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Structural study of the Diels–Alder reaction between tetrachlorodimethoxycyclopentadiene and the nickelocene-dimethyl acetylenedicarboxylate adduct. Crystal structures of the products

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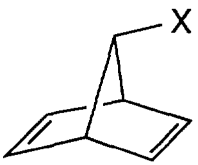
Abstract

The cyclopentadienylnickel complex (**2**) and the parent dimethyl norbornadienedicarboxylate (**4**) each react with 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene (**3**) on the less hindered *exo*-face of the dienophile to produce *anti*-sequinorbornane adducts **5** and **6**. X-ray crystal structures of these adducts have been determined and refined to *R* values of 0.029 and 0.042 respectively.

Introduction

7-Substituted norbornadienes (**1**) have often been used as synthons in synthetic pathways to diverse carbocyclic skeletons [1,2]. Convenient access to such compounds is provided by 7-metallated norbornadienes which act as precursors to variously substituted derivatives **1** [1–7]. In particular the nickel complex **2** has recently been shown [7] to undergo stereospecific carbon–nickel bond cleavage with a variety of reagents. Complex **2** is readily available from the well known reaction [8,9] of nickelocene with dimethyl acetylenedicarboxylate which selectively produces the thermodynamically more stable *syn* isomer shown.

We are currently investigating the use of **2** as an intermediate in the synthesis of more complex polycyclic molecules and herein describe the use of **2** as a dienophile in a Diels–Alder reaction with 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene (**3**). Since the electron deficient diene **3** is a masked cyclopentadienone equivalent [10,11] the products described below have the potential for further stereospecific



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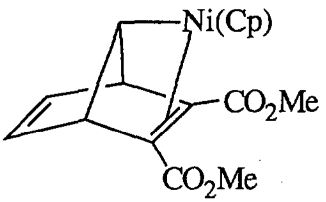

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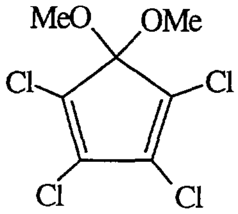

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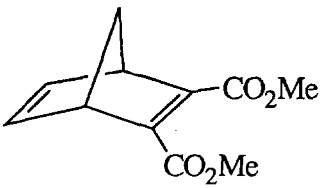


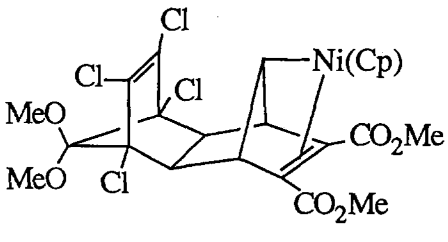
(4)

elaboration. For comparison the corresponding reaction of the non-metallated diene **4** has also been studied in order to determine the effect of the nickel on the stereochemistry, regiochemistry and rate of the Diels–Alder reaction. X-ray crystal structures of the products are also reported.

Results and discussion

The nickel complex **2** and the parent norbornadiene **4** each react smoothly with the 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene (**3**) to give the 1/1 Diels-Alder adducts **5** and **6** respectively. The structures of the products were determined by NMR spectroscopy and confirmed by the X-ray crystal structures described below.

Whereas **4** (and derivatives) undergoes cycloaddition with electron-rich dienes



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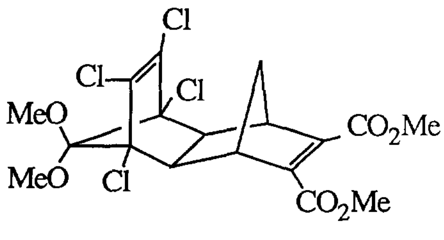

(6)

[12–14] and 1,3-dipoles [15,16] at the tetrasubstituted double bond, reaction of **4** with the electron deficient [10,11,17,18] diene **3** is expected to proceed with inverse electron demand [19–21]. Since inverse electron demand Diels–Alder reactions involve interaction between the dienophile HOMO and the diene LUMO [20,21] and since the HOMO of **4** is localised mainly on the disubstituted double bond (i.e. the ψ_2 coefficients are larger at these carbons) [15] then reaction is expected to occur at the disubstituted bond. This is indeed the case and is entirely compatible with previously reported results for related reactions [10,11,22–24]. Likewise for complex **2** regiospecific cycloaddition to the disubstituted double bond is the only reasonable reaction course in view of nickel-coordination to the tetra-substituted bond.

The observation that both dienophiles, complexed and uncomplexed, exhibit parallel stereoselectivities in cycloadditions with **3** is of considerably greater interest if viewed in context with previous stereochemical results in this area. Thus, norbornadiene (**1**, X = H) and its derivatives without bridge substituents (e.g., **4**) preferably undergo attack from the less hindered *exo*-face to produce the *anti*-sesquinorbornane skeleton [11,23,25], whereas many 7-substituted norbornadienes, especially those with a 7-oxy substituent (e.g. **1**, X = OR) afford predominantly *endo*-cycloaddition with dienes such as **3** [21,26]. The latter result can be a serious handicap in synthetic schemes which require an *endo,exo*-configuration as, for example, in **5**. Gratifyingly, the reaction of **2** with electron deficient dienes now appears to provide a potential solution to this dilemma should the carbon–nickel bond in the resultant cycloadducts undergo oxidative cleavage in a manner similar to that observed for **2** [6,7].

A reasonable explanation for the observed *exo*-face stereoselectivity of complex **2** is provided by examination of its molecular structure [27]. Thus, deformation of the bridge plane defined by carbons C(1), C(7) and C(4) towards the C(7) bonded nickel(II) enhances the steric accessability of the opposed *exo,anti*-face. In addition, displacement of the methoxycarbonyl substituents away from the nickel atom as a result of rehybridization of the C(2), C(3) olefinic carbons should sterically impede *endo,anti* attack. Both structural arguments are consistent with our observation that **2** is 2–3 times more reactive than **4** in cycloadditions with diene **3**.

In order to confirm the structures of the products and to examine their geometry in detail, X-ray crystal structures of **5** and **6** were carried out. Figures 1 and 2 show perspective views of the two structures and include the atom labelling. Tables 1 and 2 list bond lengths and angles respectively for the two structures. The structure of **5** is thus confirmed as [(9,10-η : 11-σ-3,4,5,6-tetrachloro-12,12-dimethoxy-9,10-bis(methoxycarbonyl)-*exo,endo*-pentacyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-dien-11-yl]-(η^5-cyclopentadienyl)nickel(II). A crystal structure of the precursor complex (**2**) has previously been reported [27] and, where comparable, shows similar bonding geometry. Thus the nickel atom is in a quasipentacoordinate environment in which the formally d^8 Ni^{II} atom attains an 18 electron configuration through donation of two electrons from the σ-bond to C(11), two electrons from the C(9)–C(10) π-bond and six electrons from the cyclopentadienyl anion. The Ni–C(11) bond length is typical for nickel σ-bonded to a sp^3 carbon [27,28]. The nickel atom is approximately symmetrically linked to the C(9)–C(10) bond and lies 1.822(2) Å from the midpoint of this bond which is comparable with previously reported values [27,30]. The cyclopentadienyl ring is planar with a root-mean-square deviation of 0.010 Å

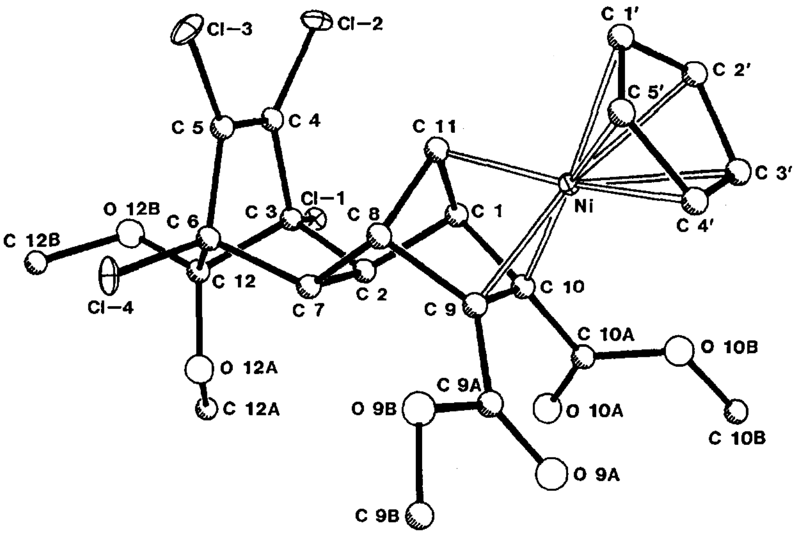

Fig. 1. Perspective view and atom labelling of the X-ray structure of **5**. Hydrogen atoms omitted for clarity.

from the meanplane of the five carbon atoms. The centroid of the ring is 1.742(2) Å from the nickel atom. Interestingly the cyclopentadienyl ring lies in the same rotational orientation as was observed in **2** [27], with the C(3′)–C(4′) bond approximately eclipsed with the C(9)–C(10) bond and with C(1′) eclipsed with C(11). The molecular mirror symmetry is destroyed in the solid state by the

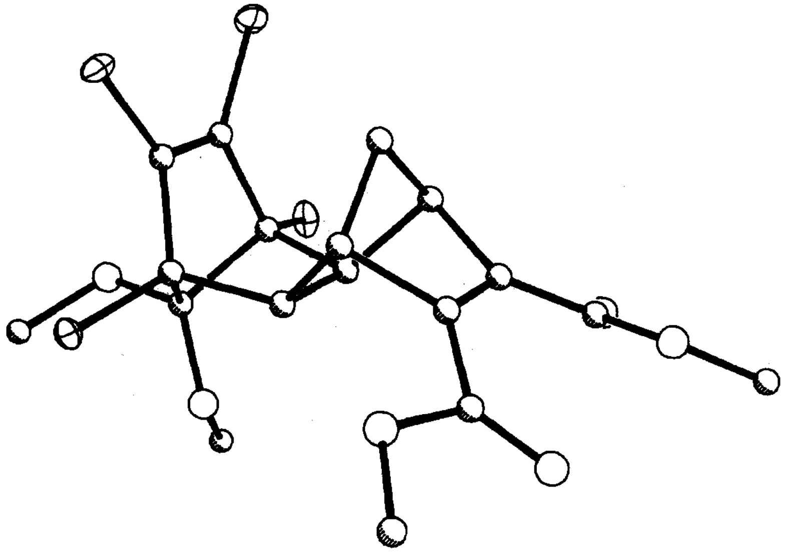

Fig. 2. Perspective view of the structure of **6**. Atom labelling as in Fig. 1. Hydrogen atoms omitted for clarity.

different relative orientations of the two methoxycarbonyl substituents, the meanplanes of the C(9) and C(10) CO_2 groups being inclined to the C(1),C(8),C(9),C(10) meanplane at angles of 21.2° and 70.7° respectively. Other geometry in the carbon skeleton is similar to that observed in **2** [27], whilst the tetrachlorodimethoxycyclopentane bonding geometry is similar to that reported in related structures [18,31–33].

The structure of **6** (Fig. 2) is confirmed as 3,4,5,6-tetrachloro-12,12-dimethoxy-9,10-bis(methoxycarbonyl)-*exo,endo*-pentacyclo[6.2.1.$1^{3,6}$.$0^{2,7}$]dodeca-4,9-diene. The most significant difference in comparable bonding geometry between the two structures is a substantial shortening of the C(9)–C(10) bond in **6** (1.344(4) Å) relative to that in **5** (1.429(3) Å). This is consistent with donation of the π-electrons of this bond to the nickel atom in **5** and the associated rehybridisation of these carbons. This is also reflected in the ^{13}C NMR spectra of the two compounds wherein the resonance for these carbons shifts from 148.3 ppm in **6** to 59.0 ppm in **5** and in other bonding geometry at these and the adjacent bridgehead carbons. Thus, for example, the carbonyl carbons C(9A), and C(10A) lie 0.262 and 0.113 Å respectively below the meanplane described by C(1),C(8),C(9),C(10) in **6**, whilst the corresponding values in **5** are 0.507 and 0.566 Å respectively, indicating much greater pyrimidalisation of the π bond in the case of **5**. Other bonding geometry in **6** is similar to that in **5** except for torsional differences associated with the rotational conformation of the methoxycarbonyl groups. Bonding of the nickel to C(11) only induces minor changes in the rest of the skeleton as reflected in the near-equivalence of the distances from C(11) to the mid-point of the C(4)–C(5) bond, viz. 2.968(2) Å and 2.959(4) for **5** and **6**, respectively.

Experimental

Infrared spectra were recorded with a Perkin–Elmer 283B spectrophotometer. NMR spectra were recorded with Varian EM 360 and JEOL FX 100 spectrometers and referenced relative to internal TMS.

Preparation of 2

To a solution of nickelocene in toluene (100 ml, 45.9 mmol, 10% w/v) in an argon atmosphere was added dimethyl acetylenedicarboxylate (6.6 ml, 54 mmol) and the resulting green solution stored at room temperature for 5 days. Removal of solvent in vacuo gave a black solid which was washed with ether and filtered. The ether solution was allowed to crystallise overnight and the resulting black crystals purified by flash chromatography on silica gel. Elution with pentane/ether (6/1) gave a light green band followed by a red band. This red band of material after removal of solvent in vacuo gave **2** as fine orange crystals (3.6 g, 24% yield), m.p. 84–85°C, ν_{max} 1720, 1690 cm^{-1}. ^1H NMR δ (C_6D_6, 60 MHz) (ppm): 6.60 (d, d $J = J' = 2$ Hz, 2H, H(5), H(6)), 5.2 (s, 5H, Cp), 3.9 ($W_{h/2}$ 8 Hz, H(1), H(4)), 3.5 (s, 6H, CO_2Me's), 2.1 (*t*, $J = J' = 3$ Hz, H(7)). ^{13}C NMR δ (ppm) 170.6 (C=O): 144.1 (C(5), C(6)), 91.1 (Cp), 67.2 (C(2), C(3)), 57.9 (C(1), C(4)), 51.5 (Me's), 26.1 (C(7)). This compound slowly decomposes in ether but is stable at room temperature in benzene, toluene, methanol and pentane the latter in which it is only slightly soluble. The compound is stable in the solid state at room temperature but decomposes in solution at temperatures above 60°C.

Preparation of **5**

A mixture of **2** (0.46 g, 1.38 mmol) and 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene (**3**) (1.09 g, 4.15 mmol) in an argon atmosphere was heated at 80 °C for 24 h. Ether was added and the black precipitate, which was not investigated further, separated from the orange-red solution. After removal in vacuo of the ether the product was purified by flash chromatography. Elution with pentane/ether (4/1) after removal of solvent gave **5** as a red solid (0.43 g, 52% yield) which was recrystallised from ether/pentane, mp, 170 °C. ν_{max} 1718 cm^{-1} (broad). ^1H NMR δ (C_6D_6) (ppm): 5.1 (s, 5H, Cp), 3.8 (d, $J = 3$ Hz, H(1), H(8)), 3.4 (s, 6H, CO_2Me's), 3.2 (s, 3H, OMe), 3.15 (s, 3H, OMe), 3.0 (s, 2H, H(2), H(7)), 2.15 (t, 1H, $J = J' = 3$ Hz, H(11)). ^{13}C NMR δ (ppm): 170.2 (C=O), 128.5 (=CCl), 114.5 (*C*(OMe)$_2$), 91.8 (Cp), 75.8 (CCl), 59.0 (=*C*CO_2Me), 57.1 (C(1), C(8)), 52.4 (OMe), 52.1 (CO_2*Me*), 52.0 (C(2), C(7)), 51.5 (OMe), 14.9 (CHNi). Exact mass calculated for $C_{23}H_{22}O_6Cl_4Ni$: 591.9524. Found: 591.9498. Anal. Found: C, 46.31; H, 3.73; Cl, 23.80. $C_{23}H_{22}O_6Cl_4Ni$ calcd.: C, 46.46; H, 3.70; Cl, 23.90%.

Preparation of **6**

A solution of **4** [34] (1.5 g, 7.2 mmol) and 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene (**3**) (1.95 g, 7.39 mmol) was heated in a sealed tube at 80 °C for 8 days. Flash chromatography on silica gel and elution with pentane/ether (3/2) gave an oily solid. The solid was washed with pentane and recrystallised from pentane-ether to give **6** as large white needles (2.79 g), 82% yield, m.p. 104–106 °C. ^1H NMR δ ($CDCl_3$, 100 MHz) (ppm): 3.75 (6H, CO_2Me's), 3.53 (s, OMe), 3.48 (s, OMe),

Table 1

Bond lengths (Å) for **5** and **6**

	5	**6**		**5**	**6**
Ni–C(9)	1.950(2)		Ni–C(10)	1.965(2)	
Ni–C(11)	1.972(2)		Ni–C(1′)	2.060(2)	
Ni–C(2′)	2.118(3)		Ni–C(3′)	2.142(3)	
Ni–C(4′)	2.147(3)		Ni–C(5′)	2.108(2)	
Cl(1)–C(3)	1.767(2)	1.767(3)	Cl(2)–C(4)	1.698(2)	1.697(3)
Cl(3)–C(5)	1.705(2)	1.699(3)	Cl(4)–C(6)	1.767(2)	1.769(2)
C(1)–C(2)	1.551(3)	1.561(4)	C(1)–C(10)	1.538(3)	1.527(4)
C(1)–C(11)	1.537(3)	1.538(4)	C(2)–C(3)	1.546(3)	1.550(4)
C(2)–C(7)	1.566(3)	1.562(3)	C(3)–C(4)	1.516(3)	1.508(4)
C(3)–C(12)	1.575(3)	1.577(3)	C(4)–C(5)	1.321(3)	1.329(4)
C(5)–C(6)	1.508(3)	1.501(3)	C(6)–C(7)	1.550(3)	1.556(3)
C(6)–C(12)	1.572(3)	1.569(3)	C(7)–C(8)	1.536(3)	1.548(4)
C(8)–C(9)	1.538(3)	1.525(4)	C(8)–C(11)	1.533(3)	1.534(4)
C(9)–C(10)	1.429(3)	1.344(4)	C(9)–C(9A)	1.474(3)	1.481(4)
C(10)–C(10A)	1.496(3)	1.485(4)	C(12)–O(12A)	1.391(3)	1.385(3)
C(12)–O(12B)	1.377(3)	1.388(3)	C(9A)–O(9A)	1.194(3)	1.197(3)
C(9A)–O(9B)	1.346(3)	1.327(3)	O(9B)–C(9B)	1.439(3)	1.438(4)
C(10A)–O(10A)	1.205(3)	1.186(4)	C(10A)–(10B)	1.322(3)	1.310(3)
O(10B)–C(10B)	1.457(2)	1.432(4)	O(12A)–C(12A)	1.444(3)	1.436(3)
O(12B)–C(12B)	1.437(3)	1.435(3)	C(1′)–C(2′)	1.401(4)	
C(1′)–C(5′)	1.433(3)		C(2′)–C(3′)	1.410(3)	
C(3′)–C(4′)	1.411(4)		C(4′)–C(5′)	1.393(4)	

Table 2

Bond angles (°) for **5** and **6**

	5	**6**		**5**	**6**
C(9)–Ni–C(10)	42.8(1)		C(9)–Ni–C(11)	68.4(1)	
C(10)–Ni–C(11)	67.8(1)		C(9)–Ni–C(1′)	150.4(1)	
C(10)–Ni–C(1′)	162.4(1)		C(11)–Ni–C(1′)	103.8(1)	
C(9)–Ni–C(2′)	118.9(1)		C(10)–Ni–C(2′)	158.4(1)	
C(11)–Ni–C(2′)	121.2(1)		C(1′)–Ni–C(2′)	39.2(1)	
C(9)–Ni–C(3′)	111.0(1)		C(10)–Ni–C(3′)	127.6(1)	
C(11)–Ni–C(3′)	158.2(1)		C(1′)–Ni–C(3′)	65.4(1)	
C(2′)–Ni–C(3′)	38.7(1)		C(9)–Ni–C(4′)	131.4(1)	
C(10)–Ni–C(4′)	115.9(1)		C(11)–Ni–C(4′)	156.4(1)	
C(1′)–Ni–C(4′)	65.5(1)		C(2′)–Ni–C(4′)	64.8(1)	
C(3′)–Ni–C(4′)	38.4(1)		C(9)–Ni–C(5′)	167.7(1)	
C(10)–Ni–C(5′)	129.4(1)		C(11)–Ni–C(5′)	120.1(1)	
C(1′)–Ni–C(5′)	40.2(1)		C(2′)–Ni–C(5′)	65.8(1)	
C(3′)–Ni–C(5′)	64.8(1)		C(4′)–Ni–C(5′)	38.2(1)	
C(2)–C(1)–C(10)	107.3(2)	101.8(2)	C(2)–C(1)–C(11)	107.9(1)	104.5(2)
C(10)–C(1)–C(11)	91.1(2)	98.4(2)	C(1)–C(2)–C(3)	118.9(2)	121.2(2)
C(1)–C(2)–C(7)	103.0(2)	102.8(2)	C(3)–C(2)–C(7)	102.1(1)	102.3(2)
Cl(1)–C(3)–C(2)	115.2(1)	114.5(2)	Cl(1)–C(3)–C(4)	113.9(2)	113.7(2)
C(2)–C(3)–C(4)	109.3(2)	110.6(2)	Cl(1)–C(3)–C(12)	116.1(2)	117.1(2)
C(2)–C(3)–C(12)	101.2(2)	100.4(2)	C(4)–C(3)–C(12)	99.2(1)	98.8(2)
Cl(2)–C(4)–C(3)	123.7(2)	124.3(2)	Cl(2)–C(4)–C(5)	128.0(2)	126.9(2)
C(3)–C(4)–C(5)	107.8(2)	108.0(2)	Cl(3)–C(5)–C(4)	127.4(2)	127.1(2)
Cl(3)–C(5)–C(6)	124.6(2)	124.9(2)	C(4)–C(5)–C(6)	107.5(2)	107.3(2)
Cl(4)–C(6)–C(5)	116.0(1)	114.8(2)	Cl(4)–C(6)–C(7)	112.5(2)	112.7(2)
C(5)–C(6)–C(7)	109.1(2)	111.1(2)	Cl(4)–C(6)–C(12)	117.1(1)	117.5(2)
C(5)–C(6)–C(12)	99.7(2)	99.5(2)	C(7)–C(6)–C(12)	100.7(1)	99.8(2)
C(2)–C(7)–C(6)	103.0(2)	103.0(2)	C(2)–C(7)–C(8)	103.6(2)	102.7(2)
C(6)–C(7)–C(8)	118.6(2)	121.2(2)	C(7)–C(8)–C(9)	105.9(2)	101.2(2)
C(7)–C(8)–C(11)	108.2(2)	105.0(2)	C(9)–C(8)–C(11)	91.7(1)	99.1(2)
Ni–C(9)–C(8)	92.7(1)		Ni–C(9)–C(10)	69.2(1)	
C(8)–C(9)–C(10)	106.4(2)	107.5(2)	Ni–C(9)–C(9A)	121.9(2)	
C(8)–C(9)–C(9A)	125.0(2)	122.4(2)	C(10)–C(9)–C(9A)	124.5(2)	129.2(2)
Ni–C(10)–C(1)	94.9(1)		Ni–C(10)–C(9)	68.0(1)	
C(1)–C(10)–C(9)	105.5(2)	107.1(2)	Ni–C(10)–C(10A)	128.0(2)	
C(1)–C(10)–C(10A)	120.5(2)	120.4(2)	C(9)–C(10)–C(10A)	126.2(2)	132.0(2)
Ni–C(11)–C(1)	94.7(1)	94.1(2)	Ni–C(11)–C(8)	92.0(1)	
C(1)–C(11)–C(8)	95.7(2)	116.9(2)	C(3)–C(12)–C(6)	90.7(2)	90.9(2)
C(3)–C(12)–O(12A)	116.8(2)	108.3(2)	C(6)–C(12)–O(12A)	106.2(2)	107.4(2)
C(3)–C(12)–O(12B)	108.2(2)	113.2(2)	C(6)–C(12)–O(12B)	119.5(2)	118.6(2)
O(12A)–C(12)–O(12b)	113.8(2)	109.7(2)	C(9)–C(9A)–O(9A)	125.7(2)	127.6(2)
C(9)–C(9A)–O(9B)	110.4(2)	115.4(3)	O(9A)–C(9A)–O(9B)	123.9(2)	122.6(2)
C(9A)–O(9B)–C(9B)	115.3(2)	113.7(2)	C(10)–C(10A)–O(10A)	121.3(2)	122.2(3)
C(10)–C(10A)–O(10B)	113.8(2)	118.0(2)	O(10A)–C(10A)–O(10B)	124.8(2)	123.9(3)
C(10A)–O(10B)–C(10B)	115.1(2)	115.9(2)	C(12)–O(12A)–C(12A)	116.3(2)	117.7(2)
C(12)–O(12B)–C(12B)	116.9(2)		Ni–C(1′)–C(2′)	72.7(1)	
Ni–C(1′)–C(5′)	71.7(1)		C(2′)–C(1′)–C(5′)	108.1(2)	
Ni–C(2′)–C(1′)	68.2(1)		Ni–C(2′)–C(3′)	71.6(1)	
C(1′)–C(2′)–C(3′)	107.7(2)		Ni–C(3′)–C(2′)	69.7(2)	
Ni–C(3′)–C(4′)	71.0(2)		C(2′)–C(3′)–C(4′)	108.1(2)	
Ni–C(4′)–C(3′)	70.6(1)		Ni–C(4′)–C(5′)	69.4(1)	
C(3′)–C(4′)–C(5′)	108.6(2)		Ni–C(5′)–C(1′)	68.1(1)	
Ni–C(5′)–C(4′)	72.4(1)		C(1′)–C(5′)–C(4′)	107.3(2)	

3.20 (d, d, $J = J' = 1.5$ Hz, H(1), H(8)), 2.74 (s, H(2), H(7)), 1.63 (J 11.2, J 1.7, J 1.7 Hz, H(11s)), 1.38 (J 11.2, $W_{h/2}$ 4 Hz, H(11a)). ^{13}C NMR δ ($CDCl_3$) (ppm): 164.1 (C=O), 148.3 (=CCO$_2$Me), 128.9 (=CCl), 115.6 (C(OMe)$_2$), 75.8 (CCl), 54.0 (C(2), C(7)), 52.5 (OMe), 52.1 (CO$_2$*Me*), 51.6 (OMe), 44.3 (C(1), C(8)), 40.2 (C(11)). Exact mass calculated for $C_{18}H_{18}O_6Cl_4$ − MeO: 438.9674. Found: 438.9715. Anal. Found: C, 45.81; H, 3.86; Cl, 29.99. $C_{18}H_{18}O_6Cl_4$ calcd.: C, 45.76; H, 3.81; Cl, 30.08%.

Crystallography

Table 3 lists crystal data and X-ray experimental details for **5** and **6**. In Tables 1 and 2 bond lengths and angles for **5** and **6** are listed. Intensity data were collected with a Nicolet R3m four-circle diffractometer by using monochromatized Mo-K_α radiation. Cell parameters were determined by least squares refinement, the setting angles of 24 accurately centered reflections ($2\theta > 27°$) being used. Throughout the data collections the intensities of three standard reflections were monitored at regular intervals; in the case of **5** there was no significant change, whilst for **6** there was a gradual decrease of 9% in these intensities and which was corrected for by scaling. The intensities were corrected for Lorentz and polarization effects and empirical absorption corrections, based on azimuthal φ scans, were applied. The space groups followed from systematic absences, although in the case of **6** signifi-

Table 3

Crystal data and X-ray experimental details

	5	**6**
Formula	$C_{23}H_{22}O_6Cl_4Ni$	$C_{18}H_{18}O_6Cl_4$
Molecular weight	594.9	472.1
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	14.314(3)	9.206(2)
b (Å)	8.472(2)	7.367(2)
c (Å)	20.566(5)	29.302(14)
β (°)	106.95(2)	92.27(3)
V (Å^3)	2385.5(9)	1986(1)
D_c (g cm^{-3})	1.656	1.579
Z	4	4
F (000)	1216	968
μ (cm^{-1})	13.1	6.3
Radiation	Mo-K_α	Mo-K_α
Wavelength (Å)	0.71069	0.71069
Temperature (°C)	−150	−150
Crystal dimensions (mm)	0.69 × 0.40 × 0.40	0.79 × 0.51 × 0.34
Scan mode	$\theta/2\theta$	ω
2θ range (°)	0–50	0–50
Unique reflections	4674	3843
Observed reflections ($I > 3\sigma(I)$)	3829	3140
Number of parameters	307	253
g	0.0002	0.0001
R	0.029	0.042
wR	0.041	0.063

Table 4

Atom coordinates ($\times 10^4$) and temperature factors ($Å^2 \times 10^3$) for **5** and **6**

5					**6**			
Atom	x	y	z	U_{eq}^{a}	x	y	z	U_{eq}^{a}
Ni	2324(1)	4020(1)	3104(1)	15(1)				
Cl(1)	4641(1)	159(1)	1519(1)	20(1)	−547(1)	7031(1)	1582(1)	35(1)
Cl(2)	3309(1)	3142(1)	778(1)	30(1)	719(1)	10912(1)	1228(1)	53(1)
Cl(3)	904(1)	2251(1)	480(1)	33(1)	4236(1)	11361(1)	1574(1)	45(1)
Cl(4)	707(1)	−1305(1)	1103(1)	28(1)	5332(1)	7671(1)	2121(1)	29(1)
C(1)	3345(2)	2268(2)	2528(1)	14(1)	2119(3)	6675(4)	696(1)	26(1)
C(2)	3269(1)	568(3)	2237(1)	13(1)	2114(3)	6160(3)	1212(1)	20(1)
C(3)	3413(2)	306(3)	1528(1)	15(1)	1349(3)	7376(3)	1562(1)	24(1)
C(4)	2819(2)	1516(3)	1035(1)	17(1)	1773(3)	9336(4)	1503(1)	31(1)
C(5)	1887(2)	1168(3)	924(1)	20(1)	3162(3)	9509(3)	1636(1)	28(1)
C(6)	1830(2)	−277(3)	1338(1)	17(1)	3696(3)	7665(3)	1783(1)	21(1)
C(7)	2162(1)	164(3)	2103(1)	15(1)	3750(3)	6352(3)	1368(1)	20(1)
C(8)	1738(2)	1658(2)	2333(1)	14(1)	4474(3)	6926(3)	923(1)	25(1)
C(9)	2179(2)	1732(3)	3109(1)	14(1)	4317(3)	5193(3)	640(1)	23(1)
C(10)	3181(2)	2163(3)	3233(1)	15(1)	2918(3)	5063(4)	495(1)	24(1)
C(11)	2349(2)	3073(2)	2233(1)	15(1)	3334(3)	8100(4)	666(1)	30(1)
C(12)	2755(2)	−1192(3)	1276(1)	16(1)	2293(3)	6938(4)	2009(1)	23(1)
C(9A)	1779(2)	925(2)	3604(1)	18(1)	5494(3)	3827(4)	621(1)	25(1)
O(9A)	2215(1)	650(2)	4182(1)	30(1)	5456(2)	2392(3)	429(1)	46(1)
O(9B)	844(1)	503(2)	3310(1)	25(1)	6637(2)	4373(3)	875(1)	54(1)
C(9B)	394(2)	−382(3)	3736(1)	31(1)	7872(4)	3177(5)	879(2)	65(1)
C(10A)	4003(2)	1732(3)	3845(1)	17(1)	2098(3)	3608(4)	246(1)	26(1)
O(10A)	4484(1)	559(2)	3854(1)	31(1)	859(3)	3300(4)	312(1)	64(1)
O(10B)	4176(1)	2795(2)	4337(1)	21(1)	2838(2)	2809(3)	−69(1)	50(1)
C(10B)	5029(2)	2483(3)	4913(1)	28(1)	2157(4)	1349(4)	−319(1)	47(1)
O(12A)	2885(1)	−2458(2)	1725(1)	18(1)	2524(2)	5122(2)	2111(1)	26(1)
C(12A)	3784(2)	−3331(3)	1839(1)	25(1)	1334(3)	4112(4)	2287(1)	41(1)
O(12B)	2821(1)	−1597(2)	643(1)	19(1)	1734(2)	7912(3)	2367(1)	33(1)
C(12B)	2177(2)	−2818(3)	285(1)	26(1)	2545(3)	7808(5)	2795(1)	43(1)
C(1′)	1739(2)	6229(3)	2834(1)	27(1)				
C(2′)	1145(2)	5460(3)	3169(1)	25(1)				
C(3′)	1727(2)	5109(3)	3834(1)	28(1)				
C(4′)	2672(2)	5716(2)	3915(1)	31(1)				
C(5′)	2691(2)	6417(3)	3306(1)	30(1)				

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

cant intensities were recorded for a number of systematically absent reflections which was shown by azimuthal scan techniques to be due to the Renninger effect [35].

The structure of **5** was solved by conventional Patterson and Fourier methods, whilst **6** was solved by direct methods. Both structures were refined by blocked cascade least-squares procedures. All non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were included in calculated positions with isotropic thermal parameters equal to the isotropic equivalent to their carrier atoms. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, with $w = [\sigma^2(F_0) + gF_0^2]^{-1}$. All calculations (including diagrams) were performed on a Nova 4X computer using SHELXTL [36].

Final atom coordinates are listed in Table 4. Tabulations of structure factors, hydrogen atom coordinates, anisotropic thermal parameters and equations of meanplanes are available from the author, P.J.S.

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