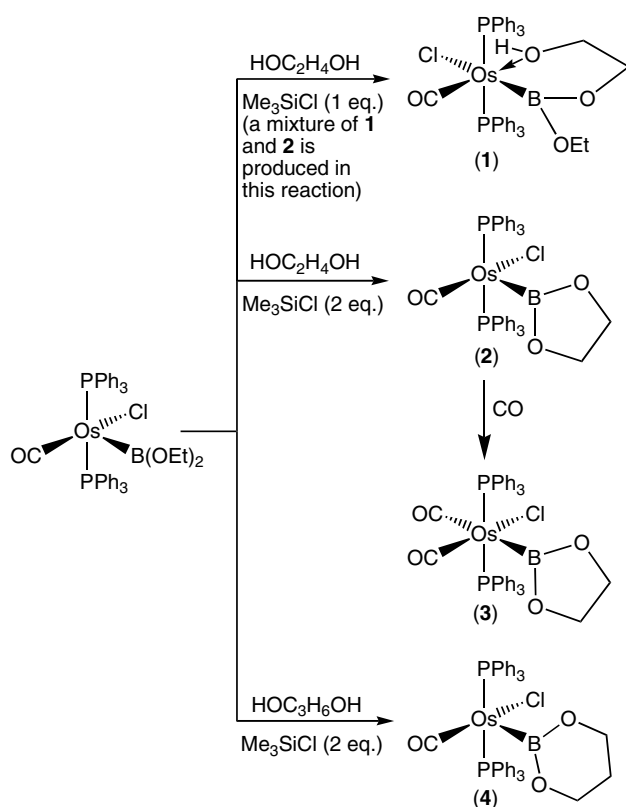
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## 2. Results and discussion

**2.1. Reaction of  $\text{Os}[\text{B}(\text{OEt})_2]\text{Cl}(\text{CO})(\text{PPh}_3)_2$  with 1,2-ethanediol in the presence of  $\text{Me}_3\text{SiCl}$  and the structures of  $\text{Os}[\text{B}(\text{OEt})(\text{OC}_2\text{H}_4\text{OH})]\text{Cl}(\text{CO})(\text{PPh}_3)_2$  (**1**) and  $\text{Os}(\text{BOC}_2\text{H}_4\text{O})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  (**2**)**

Treatment of a solution of  $\text{Os}[\text{B}(\text{OEt})_2]\text{Cl}(\text{CO})(\text{PPh}_3)_2$  with 1,2-ethanediol in the presence of one equivalent of  $\text{Me}_3\text{SiCl}$  leads to a fading of the yellow colour and a cream-coloured solid can be isolated (see Scheme 1). This proves to be a mixture of three compounds:  $\text{Os}[\text{B}(\text{OEt})(\text{OC}_2\text{H}_4\text{OH})]\text{Cl}(\text{CO})(\text{PPh}_3)_2$  (**1**) (where only one ethoxy group has exchanged with 1,2-ethanediol),  $\text{Os}(\text{BOC}_2\text{H}_4\text{O})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  (**2**) (where both ethoxy groups have exchanged and a cyclic boryl ligand is formed), and unreacted starting material. Although a bulk sample of pure **1** could not be obtained, it was possible to separate spectral data for **1** (from data for **2** and starting material) and also to grow a single crystal of **1** for X-ray analysis. The  $\nu(\text{CO})$  for compound **1** is observed at  $1916\text{ cm}^{-1}$  (cf.  $1906\text{ cm}^{-1}$  for  $\text{Os}[\text{B}(\text{OEt})_2]\text{Cl}(\text{CO})(\text{PPh}_3)_2$ ) and  $\nu(\text{OH})$  at  $3369\text{ cm}^{-1}$ . The pale colour suggests that **1** is not a coordinatively unsaturated compound and indeed this was confirmed by the crystal structure determination which confirmed the presence of a boryl ligand tethered to the osmium



Scheme 1. Reactions of  $\text{Os}[\text{B}(\text{OEt})_2]\text{Cl}(\text{CO})(\text{PPh}_3)_2$  with 1,2-ethanediol and 1,3-propanediol.

centre by coordination of the free hydroxy function. The structure also revealed that the crystalline solid was an ethanol solvate, the ethanol O atom associating with the coordinated OH function in **1**.

The molecular geometry of **1** is shown in Fig. 1 and the arrangement of the hydrogen-bonded ethanol is shown in Fig. 2. Crystal data pertaining to this structure and other structures 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 is octahedral with the two triphenylphosphine ligands mutually *trans* and the tethered boryl ligand occupying two adjacent sites with B *trans* to Cl and the coordinated OH group *trans* to CO. The Os–B distance is  $2.107(4)\text{ \AA}$ . This is longer than the Os–B distance found in the five coordinate boryl complexes,  $\text{Os}(\text{Bcat})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  (cat = 1,2- $\text{O}_2\text{C}_6\text{H}_4$ ) ( $2.019(3)\text{ \AA}$ , [6]) and  $\text{Os}(\text{BOC}_2\text{H}_4\text{O})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  (**2**) ( $2.043(4)\text{ \AA}$ , see below). It is, however, shorter than is observed when the boryl ligand is located *trans* to the  $\pi$ -acceptor CO in *cis*- $\text{Os}(\text{Bcat})\text{I}(\text{CO})_2(\text{PPh}_3)_2$  ( $2.145(5)\text{ \AA}$ , [7]) and closely similar to the distance found when *trans* to I in *trans*- $\text{Os}(\text{Bcat})\text{I}(\text{CO})_2(\text{PPh}_3)_2$  ( $2.090(3)\text{ \AA}$ , [7]). The Os–Cl bond distance in **1** ( $2.5499(8)\text{ \AA}$ ) is comparable to the Os–Cl bond distances in the related compounds where chloride is *trans* to the boryl ligand,  $\text{Os}[\text{B}(\text{OH})(\text{NHC}_5\text{H}_4\text{N})]\text{Cl}(\text{CO})(\text{PPh}_3)_2$  ( $2.5606(7)\text{ \AA}$  [5]),  $\text{Os}[\text{B}(\text{NH}n\text{-Bu})(\text{OC}_5\text{H}_4\text{N})]\text{Cl}(\text{CO})(\text{PPh}_3)_2$ , ( $2.5653(6)\text{ \AA}$  [4]) and all three are at the long end limit of the observed range for Os–Cl (mean =  $2.389$ , SD  $0.067\text{ \AA}$  [8]). Once

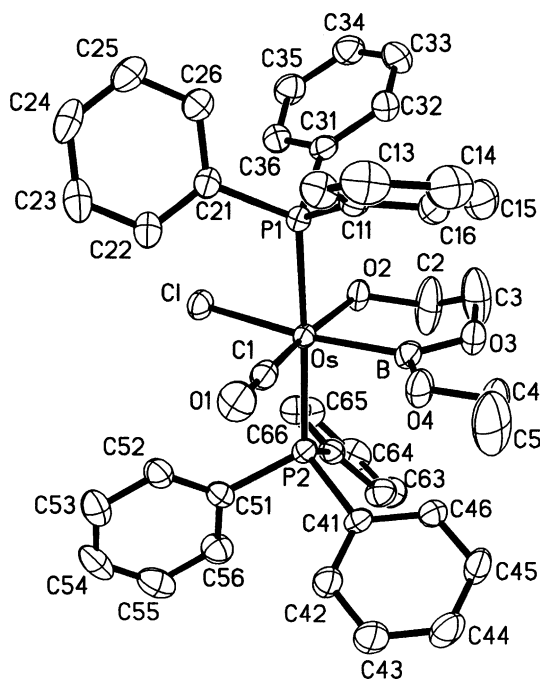


Fig. 1. Molecular geometry of  $\text{Os}[\text{B}(\text{OEt})(\text{OC}_2\text{H}_4\text{OH})]\text{Cl}(\text{CO})(\text{PPh}_3)_2$  (**1**).

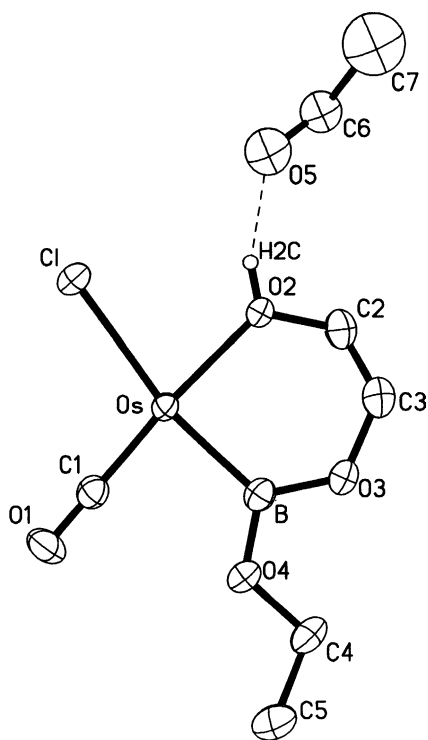


Fig. 2. The hydrogen-bond interaction between **1** and an ethanol molecule in the crystalline state.

again it is clear that boryl ligands exert a pronounced *trans* influence. An interesting feature revealed by the crystal structure of **1** is the presence of the hydrogen-

bonded ethanol (see Fig. 2). The O(2)–O(5) distance is 2.626 Å and this lies within the range observed for O–H...O hydrogen bonding interactions (2.48–2.90 Å) [9]. The B–O bond lengths and associated angles about boron are as expected.

Treatment of a solution of Os[B(OEt)<sub>2</sub>]Cl(CO)(PPh<sub>3</sub>)<sub>2</sub> with 1,2-ethanediol in the presence of two equivalents of Me<sub>3</sub>SiCl leads directly to the yellow, five-coordinate complex, Os(BOC<sub>2</sub>H<sub>4</sub>O)Cl(CO)(PPh<sub>3</sub>)<sub>2</sub> (**2**). Here, both ethoxy groups have been exchanged with the difunctional 1,2-ethanediol producing the cyclic boryl ligand (see Scheme 1). The ν(CO) for compound **2** is observed at 1912 cm<sup>-1</sup> (cf. 1906 cm<sup>-1</sup> for Os[B(OEt)<sub>2</sub>]Cl(CO)(PPh<sub>3</sub>)<sub>2</sub>). The <sup>1</sup>H NMR spectrum shows a singlet at 3.72 ppm integrating for four protons which is assigned to the ethylene bridging group of the cyclic boryl ligand. The <sup>11</sup>B NMR spectrum shows a signal at 27.8 ppm. This is significantly shielded with respect to the coordinatively saturated counterpart of **2**, viz., complex **3**, the product of CO addition to **2**. Complex **3** has a <sup>11</sup>B NMR signal at 45.0 ppm. This difference may be associated with greater Os–B π-backdonation in **2**, a conclusion supported by the structural data discussed below.

The crystal structure of **2** was determined and the molecular geometry is shown in Fig. 3. Selected bond lengths and angles for **2** are collected in Table 3. The overall geometry about osmium is square pyramidal with the two triphenylphosphine ligands mutually *trans* and

Table 1  
Data collection and processing parameters for 1–4

	1 · EtOH	2	3	4
Formula	C <sub>41</sub> H <sub>40</sub> BClO <sub>4</sub> OsP <sub>2</sub> · C <sub>2</sub> H <sub>5</sub> OH	C <sub>39</sub> H <sub>34</sub> BClO <sub>3</sub> OsP <sub>2</sub>	C <sub>40</sub> H <sub>34</sub> BClO <sub>4</sub> OsP <sub>2</sub>	C <sub>40</sub> H <sub>36</sub> BClO <sub>3</sub> OsP <sub>2</sub>
Molecular weight	895.13	849.06	877.07	863.09
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub>
<i>a</i> (Å)	12.1904(1)	9.6950(1)	19.9431(1)	9.5836(1)
<i>b</i> (Å)	16.0736(2)	14.6804(1)	10.1890(1)	14.9694(1)
<i>c</i> (Å)	20.7912(1)	13.1693(1)	19.8028(2)	13.1142(1)
β (°)	96.425(1)	109.820(1)	116.853(1)	109.273(1)
<i>V</i> (Å <sup>3</sup> )	4048.32(6)	1763.31(3)	3589.99(4)	1775.93(3)
<i>Z</i>	4	2	4	2
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.543	1.599	1.623	1.614
<i>F</i> (000)	1884	840	1736	856
μ (mm <sup>-1</sup> )	3.34	3.82	3.76	3.79
Crystal size (mm)	0.23 × 0.10 × 0.09	0.55 × 0.20 × 0.05	0.44 × 0.20 × 0.03	0.60 × 0.50 × 0.03
θ (min–max) (°)	1.6–27.4	1.6–27.4	2.1–26.4	1.6–26.4
Reflections collected	24,190	10,627	19,904	10,571
Independent reflections ( <i>R</i> <sub>int</sub> )	8894 (0.0273)	6583 (0.018)	7327 (0.060)	6229 (0.056)
Observed reflections, <i>I</i> > 2σ( <i>I</i> )	7450	6326	5260	5794
<i>A</i> (min–max)	0.514–0.753	0.227–0.832	0.288–0.895	0.209–0.895
Goodness of fit on <i>F</i> <sup>2</sup>	1.065	0.869	0.989	0.934
<i>R</i> (observed data) <sup>a</sup>	<i>R</i> 1 = 0.0290 <i>wR</i> 2 = 0.0553	<i>R</i> 1 = 0.0212 <i>wR</i> 2 = 0.0464	<i>R</i> 1 = 0.0399 <i>wR</i> 2 = 0.0776	<i>R</i> 1 = 0.0402 <i>wR</i> 2 = 0.0989
<i>R</i> (all data)	<i>R</i> 1 = 0.0416 <i>WR</i> 2 = 0.0602	<i>R</i> 1 = 0.0223 <i>wR</i> 2 = 0.0468	<i>R</i> 1 = 0.0728 <i>wR</i> 2 = 0.0889	<i>R</i> 1 = 0.0424 <i>wR</i> 2 = 0.1002

$$wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$$

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|$$

Table 2  
Selected bond lengths [Å] and angles [°] for **1**

Os–C(1)	1.817(4)
Os–B	2.107(4)
Os–O(2)	2.180(2)
Os–P(2)	2.3694(9)
Os–P(1)	2.3739(9)
Os–Cl	2.5499(8)
B–O(4)	1.370(5)
B–O(3)	1.399(5)
O(1)–C(1)	1.164(4)
O(2)–C(2)	1.417(5)
O(3)–C(3)	1.420(5)
O(4)–C(4)	1.424(4)
C(2)–C(3)	1.379(7)
C(4)–C(5)	1.489(6)
C(1)–Os–B	87.56(16)
C(1)–Os–O(2)	174.92(13)
B–Os–O(2)	87.36(13)
C(1)–Os–P(2)	89.47(12)
B–Os–P(2)	90.98(11)
O(2)–Os–P(2)	90.70(7)
C(1)–Os–P(1)	89.89(12)
B–Os–P(1)	91.27(11)
O(2)–Os–P(1)	90.13(7)
P(2)–Os–P(1)	177.64(3)
C(1)–Os–Cl	104.00(11)
B–Os–Cl	168.43(12)
O(2)–Os–Cl	81.08(7)
P(2)–Os–Cl	89.57(3)
P(1)–Os–Cl	88.38(3)
O(4)–B–O(3)	112.4(3)
O(4)–B–Os	122.1(3)
O(3)–B–Os	125.4(3)
C(2)–O(2)–Os	123.7(2)

Table 3  
Selected bond lengths [Å] and angles [°] for **2**

Os–C(1')	1.762(9)
Os–C(1)	1.764(7)
Os–B	2.043(4)
Os–P(1)	2.3661(9)
Os–P(2)	2.3751(10)
Os–Cl	2.447(3)
Os–Cl'	2.484(3)
O(1)–C(1)	1.171(9)
O(1')–C(1')	1.139(10)
B–O(3)	1.379(5)
B–O(2)	1.390(5)
O(2)–C(2)	1.454(5)
O(3)–C(3)	1.449(5)
C(2)–C(3)	1.479(8)
C(1)–Os–B	90.9(3)
C(1)–Os–P(1)	88.3(3)
B–Os–P(1)	91.31(12)
C(1)–Os–P(2)	90.6(3)
B–Os–P(2)	88.48(12)
P(1)–Os–P(2)	178.92(3)
C(1)–Os–Cl	160.0(3)
B–Os–Cl	109.03(15)
P(1)–Os–Cl	89.45(6)
P(2)–Os–Cl	91.62(6)
O(1)–C(1)–Os	177.7(8)
O(3)–B–O(2)	110.1(3)
O(3)–B–Os	124.7(3)
O(2)–B–Os	125.3(3)

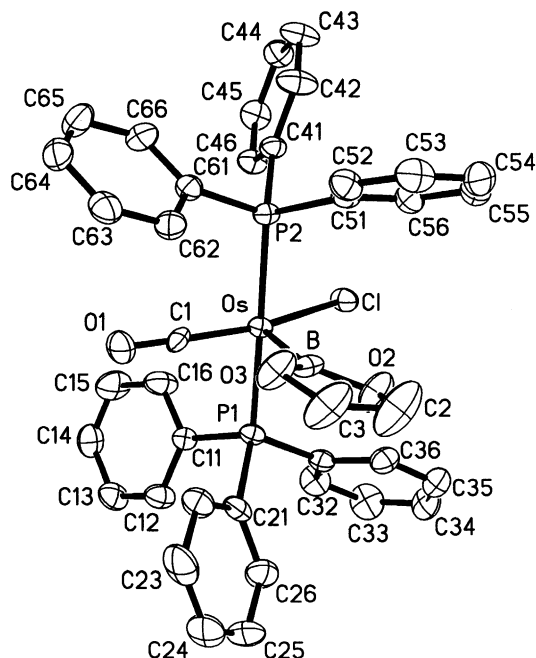


Fig. 3. Molecular geometry of  $\text{Os}(\overline{\text{BOC}_2\text{H}_4\text{O}})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  (**2**).

the cyclic boryl ligand occupying the apical position. The Os–B distance is 2.043(4) Å. This can be compared with the Os–B distances in the related five-coordinate complexes,  $\text{Os}[\text{B}(\text{OEt})_2]\text{Cl}(\text{CO})(\text{PPh}_3)_2$  (2.081(5) Å [3]) and  $\text{Os}(\text{Bcat})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  (2.019(3) Å [6]). The Os–B distance in  $\text{Os}(\overline{\text{BOC}_2\text{H}_4\text{O}})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  (**2**) is longer than the corresponding distance in  $\text{Os}(\text{Bcat})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  which is consistent with a competitive  $\pi$ -donation situation where Os–B  $\pi$ -donation is relatively stronger in the Bcat complex, and O–B  $\pi$ -donation is relatively stronger in the  $(\overline{\text{BOC}_2\text{H}_4\text{O}})$  complex. Further support for this idea is that the two B–O distances in **2** are 1.379(5) and 1.390(5) Å whereas the two B–O distances found in  $\text{Os}(\text{Bcat})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  are 1.411(4) and 1.406(4) Å. The observed Os–Cl distances in **2** (disorder between Cl and CO) are 2.447(3) and 2.484(3) Å, and are similar to other five-coordinate osmium boryl complexes where Cl is *trans* to CO.

The effectiveness of  $\text{Me}_3\text{SiCl}$  in promoting the above exchange reactions could be attributed simply to acid-catalysis by HCl (liberated through alcoholysis of the  $\text{Me}_3\text{SiCl}$ ), however, attempted exchange reactions in the presence of introduced HCl in place of  $\text{Me}_3\text{SiCl}$  were not successful. An alternative explanation could be that  $\text{Me}_3\text{SiCl}$  converts the B–O bonds in the  $\text{B}(\text{OEt})_2$  ligand to B–Cl bonds which would be expected to undergo rapid alcoholysis. We were, however, unable to detect any transient chloroboryl complexes.

2.2. Reaction of  $\text{Os}(\overline{\text{BOC}_2\text{H}_4\text{O}})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  (**2**) with CO and the structural comparison of  $\text{Os}(\overline{\text{BOC}_2\text{H}_4\text{O}})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  (**2**) and  $\text{Os}(\overline{\text{BOC}_2\text{H}_4\text{O}})\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$  (**3**)

As depicted in Scheme 1 the coordinatively unsaturated complex **2** readily takes up CO to give the colourless dicarbonyl complex,  $\text{Os}(\overline{\text{BOC}_2\text{H}_4\text{O}})\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$  (**3**). The IR spectrum of **3** shows two  $\nu(\text{CO})$  bands at 2031, 1945  $\text{cm}^{-1}$ , indicating that the CO ligands are arranged mutually *cis*. To permit a comparison between a five-coordinate and a six-coordinate boryl complex where the boryl ligands are identical, an X-ray crystal structure determination of complex **3** was undertaken.

The molecular geometry of **3** is shown in Fig. 4. Selected bond lengths and angles for **3** are collected in Table 4. The overall geometry about osmium is octahedral with the two triphenylphosphine ligands mutually *trans* and with the cyclic boryl ligand *trans* to CO. The Os–B distance is 2.179(7) Å which is considerably longer than the corresponding distance in **2** (2.043(4) Å) where there is no ligand *trans* to the boryl ligand. One factor which must contribute to this lengthening, is the presence of a competitive  $\pi$ -acceptor ligand (CO) *trans* the boryl ligand. Significantly, the Os–CO distance for this *trans* CO ligand is 1.970(6) Å, considerably longer than the Os–CO distance for the *cis* CO ligand (disordered, 1.857(12) and 1.874(16) Å).

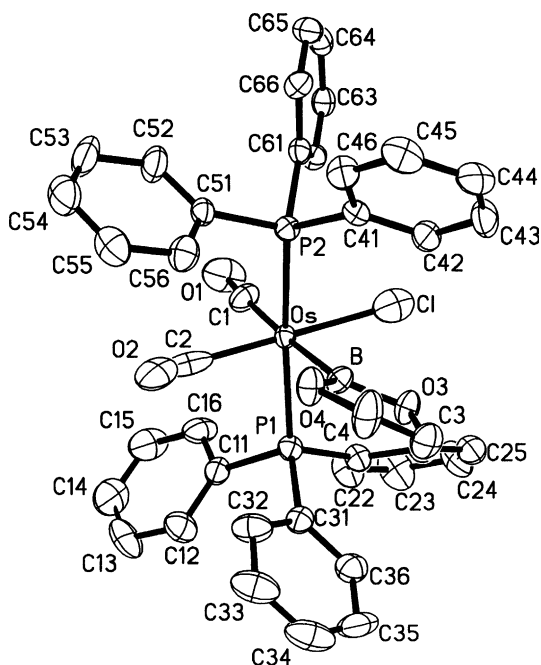


Fig. 4. Molecular geometry of  $\text{Os}(\overline{\text{BOC}_2\text{H}_4\text{O}})\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$  (**3**).

Table 4  
Selected bond lengths [Å] and angles [°] for **3**

Os–C(1)	1.970(6)
Os–C(2)	1.857(12)
Os–C(2')	1.874(16)
Os–B	2.179(7)
Os–P(2)	2.3946(15)
Os–P(1)	2.3982(16)
Os–Cl	2.433(4)
Os–Cl'	2.485(7)
B–O(3)	1.385(7)
B–O(4)	1.371(7)
O(1)–C(1)	1.143(7)
O(2)–C(2)	1.192(15)
O(2')–C(2')	0.981(16)
O(3)–C(3)	1.447(7)
O(4)–C(4)	1.441(7)
C(3)–C(4)	1.508(8)
C(1)–Os–C(2)	92.4(4)
C(1)–Os–C(2')	87.8(5)
C(1)–Os–B	177.0(3)
C(2)–Os–B	90.2(4)
C(2')–Os–B	89.7(5)
C(1)–Os–P(2)	93.56(19)
C(2)–Os–P(2)	92.4(4)
C(2')–Os–P(2)	91.3(6)
B–Os–P(2)	84.86(19)
C(1)–Os–P(1)	96.53(19)
C(2)–Os–P(1)	86.4(4)
C(2')–Os–P(1)	89.9(6)
B–Os–P(1)	85.10(19)
P(2)–Os–P(1)	169.88(5)
C(1)–Os–Cl	87.5(2)
C(1)–Os–Cl'	89.4(2)
C(2)–Os–Cl	179.8(5)
C(2')–Os–Cl'	174.8(6)
B–Os–Cl	89.83(19)
B–Os–Cl'	93.2(2)
P(2)–Os–Cl	87.76(8)
P(2)–Os–Cl'	93.21(14)
P(1)–Os–Cl	93.44(8)
P(1)–Os–Cl'	86.13(14)
O(3)–B–O(4)	111.7(5)
O(3)–B–Os	124.2(4)
O(4)–B–Os	124.1(4)

2.3. Reaction of  $\text{Os}[\text{B}(\text{OEt})_2]\text{Cl}(\text{CO})(\text{PPh}_3)_2$  with 1,3-propanediol in the presence of  $\text{Me}_3\text{SiCl}$  and the structure of  $\text{Os}(\overline{\text{BOC}_3\text{H}_6\text{O}})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  (**4**)

$\text{Os}[\text{B}(\text{OEt})_2]\text{Cl}(\text{CO})(\text{PPh}_3)_2$  reacts with 1,3-propanediol in the presence of two equivalents of  $\text{Me}_3\text{SiCl}$  in just the same way as it does with 1,2-ethanediol to give the expected five-coordinate complex with the six-membered cyclic boryl ligand,  $\text{Os}(\overline{\text{BOC}_3\text{H}_6\text{O}})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  (**4**) (see Scheme 1). The IR spectrum of this yellow compound shows a  $\nu(\text{CO})$  band at 1904  $\text{cm}^{-1}$ , significantly lower than the  $\nu(\text{CO})$  (1912  $\text{cm}^{-1}$ ) for the previously described compound from reaction with 1,2-ethanediol,  $\text{Os}(\overline{\text{BOC}_2\text{H}_4\text{O}})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  (**2**). This suggests that the five-membered cyclic boryl ligand is a better  $\pi$ -acceptor

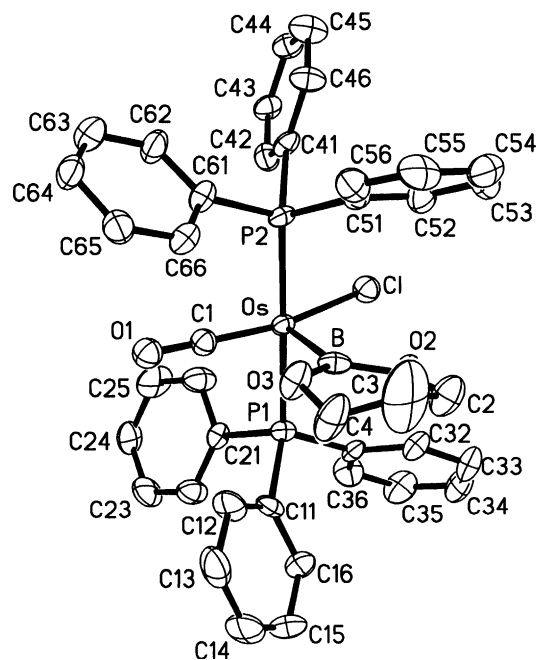


Fig. 5. Molecular geometry of  $\text{Os}(\overline{\text{BOC}_3\text{H}_6\text{O}})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  (**4**).

than the six-membered cyclic boryl ligand. This in turn suggests that the Os–B distance in complex **4** should be greater than that in complex **2** and to ascertain whether or not this prediction is true a crystal structure determination of complex **4** was undertaken.

The molecular geometry of **4** is shown in Fig. 5. Selected bond lengths and angles for **4** are collected in Table 5. The overall geometry about osmium is square pyra-

Table 5  
Selected bond lengths [Å] and angles [°] for **4**

Os–C(1')	1.736(13)
Os–C(1)	1.737(14)
Os–B	2.062(9)
Os–P(1)	2.3653(18)
Os–P(2)	2.3673(18)
Os–Cl	2.446(5)
Os–Cl'	2.454(5)
B–O(3)	1.374(10)
B–O(2)	1.374(12)
O(2)–C(2)	1.442(10)
O(3)–C(4)	1.455(10)
C(1)–Os–B	93.3(6)
C(1)–Os–P(1)	88.7(5)
B–Os–P(1)	91.4(2)
C(1)–Os–P(2)	90.2(5)
B–Os–P(2)	88.3(2)
P(1)–Os–P(2)	178.89(6)
C(1)–Os–Cl	158.9(6)
B–Os–Cl	107.7(3)
P(1)–Os–Cl	89.82(12)
P(2)–Os–Cl	91.29(12)
O(3)–B–O(2)	120.9(7)
O(3)–B–Os	119.3(6)
O(2)–B–Os	119.8(6)

midal with the two triphenylphosphine ligands mutually *trans* and the cyclic boryl ligand occupying the apical position. The Os–B distance is 2.062(9) Å. This can be compared with the value for the Os–B distance of 2.043(4) Å found for **2**. The longer distance found for the six-membered cyclic boryl ligand in **4** is compatible with there being a weaker  $\pi$ -component to the Os–B bond as suggested by the IR data. Consistent with this interpretation it can also be noted that the B–O distances in **4** (1.374(10), 1.374(12) Å) are shorter than the B–O distances in **2** (1.390(5), 1.379(5) Å). Another structural feature worth noting is that the O–B–O angle in the six-membered ring is 120.9(7)°, allowing almost perfect trigonal planarity about B, whereas the corresponding angle in the five-membered cyclic boryl ligand is restrained to 110.1(3)°. This smaller angle implies greater p-character in the B–O bonds and correspondingly greater s-character in the Os–B bond which would also be a factor contributing to the shorter Os–B bond observed in **2**.

### 3. Conclusions

Although the OEt groups in  $\text{Os}[\text{B}(\text{OEt})_2]\text{Cl}(\text{CO})(\text{PPh}_3)_2$  do not exchange with alcohols under neutral conditions, we demonstrate here that such exchanges take place readily in the presence of  $\text{Me}_3\text{SiCl}$ . By using one equivalent of  $\text{Me}_3\text{SiCl}$  in the reaction with 1,2-ethanediol it is possible to obtain, as one of several products, a compound in which there has been exchange of only one OEt group (complex **1**). However, with two equivalents of  $\text{Me}_3\text{SiCl}$  both OEt groups react forming the five-coordinate, cyclic boryl complex,  $\text{Os}(\overline{\text{BOC}_2\text{H}_4\text{O}})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ . A structural comparison of five- and six-coordinate complexes with this cyclic boryl ligand reveals a pronounced elongation of the Os–B bond when the  $\pi$ -accepting ligand CO is introduced *trans* to the boryl ligand. A further structural comparison of the five coordinate complexes,  $\text{Os}(\overline{\text{BOC}_2\text{H}_4\text{O}})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  and  $\text{Os}(\overline{\text{BOC}_3\text{H}_6\text{O}})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  which contain, respectively, five- and six-membered cyclic boryl ligands reveals a shorter Os–B bond associated with the five-membered cyclic boryl ligand. An explanation is offered in terms of the significance of both the  $\sigma$ - and  $\pi$ -components of the Os–B bond.

### 4. Experimental

#### 4.1. General procedures and instruments

Standard laboratory procedures were followed as have been described previously [10]. The compound  $\text{Os}[\text{B}(\text{OEt})_2]\text{Cl}(\text{CO})(\text{PPh}_3)_2$  [**3**] was prepared according to the literature method.

Infrared spectra (4000–400  $\text{cm}^{-1}$ ) were recorded as Nujol mulls between KBr plates on a Perkin–Elmer

Paragon 1000 spectrometer. NMR spectra were obtained on a Bruker DRX 400 at 25 °C.  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{11}\text{B}$ , and  $^{31}\text{P}$  NMR spectra were obtained operating at 400.1 ( $^1\text{H}$ ), 100.6 ( $^{13}\text{C}$ ), 128.0 ( $^{11}\text{B}$ ), and 162.0 ( $^{31}\text{P}$ ) MHz, respectively. Resonances are quoted in ppm and  $^1\text{H}$  NMR spectra referenced to either tetramethylsilane (0.00 ppm) or the proteo-impurity in the solvent (7.25 ppm for  $\text{CHCl}_3$ ).  $^{13}\text{C}$  NMR spectra were referenced to  $\text{CDCl}_3$  (77.00 ppm),  $^{11}\text{B}$  NMR spectra to  $\text{BF}_3 \cdot \text{OEt}_2$  as an external standard (0.00 ppm), and  $^{31}\text{P}$  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 $\text{Os}[\text{B}(\text{OEt})(\text{OC}_2\text{H}_4\text{OH})]\text{Cl}(\text{CO})(\text{PPh}_3)_2$ (**1**)

A mixture of  $\text{Os}[\text{B}(\text{OEt})_2]\text{Cl}(\text{CO})(\text{PPh}_3)_2$  (101 mg, 0.115 mmol), 1,2-ethanediol (6 mL) and  $\text{Me}_3\text{SiCl}$  (0.014 mL, 0.110 mmol) was stirred in THF (10 mL) for 11 min. The solvent was removed slowly in vacuo to precipitate a cream-coloured solid (70 mg) which was collected on a glass frit and washed with EtOH and hexane. The product obtained this way was always contaminated with variable amounts of both  $\text{Os}(\overline{\text{BOC}_2\text{H}_4\text{O}})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  and starting material. The ratios of  $\text{Os}[\text{B}(\text{OEt})_2]\text{Cl}(\text{CO})(\text{PPh}_3)_2$ , **1**, and **2**, appear to depend on the time taken to remove the THF in vacuo from the reaction mixture. Elemental analysis was not obtained for the above reasons, however, a single crystal of **1** was grown from a solution of the mixture so permitting structure confirmation by X-ray crystallography. IR ( $\text{cm}^{-1}$ ): 1916 vs  $\nu(\text{CO})$ ; 3369 br  $\nu(\text{OH})$ ; 1225 m, 1211 m, 1162 m, 1030 m, 1016 m, 919 w, 878 w.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 0.76 (t, 3H,  $^3J_{\text{HH}} = 7.0$  Hz,  $\text{OCH}_2\text{Me}$ ), 1.88 (br), 2.25 (br), 3.13 (br), 3.38 (q, 2H,  $^3J_{\text{HH}} = 7.0$  Hz,  $\text{OCH}_2\text{Me}$ ), 3.52 (br), 7.37 (m, 18H,  $\text{PPh}_3$ ), 7.63–7.67 (m, 12H,  $\text{PPh}_3$ ).

#### 4.3. Preparation of $\text{Os}(\overline{\text{BOC}_2\text{H}_4\text{O}})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ (**2**)

A mixture of  $\text{Os}[\text{B}(\text{OEt})_2]\text{Cl}(\text{CO})(\text{PPh}_3)_2$  (98 mg, 0.111 mmol), 1,2-ethanediol (6 mL) and  $\text{Me}_3\text{SiCl}$  (0.028 mL, 0.221 mmol) was stirred in THF (10 mL) for 30 min. The solvent was removed slowly in vacuo to give pure **2** as a yellow precipitate which was collected on a glass frit and washed with EtOH and hexane (57 mg, 60%). Anal. Calc. for  $\text{C}_{39}\text{H}_{34}\text{BClO}_3\text{OsP}_2$ : C, 55.17; H, 4.04. Found: C, 55.30; H, 4.26%. IR ( $\text{cm}^{-1}$ ): 1912 vs  $\nu(\text{CO})$ ; 1169 w, 1143 m, 1118 s, 1068 m, 940 w.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 3.72 (s, 4H,  $\text{BO}_2\text{C}_2\text{H}_4$ ), 7.36–7.39 (m, 18H,  $\text{PPh}_3$ ), 7.56–7.61 (m, 12H,  $\text{PPh}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 65.14 ( $\text{BO}_2\text{C}_2\text{H}_4$ ), 128.17 ( $t'$  [10],  $^{2,4}J_{\text{CP}} = 10$  Hz,  $o\text{-C}_6\text{H}_5$ ), 130.00 ( $p\text{-C}_6\text{H}_5$ ), 132.46 ( $t'$ ,  $^{1,3}J_{\text{CP}} = 51$  Hz,  $i\text{-C}_6\text{H}_5$ ), 134.45 ( $t'$ ,  $^{3,5}J_{\text{CP}} = 12$  Hz,  $m\text{-C}_6\text{H}_5$ ). CO not observed.  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 27.8.

#### 4.4. Preparation of $\text{Os}(\overline{\text{BOC}_2\text{H}_4\text{O}})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ (**3**)

An approximately 1:1 mixture of  $\text{Os}[\text{B}(\text{OEt})(\text{OC}_2\text{H}_4\text{OH})]\text{Cl}(\text{CO})(\text{PPh}_3)_2$  and  $\text{Os}(\overline{\text{BOC}_2\text{H}_4\text{O}})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  which had been synthesised from  $\text{Os}[\text{B}(\text{OEt})_2]\text{Cl}(\text{CO})(\text{PPh}_3)_2$  (100 mg, 0.114 mmol) following the procedure described in Section 4.2 was dissolved in THF (10 mL) and a stream of CO gas was bubbled through the solution for 5 s, turning it colourless. The solvent was concentrated to a volume of ca. 1 mL in vacuo and addition of hexane gave pure **3** as a white precipitate which was collected on a glass frit and washed with EtOH and hexane (71 mg, 71%). Anal. Calc. for  $\text{C}_{40}\text{H}_{34}\text{BClO}_4\text{OsP}_2$ : C, 54.77; H, 3.91. Found: C, 54.51; H, 3.57%. IR ( $\text{cm}^{-1}$ ): 2031 s, 1945 s  $\nu(\text{CO})$ ; 1160 m, 1126 s, 1111 m, 941 w.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 3.24 (s, 4H,  $\text{BO}_2\text{C}_2\text{H}_4$ ), 7.34–7.39 (m, 18H,  $\text{PPh}_3$ ), 7.69–7.74 (m, 12H,  $\text{PPh}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 64.67 ( $\text{BO}_2\text{C}_2\text{H}_4$ ), 127.82 ( $t'$ ,  $^{2,4}J_{\text{CP}} = 10$  Hz,  $o\text{-C}_6\text{H}_5$ ), 129.97 ( $p\text{-C}_6\text{H}_5$ ), 133.87 ( $t'$ ,  $^{1,3}J_{\text{CP}} = 54$  Hz,  $i\text{-C}_6\text{H}_5$ ), 133.99 ( $t'$ ,  $^{3,5}J_{\text{CP}} = 11$  Hz,  $m\text{-C}_6\text{H}_5$ ). CO not observed.  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 45.0.

#### 4.5. Preparation of $\text{Os}(\overline{\text{BOC}_3\text{H}_6\text{O}})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ (**4**)

A mixture of  $\text{Os}[\text{B}(\text{OEt})_2]\text{Cl}(\text{CO})(\text{PPh}_3)_2$  (99 mg, 0.113 mmol), 1,3-propanediol (6 mL) and  $\text{Me}_3\text{SiCl}$  (0.028 mL, 0.221 mmol) was stirred in THF (10 mL) for 15 min. The THF was removed in vacuo affording a yellow precipitate which was collected on a glass frit and washed with EtOH and hexanes. The product was recrystallised from  $\text{CH}_2\text{Cl}_2$ /hexane to give pure **4** (85 mg, 87%).  $^1\text{H}$  NMR spectroscopy showed 0.25 equivalents of  $\text{CH}_2\text{Cl}_2$  present as solvate. Anal. Calc. for  $\text{C}_{46}\text{H}_{37}\text{BClO}_3\text{OsP}_2 \cdot 0.25\text{CH}_2\text{Cl}_2$ : C, 54.66; H, 4.16. Found: C, 54.85; H, 3.88%. IR ( $\text{cm}^{-1}$ ): 1904 vs  $\nu(\text{CO})$ ; 1258 w, 1250 m, 1144 s, 1120 s, 1019 w.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 1.30 (quin, 2H,  $^3J_{\text{HH}} = 5.5$  Hz,  $\text{BO}_2\text{C}_3\text{H}_6$ ), 3.61 (t, 4H,  $^3J_{\text{HH}} = 5.5$  Hz,  $\text{BO}_2\text{C}_3\text{H}_6$ ), 7.35–7.38 (m, 18H,  $\text{PPh}_3$ ), 7.55–7.61 (m, 12H,  $\text{PPh}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 27.66 ( $\text{BO}_2\text{C}_3\text{H}_6$ ), 62.01 ( $\text{BO}_2\text{C}_3\text{H}_6$ ), 128.00 ( $t'$ ,  $^{2,4}J_{\text{CP}} = 10$  Hz,  $o\text{-C}_6\text{H}_5$ ), 139.80 ( $p\text{-C}_6\text{H}_5$ ), 133.04 ( $t'$ ,  $^{1,3}J_{\text{CP}} = 49$  Hz,  $i\text{-C}_6\text{H}_5$ ), 134.57 ( $t'$ ,  $^{3,5}J_{\text{CP}} = 11$  Hz,  $m\text{-C}_6\text{H}_5$ ). CO not observed.  $^{11}\text{B}$  NMR ( $\text{CDCl}_3/\text{CH}_2\text{Cl}_2$ ,  $\delta$ ): 23.5.  $^{31}\text{P}$  NMR ( $\text{CDCl}_3/\text{CH}_2\text{Cl}_2$ ,  $\delta$ ): 29.79 (s).

#### 4.6. X-ray crystal structure determinations for complexes **1**, **2**, **3**, and **4**

Data were collected on a Siemens SMART CCD diffractometer at 200 K with graphite-monochromated Mo  $\text{K}\alpha$  radiation ( $\lambda$  0.71073 Å) using  $\omega$  scans. Data were corrected for Lorentz and polarisation effects and absorption corrections applied using symmetry related measurements [11]. The structures were solved using SHELXS [12] and refined by full-matrix least squares

using SHELXL [13] with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were included in calculated positions and refined with a riding model. **2** and **4** are isostructural, even though **4** has an additional methylene group in the cyclic boryl ligand. Structures **2**, **3**, and **4** all have disorder between the chlorine and carbonyl groups and these structures have been refined with these two groups half-weighted in the two alternate positions. In addition, the central carbon atom of the bridging C<sub>3</sub>H<sub>6</sub> group of the cyclic boryl ligand in **4** is disordered and has also been refined, half-weighted, in two alternative sites. **2** and **4** are chiral and coincidentally are opposite enantiomers, the absolute structure parameters [14] being 0.010(4) and –0.016(9) for **2** and **4**, respectively. Crystal data and refinement details for all three structures are given in Table 1.

## 5. Supplementary material

Crystallographic data (excluding structure factors) for **1**, **2**, **3**, and **4** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. 224972–224975. 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](mailto:deposit@ccdc.cam.ac.uk) or [www: http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

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