Reaction of an oxaruthenacycle with DMAD. Stoichiometric transformations of 2,6-xylenol to allylic phenols and benzopyrans *via* sp^3 C–H bond cleavage reaction†‡

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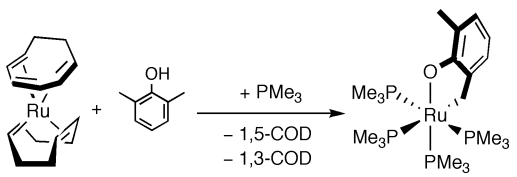
Insertion of a dimethyl acetylenedicarboxylate (DMAD) into the Ru–C bond in a cycloruthenated complex Ru[OC_6H_3(2-CH_2)(6-Me)-κ^2O,C](PMe_3)$_4$ (**2**) has been achieved to give a seven-membered oxaruthenacycle Ru[OC_6H_3{2-$CH_2C(CO_2Me)$=C(CO_2Me)}(6-Me)-κ^2O,C](PMe_3)$_3$ (**3**) in 47% yield. The molecular structure of **3** by X-ray analysis shows an agostic interaction between the ruthenium and one of the benzylic methylene protons. Complex **3** shows fluxional behaviour in solution and the variable temperature NMR studies suggest this fluxionality to be responsible for the turnstile rotation of three PMe_3 ligands and the rotation of the α-methoxycarbonyl group. Heating of a toluene solution of **3** at 100 °C for 2 h results in the 1,3-H shift reaction in **3** to give a κ^1O,η^3-C,C',C'' allylic complex Ru[OC_6H_3{2-CHC(CO_2Me)CH(CO_2Me)}(6-Me)-κ^1O,η^3C,C',C''](PMe_3)$_3$ (**6**) (80–90%), whose molecular structure is revealed by X-ray analysis. Acidolyses of **3** and **6** give 2-[(*Z*)-2′,3′-bis(methoxycarbonyl)allyl]-6-methylphenol (**7**) (88%) and 2-[(*Z*)-2′,3′-bis(methoxycarbonyl)propenyl]-6-methylphenol (**8**) (47%), respectively, and iodolyses of **3** and **6** produce 2,3-bis(methoxycarbonyl)-8-methyl-4*H*-benzopyran (**9**) (24%) and 2,3-bis(methoxycarbonyl)-8-methyl-2*H*-benzopyran (**10**) (48%), respectively.

Introduction

The carbon–hydrogen bond cleavage reaction by transition-metal complexes has attracted current attention because of its potential for direct functionalization of organic molecules.[1] Much effort has been paid to such chemistries since Chatt and Davidson discovered the first C–H bond cleavage reaction by a zerovalent ruthenium complex.[2] Among these studies, although several effective catalytic molecular transformations involving a sp^2 C–H bond cleavage are documented, those involving a sp^3 C–H bond cleavage are still limited to date.[3] We have reported sp^3 C–H bond cleavage reactions of 2,6-xylenol and the related phenols by low valent ruthenium complexes. For example, treatment of a zerovalent ruthenium complex Ru(η^4-1,5-COD)(η^6-1,3,5-COT) (**1**) with 2,6-xylenol in the presence of PMe_3 produced an oxaruthenacycle complex **2** by the sp^3 C–H bond cleavage reaction [eqn. (1)].[4]

As part of an extensive study of this chemistry, we tried to develop the reaction of **2** with unsaturated compounds. During the course of this study, we found that DMAD readily inserted into the Ru–C bond in **2** under ambient conditions. Since chelation-assisted catalytic insertion of alkynes into the C–H bond without the need to sacrifice any extra functional group is very limited,[5] such a stoichiometiric study would provide useful information for the reactivity of the oxaruthenacycle and the formation of functionalized molecules at the molecular level. Herein we would like to present a stepwise transformation of an oxaruthenacycle **2** as well as fluxional behaviours of the resulting complexes.

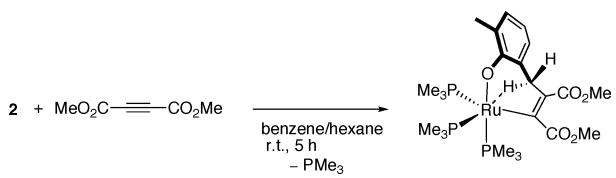


1 **2** (1)

Results and discussion

Reaction of oxaruthenacycle with DMAD and the molecular strucutre of 3

Treatment of an oxaruthenacycle complex **2** with DMAD in a mixture of benzene/hexane at room temperature followed by the work up procedure resulted in the formation of the insertion product in 47% yield [eqn. (2)].



3
47% (2)

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† Electronic supplementary information (ESI) available: Variable-temperature $^{31}P\{^1H\}$ NMR spectra of **3** in acetone-d_6. CCDC reference numbers 711077–711078. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b821179e

‡ Abbreviations used in this article. COD = cyclooctadiene, C_8H_{12}. COT = cyclooctatriene, C_8H_{10}. DMAD = dimethyl acetylenedicarboxylate, $MeO_2CC{\equiv}CCO_2Me$. TCNE = tetracyanoethylene, $(NC)_2C{=}C(CN)_2$.

It is notable that when this reaction took place in the presence of an excess amount of DMAD in benzene, a complex mixture was obtained. To obtain a single product, we performed this reaction in a mixture of benzene/hexane to promote deposition of the mono insertion product.

Single crystals suitable for the X-ray structure analysis were obtained by the recrystallisation of **3** from the cold CH_2Cl_2/hexane solution. The molecular structure of **3** is given in Fig. 1 and selected bond distances and angles are listed in Table 1.

The molecular structure of **3** shows that a DMAD molecule is inserted into the Ru–C bond to form a seven-membered oxaruthenacycle, which seems to be formally a coordinatively unsaturated complex. However, the distance Ru(1)–C(8) [2.730(5) Å] suggests the presence of an agostic interaction of the methylene group (*vide infra*), which is also supported by a weak band at 2541 cm^{-1} assignable to the stretching vibration of the agostic C–H bond in the IR spectrum.[6] Agosctic Ru(II)–C bond distances are reported in the range 2.395(4)–3.445(4) Å.[7,8] Therefore, the present Ru(1)–C(8) bond distance is good evidence for the agostic interaction. By taking into account this interaction and the bond angles P(1)–Ru(1)–P(2) [96.43(6)°], P(1)–Ru(1)–P(3) [96.82(7)°], P(1)–Ru(1)–O(1) [83.22(12)°] and P(3)–Ru(1)–O(1) [173.14(13)°], complex **3** is best regarded as a distorted octahedral geometry. The bond distance C(9)–C(10) [1.358(9) Å] and the dihedral angle C(8)–C(9)–C(10)–Ru(1) [2.4(6)°] show the double bond character between C(9)–C(10) and the C(8), C(9), C(10) and Ru(1) atoms locate on almost the same plane. The dihedral angles C(10)–C(9)–C(11)–O(2) [177.7(6)°] and C(9)–C(10)–C(13)–O(4) [–93.0(9)°] indicate that while the carbonyl group of C(11)–O(2) locates on the same plane to the C(9)–C(10) double bond, the carbonyl

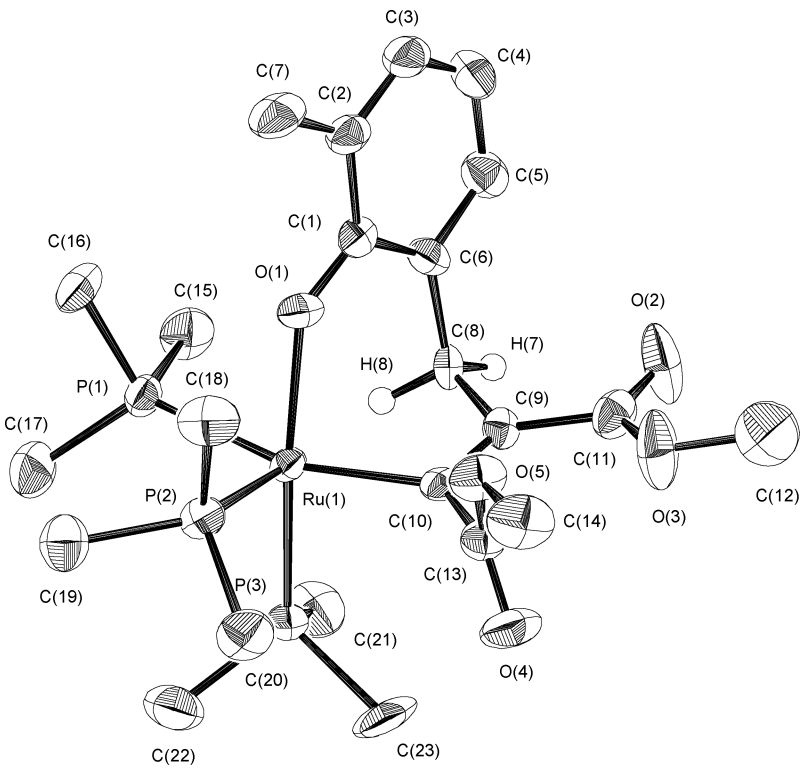


Fig. 1 Molecular structure of **3** showing atomic numbering schemes. Ellipsoids represent 50% probability. All hydrogen atoms except the methylene protons at C(8) and an incorporated CH_2Cl_2 molecule are omitted for clarity.

Table 1 Selected bond distances (Å) and angles (deg) of **3**

Ru(1)–P(1)	2.3549(18)	Ru(1)–P(2)	2.2152(17)
Ru(1)–P(3)	2.2685(19)	Ru(1)–O(1)	2.128(4)
Ru(1)–C(10)	2.098(6)	O(2)–C(11)	1.256(9)
O(3)–C(11)	1.264(9)	O(3)–C(12)	1.435(19)
O(4)–C(13)	1.198(8)	C(6)–C(8)	1.509(9)
C(8)–C(9)	1.515(8)	C(9)–C(10)	1.358(9)
C(9)–C(11)	1.477(9)	C(10)–C(13)	1.466(9)
Ru(1)–C(8)	2.730(5)		
P(1)–Ru(1)–P(2)	96.43(6)	P(1)–Ru(1)–P(3)	96.82(7)
P(1)–Ru(1)–O(1)	83.22(12)	P(1)–Ru(1)–C(10)	160.85(18)
P(3)–Ru(1)–O(1)	173.14(13)	Ru(1)–O(1)–C(1)	124.5(4)
C(6)–C(8)–C(9)	111.0(5)	C(8)–C(9)–C(10)	118.0(5)
Ru(1)–C(10)–C(9)	105.9(4)	C(8)–C(9)–C(10)–Ru(1)	2.4(6)
C(9)–C(10)–C(13)–O(4)	–93.0(9)	C(10)–C(9)–C(11)–O(2)	177.7(6)

C(13)–O(4) is vertical. This fact suggests steric repulsion among the α-methoxycarbonyl group, the equatorial and axial PMe_3 ligands, and the β-methoxycarbonylcarbonyl group.

The methyl ester carbon C(12) was disordered and the alternative carbon C(25), which is not shown in Fig. 1, was bonded to O(2). The best calculated population of C(12)/C(25) was 50/50. On the other hand, no disorder was found for C(14). Ru(1)–P(1) [2.3549(18) Å] which is remarkably longer than Ru(1)–P(2) [2.2152(17) Å] or Ru(1)–P(3) [2.2685(19) Å], suggesting a strong *trans* influence of C(10).

A similar treatment of **2** with phenylacetylene quantitatively released 2,6-xylenol,[4b] and neither reaction of diphenylacetylene nor methyl propiolate with **2** did not proceed under the same conditions.

Fluxional behaviour of 3 in a solution

Complex **3** shows a fluxional behaviour in solution. At 20 °C in acetone-d_6, no apparent signals assignable to **3** are observed in the $^{31}P\{^1H\}$ NMR spectrum. On cooling the solution to 0 °C, broad peaks are observed at δ −3.0 (br, 1P), 14.8 (br, 1P) and 43.8 (br, 1P). The highest-field resonance at δ −3.0 is assigned to the PMe_3 *trans* to C having a very strong *trans* influence,[9] that is also consistent with the longest Ru(1)–P(1) bond in the solid state (Table 1). The signal at δ 14.8 is assignable to the PMe_3 ligands *trans* to O. It is notable that the reported PMe_3 resonances *trans* to OAr in octahedral *cis*-$RuH(OAr)(PMe_3)_4$ are in the range δ 15.2–16.4.§ The signal at δ 43.8 is assigned to the PMe_3 *trans* to the agostic hydrogen. This is also consistent with the shortest Ru(1)–P(2) bond in the solid sate (Table 1). These three peaks become sharper on further cooling to −40 °C to show an AMX spin system at δ −2.0 (t, $^2J_{P\text{-}P}$ = 23 Hz, 1P), 15.6 (dd, $^2J_{P\text{-}P}$ = 47, 23 Hz, 1P) and 44.6 (br.dd, $^2J_{P\text{-}P}$ = 47, 23 Hz, 1P) but further cooling until −60 °C results in the specific broadening of the signal at δ 45.0 (half-width = 179 Hz), which is finally divided into two signals at δ 45.3 and 46.5 in a 7/3 ratio at −80 °C.

In the ^1H NMR spectrum of **3** in acetone-d_6 at 20 °C, a broad signal assignable to the three PMe_3 is observed around δ 1.4–1.6 (27H) (Fig. 2). The most significant feature of **3** in the ^1H NMR spectrum is a doublet at δ −1.40 ($^2J_{H\text{-}H}$ = 15.6, 1H) and a doublet of quartets at δ 3.26 ($^2J_{H\text{-}H}$ = 15.6, $^5J_{H-P}$ = 1.5, 1H). The ^1H–^1H COSY suggests these signals being tied up with each other and they are assigned as the geminal methylene protons.

This large splitting and the high-field shift of one of these protons are due to the agostic interaction and the signal at δ −1.40 is assignable to the agostic proton. It is notable that while the *exo* (non-agostic) methylene proton has coupled to three equivalent phosphorus atoms, the *endo* methylene proton apparently does not have spin coupling to any phosphorus atoms despite the

§ The reported PMe_3 resonances for *trans* to OAr in $RuH(OAr)(PMe_3)_4$ in the $^{31}P\{^1H\}$ NMR are as follows: δ 15.2 (Ar = C_6H_4OMe-4, in C_6D_6) [ref. 23], δ 15.2 (Ar = C_6H_4Me-2, in C_6D_6) [ref. 4*b*], δ 15.3 (Ar = $C_6H_4CHMe_2$-2, in C_6D_6) [ref. 4b], δ 15.3 (Ar = C_6H_4Me-4, in CD_2Cl_2) [ref. 24] and δ 16.4 (Ar = Ph, in CD_2Cl_2) [ref. 24].

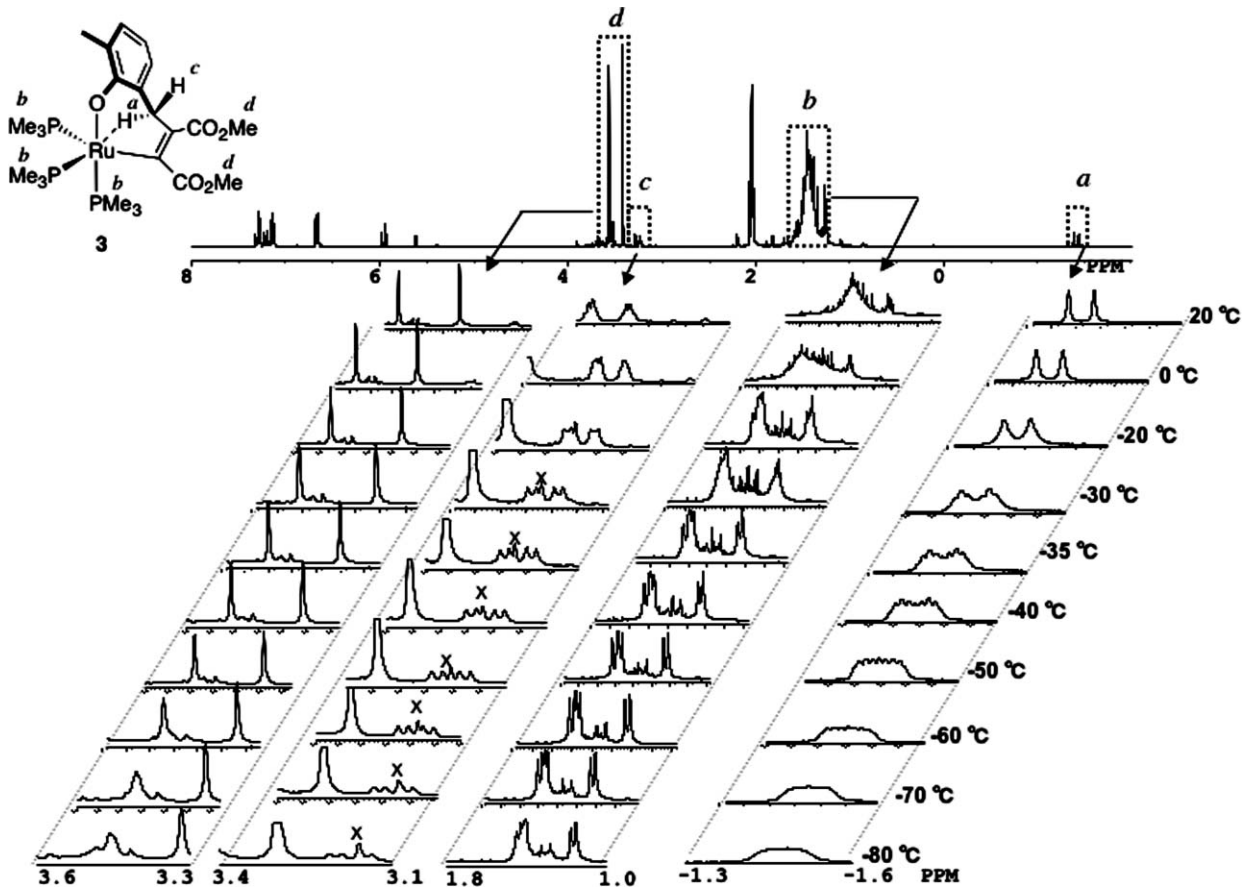


Fig. 2 Variable-temperature ^1H NMR spectra of **3** in acetone-d_6 (300 MHz). X indicates an impurity.

agostic interaction. Therefore, the H–P spin coupling for the *exo* methylene proton is considered to be transferred through the $^{5}J_{H-P}$ bonds. On the other hand, the *endo* methylene proton does not have any apparent H–P couplings probably because of the small averaged three $^{2}J_{H-P}$ spin couplings through agostic interaction at this temperature. On cooling the solution at −50 °C, these geminal methylene signals changed to a doublet of doublets of triplets at δ −1.40 ($^{2}J_{H-H}$ = 15.7, $^{2}J_{H-P}$ = 8.1, $^{2}J_{H-P}$ = 3.9 Hz, 1H) and a doublet of doublets at δ 3.24 ($^{2}J_{H-H}$ = 15.7, $^{4}J_{H-P}$ = 6.0 Hz, 1H), without changing the chemical shift. Further cooling of the solution results in the significant broadening of these methylene signals. For the methoxy resonances in the ester groups sharp two singlets are observed at δ 3.42 (3H, half width = 0.96 Hz) and 3.57 (3H, half width = 0.96 Hz) at 20 °C. On cooling the solution, the latter signal causes broadening (half-width = 8.4 Hz) at −80 °C, while the former remains relatively sharp (half-width = 2.5 Hz). Unfortunately, we do not know which methoxycarbonyl group is assigned to this broadening signal.

It is notable that in the ^{13}C NMR spectrum of **3** in chloroform-d_1 at 18 °C, a doublet of doublets at δ 26.9 (dd, $^{1}J_{C-H}$ = 126, 98 Hz) is assignable to the *ortho*-methylene carbon. The small $^{1}J_{C-H}$ value ($^{1}J_{C-H}$ = 98 Hz), being a typical diminished $^{1}J_{C-H}$ value (75–100 Hz),[10] suggests the presence of agostic interaction. In addition, this fact supports the presence of agostic interaction even around room temperature.

These fluxional behaviours can be explained as follows (Fig. 3). Complex **3** has an agostic interaction at room temperature and the fluxionality is due to the rapid site exchanging of the three PMe_3 ligands. Since the J_{H-P} spin coupling between one of the methylene protons and three equivalent phosphorus atoms remains intact throughout this temperature range at almost the same chemical shift, the site exchange is operated in the octahedral geometry by a turnstile mechanism.[11] Around −40 °C, the site exchange of the PMe_3 ligands almost stopped. However, as described above, further fluxional behaviour should be involved in this complex. At −80 °C, the PMe_3 ligand *trans* to the agostic ligand is separated into two broad resonances in the $^{31}P\{^{1}H\}$ NMR and one of the methoxy resonances also shows significant broadening at the same time. The fluxionality observed below −40 °C is independent from the agostic interaction because the *exo* and *endo* methylene protons basically do not change their chemical shifts in this temperature range (20 to −80 °C). The most probable reason for this fluxionality is a slow down of the rotation of one of the methoxycarbonyl groups. As described above, we have observed two orientations of the β–methoxycarbonyl group by X-ray analysis. One may relate this finding with the fluxionality. However, we believe this is a less likely scenario because the orientation of the β–methoxycarbonyl group would not perturb the PMe_3 *cis* to C so much.¶ The more pertinent explanation for this fluxionality is therefore attributable to the slow down in rotation of the α–methoxycarbonyl group as depicted in Fig. 3. The α–methoxycarbonyl resonance and the PMe_3 resonance *cis* to C are separated into two peaks at low temperature, although the frozen NMR spectum could not be obtained under experimental conditions. Probably, the α–methoxycarbonyl group has two stable orientations in the equatorial plane around −80 °C

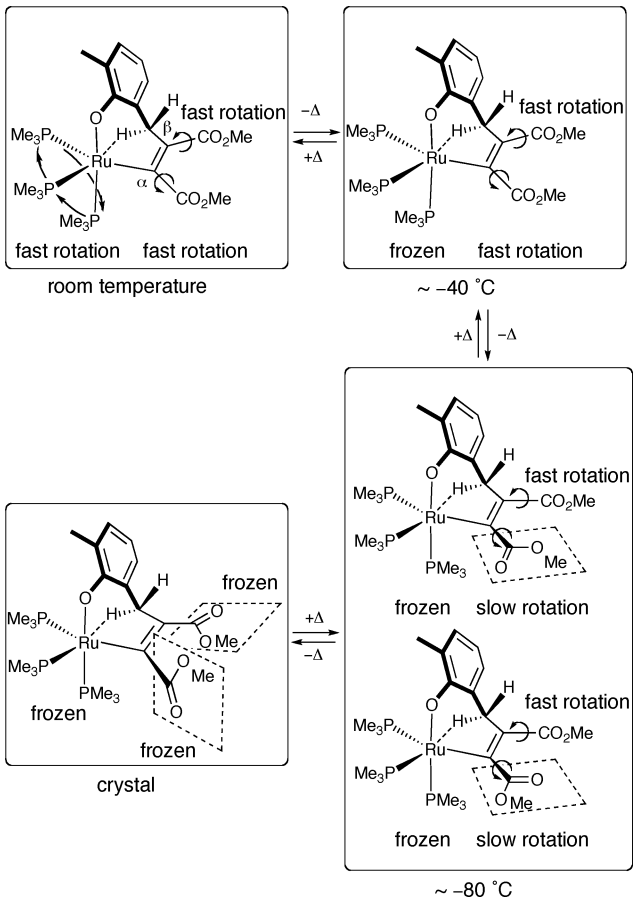


Fig. 3 Possible behaviours of **3**. At room temperature, PMe_3 and α-methoxycarbonyl groups rotate and the rotation of PMe_3 was frozen around −40 °C. Around −80 °C, the rotation of the α-methoxycarbonyl group slows down. In a crystal, X-ray analysis shows the α-methoxycarbonyl group locates in the vertical to the equatorial plane.

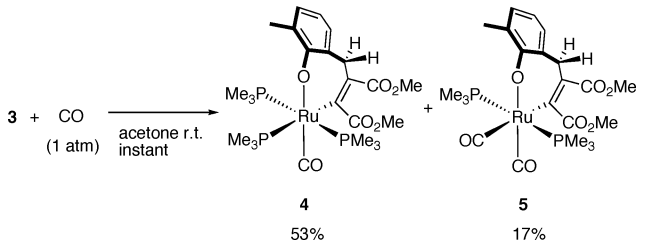
because only the PMe_3 *cis* to C shows significant change below −40 °C. These rotamers would be stabilized by conjugation with the neighbouring C=C bond.

The ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra would be affected by the proximal/distal methyl ester group toward the PMe_3 ligand *cis* to C. However, X-ray analysis of **3** showed that the α-methoxycarbonyl group takes from the C=C plane despite loss of the conjugated system in the solid state (Fig. 1). This may be caused by the packing of **3** in a unit cell because of the steric repulsion by the equatorial PMe_3 and the β-methoxycarbonyl groups.

The fluxional complex **3** was instantly converted to a stable complex by exposure to an atmosphere of CO. By exposure of an acetone solution of **3** to CO (0.1 MPa) at room temperature, the orange colour was immediately bleached. After evaporation of the solution followed by washing with cold pentane, a mixture of saturated carbonyl complexes was obtained as a colourless powder of **4** (53%) and **5** (17%) [eqn. (3)]. Unfortunately the $^{31}P\{^{1}H\}$ NMR spectrum of these complexes did not give useful structural information because of broadening. The ^{1}H NMR spectrum suggests the presence of two independent species. Since both complexes have a virtual triplet assignable to the PMe_3 ligand, these compounds have a couple of mutually *trans* PMe_3 ligands, respectively. The presence of the third PMe_3 is observed only for the

¶ Since the anisotropic displacement parameter U_{ani} for P(1) [0.0301(4)] is comparable to P(2) [0.0323(4)] and P(3) [0.0300(4)], the 50/50 disorder of the β-methoxycarbonyl group does not affect the P(1) atom.

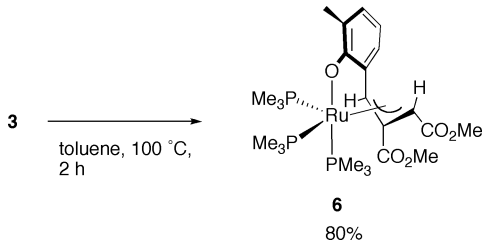
major species in the ^{1}H NMR spectrum in relatively high magnetic field at δ 1.07 (d), that is characteristic PMe_3 *trans* to the carbon having a strong *trans* influence. Therefore, overall structures for **4** and **5** are assigned as shown in eqn. (3). Consistently, the methylene protons appeared at δ 3.81 for **4** and δ 3.71 for **5** as a singlet, respectively, although they are observed as slightly broad signals, probably due to flipping of the seven-membered oxaruthenacycle ring. This fact also suggests the apparent C_s symmetry of **4** and **5** in solution. The IR spectrum of the mixture of **4** and **5** shows three bands assignable to the metal carbonyls at 2052 (s, *ν*CO), 1962 (s, *ν*CO) and 1922 (vs, *ν*CO) cm^{-1} in KBr, suggesting the presence of three different metal carbonyl groups.



(3)

1,3-Hydrogen shift to give an η^3–allylic complex

Heating of the fluxional complex **3** due to agostic interaction caused a unique 1,3-H shift reaction. Namely, the NMR study for heating of a toluene solution of **3** at 100 °C for 2 h produced an η^3-allylic complex **6** in 80% yield [eqn. (4)]. Complex **6** was also prepared directly from **2** without isolation of **3** in 90% isolated yield.



(4)

Complex **6** shows an AXY pattern in the ^{31}P{^{1}H} NMR suggesting the presence of three inequivalent phosphorus atoms. The ^{1}H NMR shows a terminal allylic proton at δ 5.41 (s, 1H) and an *ortho* methine proton at δ 2.74 (d, 1H). However, the most direct evidence for the molecular structure of **6** was obtained by X-ray analysis (Fig. 4) and the selected molecular distances and angles are listed in Table 2. The comparable bond distances Ru(1)–C(8), Ru(1)–C(9) and Ru(1)–C(10) (2.202–2.257 Å), the almost equal distances C(8)–C(9) [1.413(8) Å] and C(9)–C(10) [1.429(8) Å],

Table 2 Selected bond distances (Å) and angles (deg) of **6**

Ru(1)–P(1)	2.3344(16)	Ru(1)–P(2)	2.3277(16)
Ru(1)–P(3)	2.3026(16)	Ru(1)–O(1)	2.144(4)
Ru(1)–C(8)	2.252(5)	Ru(1)–C(9)	2.202(6)
Ru(1)–C(10)	2.257(5)	C(8)–C(9)	1.413(8)
C(9)–C(10)	1.429(8)		
P(1)–Ru(1)–P(2)	100.55(5)	P(1)–Ru(1)–P(3)	91.58(5)
P(1)–Ru(1)–O(1)	83.22(13)	P(1)–Ru(1)–C(9)	128.20(17)
P(2)–Ru(1)–C(9)	130.66(17)	P(3)–Ru(1)–O(1)	172.96(13)
C(6)–C(8)–C(9)	124.3(5)	C(8)–C(9)–C(10)	122.0(5)
C(9)–C(10)–C(13)	121.2(5)		

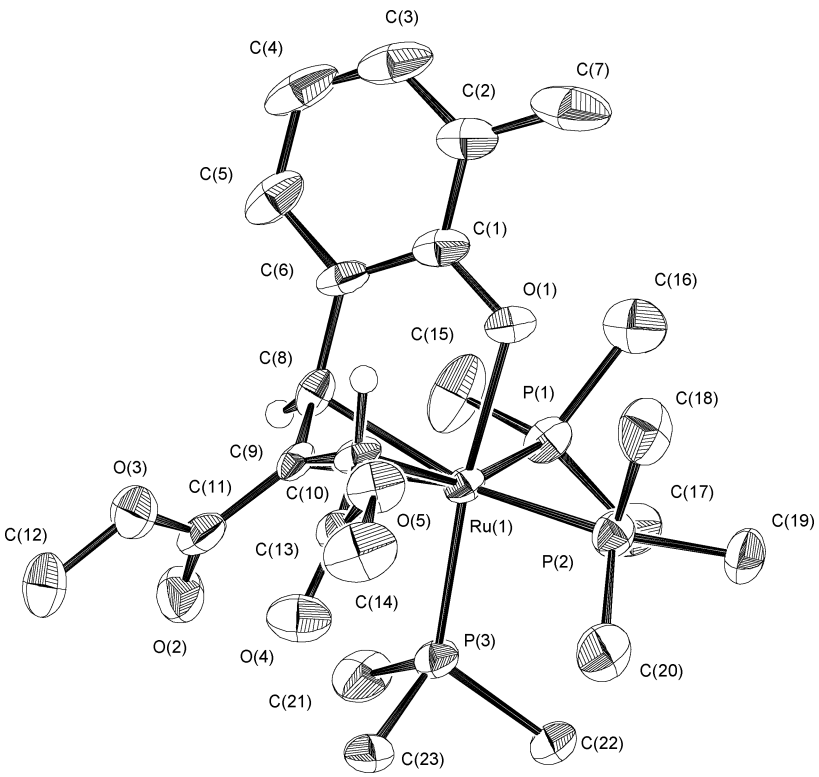
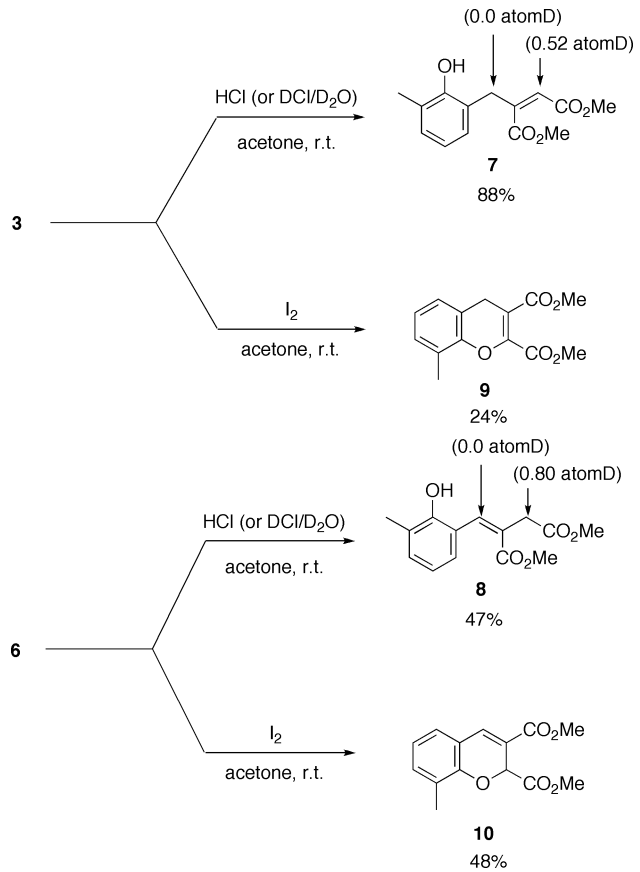


Fig. 4 Molecular structure of **6** with numbering schemes. All hydrogen atoms except allylic protons and an incorporated CH_2Cl_2 molecule are omitted for clarity. Ellipsoids represent 50% probability.

and bond angles C(6)–C(8)–C(9) [124.3(5)°], C(8)–C(9)–C(10) [122.0(5)°] and C(9)–C(10)–C(13) [121.2(5)°] indicate formation of an η^3-allylic fragment. The stereochemistry of the allyic moiety is *anti* to the aryl fragment and *syn* to the terminal methoxycarbonyl group. The molecular structure of **6** is best regarded as a trigonal bipyramidal complex with κ^1O and η^3-allylic bondings. Since a benzylic methylene proton in complex **3** has an agostic interaction with Ru, one of the most reasonable explanations for the formation mechanism of **6** is the C–H bond cleavage reaction of the agostic proton in **3** followed by the migration of the resulting hydride to the terminal carbon to give **6**.

Acidolysis and iodolysis of complexes 3 and 6

Acidolysis of **3** by dry HCl gas in acetone produced 2-[(*Z*)-2′,3′-bis(methoxycarbonyl)allyl]-6-methylphenol (**7**) in 88% yield. Compound **7** was characterised by ^{1}H NMR, GLC and GC-MS. Similar treatment of **3** with DCl/D_2O resulted in the deuteration of the methine proton at the 3′-proton (Scheme 1). On the other hand, acidolysis of **6** by dry HCl gas gave 2-[(*Z*)-2′,3′-bis(methoxycarbonyl)propenyl]-6-methylphenol (**8**) in 47% yield and treatment of **6** with DCl/D_2O led to the deuteration of the terminal methylene group at the 3′-position.‖ Although Miura and his coworkers reported formation of dibenzopyran derivatives by



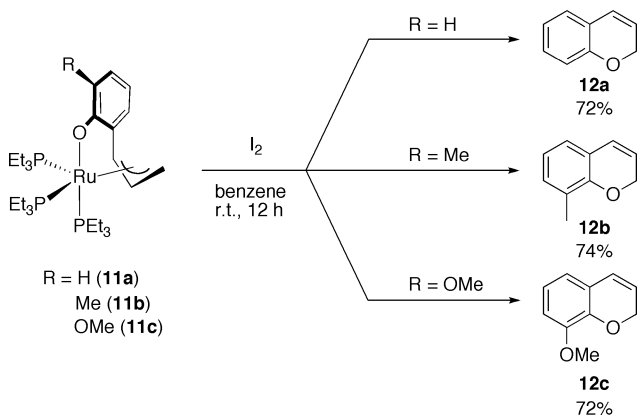
Scheme 1

‖ Selective incorporation of deuterium at the terminal methine and methylene position suggests strong linkage between these carbons and the Ru centre. However, the reason why their deuterium contents have diminished is not clear at present.

an sp^2 C–H bond cleavage reaction of 2-phenylphenol followed by an insertion alkyl acrylates/β–hydrogen elimination followed by Michael type nucleophilic cyclisation,[12] no cyclisation occurred from **7** or **8** in the present system under these conditions.

Reductive elimination from a metallacycle-like present system seems to be a promising way to produce heterocycles. However, divalent ruthenium requires high energy for reductive elimination[13] and reductive elimination between carbon and electronegative atoms is difficult.[14] Despite these facts, it is interesting to introduce a rare example of Pfeffer and his co-workers, where a Ru(II) complex RuCl(η^6-C_6H_6)($NMe_2CH_2C_6H_4$-κ^2N,C) reacted with internal alkynes to yield an isoquinolinium derivative and Ru(0) at room temperature,[15] where spontaneous C–N reductive elimination was expected to be involved. Ryabov and his co-workers demonstrated that Pfeffer's reaction involved a C–N bond reductive elimination step by kinetic studies.[16] Therefore, it is worth studying the production of benzopyran derivatives from **3** and **6**. However, they were thermally stable complexes and treatments of them with TCNE or atmospheric oxygen led to complex decomposition. When iodine was employed as an oxidant, 2,3-bis(methoxycarbonyl)-8-methyl-4*H*-benzopyran (**9**) and 2,3-bis(methoxycarbonyl)-8-methyl-2*H*-benzopyran (**10**) were obtained from **3** and **6** in 24% and 48% yields, respectively.

In relation to the iodolysis of **6**, we have briefly reported formation of a similar η^3-allylic complex Ru[OC_6H_4(2-CHCHCH$_2$)-κ^1O,η^3-C,C',C''](PEt_3)$_3$ (**11a**) by the reaction of **1** with 2-allylphenol in the presence of PEt_3.[4a] It is interesting to compare the iodolysis of **6** to that of **11a** because they have a comparable κ^1,η^3-structure. Reaction of **1** with 2-allyl-6-methylphenol and 2-allyl-6-methoxyphenol in the presence of PEt_3 produced corresponding allylic complexes Ru[OC_6H_4(2-CHCHCH$_2$)(6-Me)-κ^1O,η^3-C,C',C''](PEt_3)$_3$ (**11b**) and Ru[OC_6H_4(2-CHCHCH$_2$)(6-OMe)-κ^1O,η^3-C,C',C''](PEt_3)$_3$ (**11c**) in 38% and 42% yields, respectively. Iodolysis of **11a–c** at room temperature also led to the formation of 2*H*-benzopyrans in moderate yields (72–74%) (Scheme 2). These benzopyrans were characterised by the authentic samples prepared by literature methods.[17,18]



Scheme 2

These reactions suggest that iodine is an effective oxidant to promote reductive elimination between the terminal allylic carbon and aryloxo oxygen and the C–O reductive elimination is a common nature of these κ^1O,η^3-allylic complexes. Although the detailed mechanism for the reductive elimination is so far unclear,

intramolecular nucleophilic attack of the aryloxo oxgen to the η^3-allylic moiety is a possible pathway.[14]

Conclusions

In conclusion, the present work provides a stoichiometric transformation reaction of 2,6-xylenol *via* a sp^3 C–H bond cleavage reaction of the *ortho* methyl group, where each step can be unequivocally characterised in detail by NMR and X-ray analyses. An insertion reaction of a ruthenacycle complex **3** with DMAD followed by the 1,3-H shift reaction led to the formation of an η^3-allylic complex **6**. Although a strong oxidant such as iodine is required for the reaction, this process gives 2*H*-benzopyran derivatives suggesting reductive elimination between the terminal allylic carbon and oxygen. Such C–O bond formation by reductive elimination is generally rare, although reductive elimination between acyl and alkoxo/aryloxo groups is well documented.[4a] These stoichiometric reactions represent production of benzopyran derivatives from 2,6-xylenol or 2-allylphenol *via* an sp^3 C–H bond cleavage reaction.

Experimental

General procedures

All manipulations were carried out under dry nitrogen using standard Schlenk and vacuum line techniques. Benzene, toluene, hexane and Et_2O were dried over anhydrous calcium chloride and then distilled from sodium wire under nitrogen with benzophenone ketyl as an indicator. Acetone and dichloromethane were dried over anhydrous Drierite and distilled over Drierite under nitrogen. Complex **1** was prepared according to the reported method.[4a,b] DMAD was used as received. Compound **12a** was prepared according to the literature method by the reduction of 4-chromanone with $LiAlH_4$ followed by dehydration.[17] Compounds **12b** and **12c** were prepared according to the literature method by the Claisen rearrangement reactions of 2-methylphenyl propargyl ether derived from *ortho*-cresol and 2-methoxyphenyl proargyl ether derived from 2-methoxyphenol.[18] PMe_3 and PEt_3 were prepared by the reaction of $P(OPh)_3$ with MeMgI or EtMgBr.[19] Aluminium oxide was purchased from Merck (90 active neutral, active stage I, 70–230 mesh) and was used as received.

Deuterated solvents for use in NMR experiments were purchased from Kanto Chemical and dried with sodium wire for benzene-d_6 and Drierite for acetone-d_6 and were directly vacuum transferred into an NMR tube. NMR spectra were recorded on a JEOL LA-300 or ECX-400 spectrometers (300.4 MHz or 399.8 MHz for ^{1}H) with chemical shifts reported in ppm downfield from TMS for ^{1}H and from 85% H_3PO_4 in D_2O for ^{31}P NMR. IR spectra were recorded on a JASCO FT/IR-410 spectrometer using KBr disks. Elemental analyses were carried out using a Perkin-Elmer 2400 series II CHN analyzer. GC-MS spectra were performed on a Shimadzu QP2000 equipped with a capillary column (TC-1, 0.25 mm × 30 m).

Reaction of 2 with DMAD. Ru[OC_6H_3(2-CH_2)(6-Me)-κ^2*O,C*](PMe_3)$_4$ (**2**) (133.1 mg, 0.2535 mmol) was placed in a 25 ml Schlenk tube, into which hexane (4 ml) and benzene (2 ml) were added to give a yellow solution. DMAD (52.8 µl, 0.431 mmol) was added and the solution turned red instantly. The resulting solution was stirred at room temperature for 5 h to give an orange precipitate. The resulting precipitate was washed with hexane and was recrystallised from cold CH_2Cl_2 to give an orange agostic complex Ru[OC_6H_3{2-CH_2C(CO_2Me)=C(CO_2Me)}(6-Me)-κ^2*O,C*](PMe_3)$_3$ (**3**) in 47% yield (70.3 mg, 0.119 mmol). ^{1}H NMR (300 MHz, acetone-d_6, 20 °C): δ −1.40 (d, $^2J_{H-H}$ = 15.6 Hz, 1H, agostic *ortho*-CH_2), 1.4–1.5 (br, 27H, P*Me*$_3$), 2.1 (overlapped, *ortho-Me*), 3.26 (dq, $^2J_{H-H}$ = 15.6, $^5J_{H-P}$ = 1.5 Hz, 1H, *ortho*-CH_2), 3.42 (s, 3H, β-CO_2*Me*), 3.57 (s, 3H, α-CO_2*Me*), 5.96 (t, $^3J_{H-H}$ = 7.2 Hz, 1H, *para*-C_6H_3), 6.67 (d, $^3J_{H-H}$ = 7.2 Hz, 2H, *meta*-C_6H_3). ^{1}H NMR (300 MHz, acetone-d_6, −50 °C): δ −1.41 (ddt, $^2J_{H-H}$ = 15.9, $^5J_{H-P}$ = 7.8, $^5J_{H-P}$ = 3.9 Hz, 1H, agostic *ortho*-CH_2), 2.00 (br s, 9H, P*Me*$_3$), 2.02–2.06 (overlapped with signals due to acetone, PMe_3), 2.07 (s, *ortho-Me*), 3.26 (dd, $^2J_{H-H}$ = 15.9, $^5J_{H-P}$ = 6.3 Hz, 1H, *ortho*-CH_2), 3.38 (s, 3H, β-CO_2*Me*), 3.53 (s, 3H, α-CO_2*Me*), 5.95 (t, $^3J_{H-H}$ = 7.2 Hz, 1H, *para*-C_6H_3), 6.63 (d, $^3J_{H-H}$ = 7.2 Hz, 2H, *meta*-C_6H_3). ^{13}C{^{1}H} NMR (100.5 MHz, chloroform-d_1, 18 °C): δ 17.4 (s, *ortho*-CH_3),18–27 (br.m, PCH_3), 26.9 (s, *ortho*-CH_2), 50.9 (s, CO_2CH_3), 51.1 (s, CO_2CH_3), 109.9 (s, aromatic), 120.2 (s, aromatic), 125.5 (s, aromatic), 127.4 (s, aromatic), 127.9 (s, aromatic), 129.2 (s, aromatic), 162.7 (s, *C*=O or *C*=C), 169.9 (s, *C*=O or *C*=C), 178 (br, *C*=C), 179.1 (s, *C*=O or *C*=C). ^{13}C NMR (100.5 MHz, chloroform-d_1, 18 °C): δ 17.4 (q, $^1J_{C-H}$ = 130 Hz, *ortho*-CH_3), 15–27 (m, PCH_3), 26.9 (dd, $^2J_{C-H}$ = 126, 98 Hz, *ortho*-CH_2),50.9 (q, $^1J_{C-H}$ = 145 Hz, CO_2CH_3), 51.1 (q, $^1J_{C-H}$ = 145 Hz, CO_2CH_3), 110.0 (d, $^1J_{C-H}$ = 159 Hz, aromatic), 120.3 (s, aromatic), 125.5 (s, aromatic), 127.4 (d, $^1J_{C-H}$ = 155 Hz, aromatic), 127.9 (s, aromatic), 129.2 (d, $^1J_{C-H}$ = 160 Hz, aromatic), 162.6 (s), 169.9 (s), 178 (br), 179.1 (s). ^{31}P{^{1}H} NMR (121 MHz, acetone-d_6, 20 °C): no apparent peak. ^{31}P{^{1}H} NMR (121 MHz, acetone-d_6, −50 °C): δ −1.6 (t, $^2J_{P-P}$ = 23 Hz, 1P), 15.9 (dd, $^2J_{P-P}$ = 47, 23 Hz, 1P) and 45.0 (br, 1P). IR (KBr, cm^{-1}): 3044 (w), 2969 (w), 2905 (m), 2541 (w), 1681 (vs), 1575 (s), 1457 (s), 1424 (s), 1299 (s), 1218 (s), 1123 (s), 969 (s), 942 (vs), 856 (m), 740 (s), 721 (m), 672 (m). Anal. Calcd for $C_{23}H_{41}O_5P_3Ru$: C, 46.70; H, 6.99. Found: C, 46.74; H, 6.81.

Reaction of 3 with CO. Complex **3** (27.5 mg, 0.0464 mmol) was placed in a 25 ml Schlenk tube into which acetone (2 ml) was added to give an orange solution. Carbon monoxide (0.1 Mpa) was exposed to the solution at room temperature and the colour was instantly bleached within 1–2 min. The solution was evaporated to give a white solid which was washed with cold pentane to give colourless solid (17.8 mg). The NMR analyses of this product suggests a mixture of *mer*-Ru[OC_6H_3{2-CH_2C(CO_2Me)=C(CO_2Me)}(6-Me)-κ^2*O,C*](PMe_3)$_3$(CO) (**4**) and *cis,trans,cis*-Ru[OC_6H_3{2-CH_2C(CO_2Me)=C(CO_2Me)}(6-Me)-κ^2*O,C*](PMe_3)$_2$(CO)$_2$ (**5**) in 53% and 17% yields, respectively. **4**: ^{1}H NMR (300 MHz, benzene-d_6, r.t.): δ 1.07 (d, $^2J_{H-P}$ = 7 Hz, 9H, P*Me*$_3$), 1.14 (vt, $^2J_{H-P}$ = $^4J_{H-P}$ = 3.9 Hz, 18H, mutually *trans* P*Me*$_3$), 2.25 (s, 3H, 6-*Me*), 3.57 (s, 3H, CO_2*Me*), 3.75 (s, 3H, CO_2*Me*), 3.81 (br.s, 2H, 2-CH_2), 6.78 (t, $^3J_{H-H}$ = 7 Hz, 1H, aromatic), 7.1–7.2 (overlapped with signal due to benzene). ^{31}P{^{1}H} NMR (121 MHz, benzene-d_6, r.t.): δ −16.3 (t, ^2J = 28 Hz, 1P, *P*Me$_3$), −10.5 (br, 2P, *P*Me$_3$). **5**: ^{1}H NMR (300 MHz, benzene-d_6, r.t.): δ 1.09 (vt, $^2J_{H-P}$ = $^4J_{H-P}$ = 3.9 Hz, 18H, mutually *trans* P*Me*$_3$), 2.41 (s, 3H, 6-*Me*), 3.50 (s, 3H, CO_2*Me*), 3.66 (s, 3H, CO_2*Me*), 3.77 (br.s, 2H, 2-CH_2), 7.1–7.2 (overlapped with signal due to benzene), 7.4 (d, $^3J_{H-H}$ = 7 Hz, 1H, aromatic). ^{31}P{^{1}H} NMR (121 MHz, benzene-d_6, r.t.):

δ −9.0 (s, 2P, PMe_3). IR spectrum of a mixture of **4** and **5** in KBr (cm^{-1}): 2982 (m), 2944 (m), 2914 (m), 2052 (s, νCO), 1962 (s, νCO), 1922 (vs, νCO), 1703 (vs, νC=O), 1587 (m), 1558 (m), 1421 (s), 1286 (s), 1196 8 s), 1167 (s), 1101 (s), 1085 (s), 1020 (m), 949 (vs), 851 (s), 755 (s), 671 (m).

Preparation of 6.

(Method A). Complex **2** (79.9 mg, 0.1349 mmol) was placed in a 25 ml Schlenk tube into which hexane (5 ml) and benzene (3 ml) were added. DMAD (55.0 μl, 0.449 mmol) was added to the solution and the reaction mixture was stirred at room temperature for 5 h. The resulting precipitate was collected and washed with hexane. Then, toluene (3 ml) was added and the solution was heated at 100 °C for 10 h. After the reaction, the product was separated through column chromatography using neutral alumina and the yellow band was collected. The resulting yellow fraction was evaporated to give analytically pure yellow solid of Ru[OC_6H_3{2-CHC(CO_2Me)CH(CO_2Me)}(6-Me)-κ^1*O*,η^3-*C,C′,C″*](PMe_3)$_3$ (**6**) in 90% yield (71.8 mg, 0.121 mmol).

(Method B). Complex **3** (1.4 mg, 0.0024 mmol) was dissolved in toluene-d_8 (0.6 ml) and the solution was heated at 100 °C for 2 h. The NMR spectrum showed formation of **6** in 80% yield.

^{1}H NMR (300 MHz, benzene-d_6, r.t.): δ 1.02 (d, $^2J_{H-P}$ = 8.4 Hz, 9H, P*Me*$_3$), 1.15 (d, $^2J_{H-P}$ = 8.4 Hz, 9H, P*Me*$_3$), 1.28 (d, $^2J_{H-P}$ = 8.4 Hz, 9H, P*Me*$_3$), 2.26 (s, 3H, *ortho-Me*), 2.74 (d, $^3J_{H-P}$ = 3.3 Hz, 1H, *syn*-C*H*Ar), 3.43 (s, 3H, CO_2*Me*), 3.59 (s, 3H, CO_2*Me*), 5.41 (s, 1H, *anti*-C*H*CO_2Me), 6.54 (t, $^3J_{H-H}$ = 7.4 Hz, 1H, *para*-C_6H_3), 7.04 (d, $^3J_{H-H}$ = 6.9 Hz, 1H, *meta*-C_6H_3), 7.14 (overlapped, *meta*-C_6H_3). ^{13}C{^{1}H} NMR (74.5 MHz, benzene-d_6, r.t.): δ 17.15 (s, 6-*Me*), 19.4 (dd, $^1J_{C-P}$ = 22, $^3J_{C-P}$ = 8 Hz, P*Me*$_3$), 20.78 (dd, $^1J_{C-P}$ = 21, $^3J_{C-P}$ = 6 Hz, P*Me*$_3$), 22.7 (d, $^1J_{C-P}$ = 28 Hz, P*Me*$_3$), 50.18 (s, O*Me*), 52.50 (s, O*Me*), 52.77 (d, $^2J_{C-P}$ = 18 Hz, *C*H), 80.17 (d, $^2J_{C-P}$ = 17 Hz, *C*H), 110.58 (s, *C*CO_2Me), 112.42 (s, C_6H_3), 126.5 (d, $^4J_{C-P}$ = 3 Hz, 3-C_6H_3), 127.2 (s, 2- or 6-C_6H_3), 129.02 (s, 6- or 2-C_6H_3), 129.78 (s, 5-C_6H_3), 168.9 (d, $^3J_{C-P}$ = 8 Hz, 1-C_6H_3), 172.4 (d, $^3J_{C-P}$ = 5 Hz, *C*O_2Me), 174.2 (s, *C*O_2Me). ^{31}P{^{1}H} (121 MHz, benzene-d_6, r.t.): δ 3.03 (dd, $^2J_{P-P}$ = 38, 26 Hz, 1P, *P*Me_3), 3.18 (dd, $^2J_{P-P}$ = 38, 26 Hz, 1P, *P*Me_3), 7.93 (t, $^2J_{P-P}$ = 38 Hz, 1P, *P*Me_3). Anal. Calcd for $C_{23}H_{41}O_5P_3Ru$: C, 46.70; H, 6.99. C, 46.87; H, 6.68.

Acidolysis of 3. Complex **3** (4.8 mg, 0.0081 mmol) was placed in a 25 ml Schlenk tube into which acetone (3 ml) was added. Dry HCl gas was exposed to the solution using a manometer (0.139 mmol, 17.1 equiv) and the solution colour instantly turned pale yellow with deposition of precipitate. The liquid phase was separated form the precipitate and volatile matter was removed under vacuum to give 2-[(*Z*)-2′,3′-bis(methoxycarbonyl)allyl]-6-methylphenol (**7**) in 88% yield. ^{1}H NMR (300 MHz, benzene-d_6, r.t.): δ 1.90 (s, 3H, 6-*Me*), 3.22 (s, 3H, CO_2*Me*), 3.40 (s, 3H, CO_2*Me*), 3.46 (d, $^4J_{H-H}$ = 1.5 Hz, 2H, 2-CH_2), 5.78 (t, $^4J_{H-H}$ = 1.5 Hz, 1H, C*H*CO_2Me), 6.69 (t, $^3J_{H-H}$ = 7.5 Hz, 1H, 4-C*H*), 6.77 (dd, $^3J_{H-H}$ = 7.2, $^4J_{H-H}$ = 2.1 Hz, 1H, 3- or 5-C*H*), 6.85 (dd, $^3J_{H-H}$ = 7.2, $^4J_{H-H}$ = 2.1 Hz, 1H, 5- or 3-C*H*). GC-MS (EI): *m*/*z* = 264 (M^+).

Acidolysis of **3** (4.3 mg, 0.0072 mmol) with 3 drops of DCl/D_2O (37 wt%) in benzene-d_6 caused incorporation of D atoms at 52% at the terminal methine in **7** and no incorporation was observed at the benzylic position.

Acidolysis of 6. Complex **6** (67.4 mg, 0.114 mmol) was placed in a 25 ml Schlenk tube into which acetone (3 ml) was added. Dry HCl gas was exposed to the solution using a manometer (0.228 mmol, 2 equiv) and the solution was instantly bleached with deposition of precipitate. The liquid phase was separated from the precipitate and volatile matter was removed under vacuum to give 2-[(*Z*)-2′,3′-bis(methoxycarbonyl)propenyl]-6-methylphenol (**8**) in 47% yield. ^{1}H NMR (300 MHz, benzene-d_6, r.t.): δ 2.13 (s, 3H, 6-*Me*), 3.25 (s, 3H, CO_2*Me*), 3.34 (s, 2H, C$H_2$$CO_2$Me), 3.36 (s, 3H, CO_2*Me*), 6.18 (br, 1H, O*H*), 6.70 (t, $^3J_{H-H}$ = 7 Hz, 1H, 4-C*H*), 6.90 (d, $^3J_{H-H}$ = 7 Hz, 1H, 3- or 5-C*H*), 6.93 (d, $^3J_{H-H}$ = 7 Hz, 1H, 5- or 3-C*H*), 8.00 (s, 1H, C*H*=C). GC-MS (EI): *m*/*z* = 264 (M^+).

Acidolysis of **6** (7.0 mg, 0.012 mmol) with 3 drops of DCl/D_2O (37 wt%) in benzene-d_6 caused incorporation of D atoms at 80% at the terminal methine in **8** and no incorporation was observed at the benzylic position.

Iodolysis of 3. Complex **3** (17.0 mg, 0.0287 mmol) was placed in a 25 ml Schlenk tube into which acetone (3 ml) was added. Addition of iodine (12.4 mg, 0.0488 mmol) to the solution caused an immediate colour change to dark brown. The solution was stirred at room temperature for 12 h during which deposition of precipitate was observed. After removal of the precipitate, all volatile matter was removed under reduced pressure to give 2,3-bis(methoxycarbonyl)-8-methyl-*4H*-benzopyran (**9**) in 24% yield. ^{1}H NMR (300 MHz, benzene-d_6, r.t.): δ 2.06 (s, 3H, 8-*Me*), 3.09 (s, 3H, CO_2*Me*), 3.32 (s, 3H, CO_2*Me*), 3.89 (s, 2H, 4-CH_2), 6.70 (t, $^3J_{H-H}$ = 7 Hz, 1H, 6-C*H*), 6.88 (d, $^3J_{H-H}$ = 7 Hz, 1H, 5- or 7-C*H*), 7.22 (d, $^3J_{H-H}$ = 7 Hz, 1H, 7- or 5-C*H*). GC-MS (EI): *m*/*z* = 262 (M^+).

Preparation of 11a. Preparation of **11a** was briefly reported in a previous communication.[4a] Complex **1** (383 mg, 1.21 mmol) was placed in a 25 ml Schlenk tube into which benzene (4 ml), PEt_3 (540 μl, 3.65 mmol) and 2-allylphenol (160 μl, 1.22 mmol) were added in this order. The solution was stirred at 50 °C for 12 h, during which the yellow solution turned orange. After removal of volatile matter, the resulting solid was dried under vacuum. The solid was extracted with Et_2O and purified by a chromatography with neutral alumina. The yellow fraction was collected and the solution was concentrated. Setting aside the solution at −20 °C for a night gave yellow blocks of **11a** in 39% yield (227.4 mg). ^{1}H NMR (300 MHz, benzene-d_6, r.t.): δ 0.72 (dt, $^3J_{H-P}$ = 12.2, $^3J_{H-H}$ = 7.6 Hz, 9H, PCH_2CH_3), 1.01 (dt, $^3J_{H-P}$ = 12.2, $^3J_{H-H}$ = 7.6 Hz, 9H, PCH_2CH_3), 1.10 (dt, $^3J_{H-P}$ = 12.2, $^3J_{H-H}$ = 7.6 Hz, 9H, PC$H_2$$CH_3$), 1.25 (dq, $^2J_{H-P}$ = 14.6, $^3J_{H-H}$ = 7.6 Hz, 3H, PC$H_2$$CH_3$), 1.57 (dq, $^2J_{H-P}$ = 14.6, $^3J_{H-H}$ = 7.6 Hz, 3H, PC$H_2$$CH_3$), 1.73 (dq, $^2J_{H-P}$ = 14.6, $^3J_{H-H}$ = 7.6 Hz, 3H, PC$H_2$$CH_3$ and overlapped 1H), 1.88 (dq, $^2J_{H-P}$ = 14.6, $^3J_{H-H}$ = 7.6 Hz, 3H, PC$H_2$$CH_3$), 2.01 (dq, $^2J_{H-P}$ = 14.6, $^3J_{H-H}$ = 7.6 Hz, 9H, PC$H_2$$CH_3$), 3.03 (m, 1H, benzylic C_3H_4), 4.63 (dq, $^3J_{H-P}$ = 19.7, $^3J_{H-H}$ = $^3J_{H-P}$ = 7.4 Hz, 1H, *central*-C_3H_4), 5.60 (dt, $^3J_{H-H}$ = 7.4, $^3J_{H-P}$ = 3.5 Hz, 1H, *terminal-anti*-C_3H_4), 6.67 (td, $^3J_{H-H}$ = 7.2, $^4J_{H-H}$ = 1.2 Hz, 1H, C_6H_4), 6.80 (d, $^3J_{H-H}$ = 8.1 Hz, 1H, C_6H_4), 7.16 (overlapped with benzene, C_6H_4), 7.46 (dd, $^3J_{H-H}$ = 7.5, $^4J_{H-H}$ = 1.8 Hz, 1H, C_6H_4). ^{13}C{^{1}H} NMR (74.5 MHz, benzene-d_6, r.t.): δ 9.0 (d, *J* = 4 Hz), 9.4 (d, *J* = 4 Hz), 9.6 (d, *J* = 4 Hz), 21.2 (d, *J* = 18 Hz), 22.4 (d, *J* = 18 Hz), 22.9 (d, *J* = 18 Hz), 47.1 (dd, *J* = 23, 3 Hz), 71.4 (dd, *J* = 23, 3 Hz), 92.5 (s), 111.8 (s), 118.2 (d, *J* = 5 Hz), 127.2 (s), 130.7 (s), 172.2 (d, *J* = 8 Hz). ^{31}P{^{1}H} NMR (122 MHz, benzene-d_6, r.t.): δ 21.0 (dd, $^2J_{P-P}$ = 32,

12 Hz, 1P, PEt_3), 22.6 (dd, $^2J_{P-P}$ = 32, 12 Hz, 1P, PEt_3), 32.8 (t, $^2J_{P-P}$ = 32 Hz, 1P, PEt_3). Anal. Calcd for $C_{27}H_{53}OP_3Ru$: C, 55.18; H, 9.09. Found: C, 55.10; H, 8.92.

Preparation of 11b. Similar to **11a**, **11b** was prepared by the reaction of **1** (242.0 mg, 0.767 mmol), 2-allyl-6-methylphenol (126.0 μl, 0.843 mmol) in the presence of PEt_3 (340.0 μl, 2.302 mmol) at 50 °C for 12 h. Complex **11b** was obtained as yellow blocks from cold Et_2O in 38% yield (177.6 mg). ^{1}H NMR (300 MHz, benzene-d_6, r.t.): δ 0.72 (dt, $^3J_{H-P}$ = 11.7, $^3J_{H-H}$ = 7.5 Hz, 9H, PCH_2CH_3), 0.98 (dt, $^3J_{H-P}$ = 12.6, $^3J_{H-H}$ = 7.5 Hz, 9H, PCH_2CH_3), 1.10 (dt, $^3J_{H-P}$ = 12.3, $^3J_{H-H}$ = 7.5 Hz, 9H, PCH_2CH_3 and overlapped 3H), 1.29 (dq, $^2J_{H-P}$ = 14.3, $^3J_{H-H}$ = 7.5 Hz, 3H, PCH_2CH_3), 1.57 (dq, $^2J_{H-P}$ = 14.3, $^3J_{H-H}$ = 7.5 Hz, 3H, PCH_2CH_3), 1.75 (dq, $^2J_{H-P}$ = 14.3, $^3J_{H-H}$ = 7.5 Hz, 3H, PCH_2CH_3), 1.92 (dq, $^2J_{H-P}$ = 14.3, $^3J_{H-H}$ = 7.5 Hz, 3H, PCH_2CH_3), 2.06 (dq, $^2J_{H-P}$ = 14.3, $^3J_{H-H}$ = 7.5 Hz, 3H, PCH_2CH_3), 2.39 (s 3H, 6-*Me*), 2.96 (m, 1H, benzylic C_3H_4), 4.64 (dq, $^3J_{H-P}$ = 11.8, $^3J_{H-H}$ = $^3J_{H-P}$ = 7.7 Hz, 1H, *central*- C_3H_4), 5.59 (dt, $^3J_{H-H}$ = 7.7, $^3J_{H-P}$ = 3.3 Hz, 1H, *terminal-anti*-C_3H_4), 6.65 (t, $^3J_{H-H}$ = 7.2 Hz, 1H, C_6H_3), 7.10 (d, $^3J_{H-H}$ = 7.2 Hz, 1H, C_6H_3), 7.37 (d, $^3J_{H-H}$ = 7.2 Hz, 1H, C_6H_3). ^{31}P{^{1}H} NMR (122 MHz, benzene-d_6, r.t.): δ 21.4 (dd, $^2J_{P-P}$ = 31, 14 Hz, 1P, PEt_3), 23.4 (dd, $^2J_{P-P}$ = 31, 14 Hz, 1P, PEt_3), 32.6 (t, $^2J_{P-P}$ = 31 Hz, 1P, PEt_3). Anal. Calcd for $C_{28}H_{55}OP_3Ru$: C, 55.89; H, 9.21. Found: C, 56.12; H, 9.50.

Preparation of 11c. Similar to **11a**, **11c** was prepared by the reaction of **1** (199.5 mg, 0.632 mmol), 2-allyl-6-methoxyphenol (107.0 μl, 0.696 mmol) in the presence of PEt_3 (280.0 μl, 1.896 mmol) at 50 °C for 12 h. Complex **11b** was obtained as yellow blocks from cold Et_2O in 42% yield (164.7 mg). ^{1}H NMR (300 MHz, benzene-d_6, r.t.): δ 0.72 (dt, $^3J_{H-P}$ = 11.7, $^3J_{H-H}$ = 7.6 Hz, 9H, PCH_2CH_3), 1.03 (dt, $^3J_{H-P}$ = 12.6, $^3J_{H-H}$ = 7.6 Hz, 9H, PCH_2CH_3), 1.23 (dt, $^3J_{H-P}$ = 14.8, $^3J_{H-H}$ = 7.6 Hz, 9H, PCH_2CH_3), 1.60 (dq, $^2J_{H-P}$ = 14.9, $^3J_{H-H}$ = 7.6 Hz, 3H, PCH_2CH_3), 1.79 (dq, $^2J_{H-P}$ = 14.9, $^3J_{H-H}$ = 7.6 Hz, 3H, PCH_2CH_3 and overlapped 1H), 1.93 (dq, $^2J_{H-P}$ = 14.9, $^3J_{H-H}$ = 7.6 Hz, 3H, PCH_2CH_3), 2.11 (dq, $^2J_{H-P}$ = 14.9, $^3J_{H-H}$ = 7.6 Hz, 3H, PCH_2CH_3), 3.12 (m, 1H, benzylic C_3H_4), 3.68 (s, 3H, O*Me*), 4.63 (dq, $^3J_{H-P}$ = 12.0, $^3J_{H-H}$ = $^3J_{H-P}$ = 7.4 Hz, 1H, *central*-C_3H_4), 5.58 (dt, $^3J_{H-H}$ = 7.4, $^3J_{H-H}$ = $^3J_{H-P}$ = 3.4 Hz, 1H, *terminal-anti*-C_3H_4), 6.68 (t, $^3J_{H-H}$ = 7.5 Hz, 1H, C_6H_3), 6.74 (dd, $^3J_{H-H}$ = 7.5, $^4J_{H-H}$ = 1.5 Hz, 1H, C_6H_3), 7.21 (dd, $^3J_{H-H}$ = 7.5, $^4J_{H-H}$ = 1.5 Hz, 1H, C_6H_3). ^{31}P{^{1}H} NMR (122 MHz, benzene-d_6, r.t.): δ 21.3 (dd, $^2J_{P-P}$ = 31, 13 Hz, 1P, PEt_3), 22.7 (dd, $^2J_{P-P}$ = 31, 13 Hz, 1P, PEt_3), 32.9 (t, $^2J_{P-P}$ = 31 Hz, 1P, PEt_3). Anal. Calcd for $C_{28}H_{55}O_2P_3Ru$: C, 54.44; H, 8.97. Found: C, 54.70; H, 8.77.

Iodolysis of 11a. Complex **11a** (74.8 mg, 0.127 mmol) was dissolved in benzene (2 ml) into which iodine (48.5 mg, 0.191 mmol) was added. The yellow solution instantly turned red. After stirring the solution at room temperature for 12 h, the product was purified by column chromatography using neutral alumina with Et_2O as eluent to give 2*H*-benzopyran (**12a**) in 72% yield. The product was identified by comparison with an authentic sample. ^{1}H NMR (300 MHz, benzene-d_6, r.t.): δ 4.39 (dd, $^3J_{H-H}$ = 3, $^4J_{H-H}$ = 2 Hz, 2H, 2-CH_2), 5.17 (dt, $^3J_{H-H}$ = 10, 3 Hz, 1H, 3-C*H*), 6.10 (dt, $^3J_{H-H}$ = 10, $^4J_{H-H}$ = 2 Hz, 1H, 4-C*H*), 6.75–6.89 (m, 3H, aromatic).

Iodolysis of 11b. Complex **11b** (41.5 mg, 0.0689 mmol) reacted with iodine (30.2 mg, 0.118 mmol) in benzene-d_6 (0.6 ml) in the presence of 1,4-dioxane as an internal standard. The product was identified as 8-methyl-2*H*-benzopyran (**12b**) by comparison with an authentic sample and the yield was estimated as 74%. ^{1}H NMR (300 MHz, benzene-d_6, r.t.): δ 2.19 (s, 3H, 8-*Me*), 4.42 (dd, $^3J_{H-H}$ = 3, $^4J_{H-H}$ = 2 Hz, 2H, 2-CH_2), 5.20 (dt, $^3J_{H-H}$ = 10, 3 Hz, 1H, 3-C*H*), 6.15 (dt, $^3J_{H-H}$ = 10, $^4J_{H-H}$ = 2 Hz, 1H, 4-C*H*), 6.69–6.89 (m, 3H, aromatic).

Iodolysis of 11c. Complex **11c** (38.5 mg, 0.0623 mmol) reacted with iodine (24.2 mg, 0.0954 mmol) in benzene-d_6 (0.6 ml) in the presence of 1,4-dioxane as an internal standard. The product was identified as 8-methoxy-2*H*-benzopyran (**12c**) by comparison with an authentic sample and the yield was estimated as 72%. ^{1}H NMR (300 MHz, benzene-d_6, r.t.): δ 3.39 (s, 3H, 8-O*Me*), 4.42 (dd, $^3J_{H-H}$ = 3, $^4J_{H-H}$ = 2 Hz, 2H, 2-CH_2), 5.20 (dt, $^3J_{H-H}$ = 10, 3 Hz, 1H, 3-CH), 6.15 (dt, $^3J_{H-H}$ = 10, $^4J_{H-H}$ = 2 Hz, 1H, 4-C*H*), 6.49–6.55 (d, $^3J_{H-H}$ = 8 Hz, 2H, 5- and 7-C*H*), 6.70 (t, $^3J_{H-H}$ = 8 Hz, 1H, 6-C*H*).

X-Ray analyses of 3 and 6. A rigaku AFC-7R diffractometer with graphite-monochromated Mo-K_α (λ = 0.71069 Å) was used for data collection. Single crystals of **3** suitable for X-ray analysis were obtained by the recrystallisation of analytically pure solid of **3** from cold CH_2Cl_2/hexane. The single crystals of **3** were sensitive to X-ray irradiation and they decomposed during the data collection regardless of the measurement temperature. The best crystallographic data were collected as follows. A selected crystal of **3** was mounted in a flame-sealed glass capillary (GLASS, 0.7 mm ϕ) under argon. During the data collection, −55.5% decay of the standard reflections were observed. The collected data were solved by Direct methods (SIR92), and refined by a full-matrix least-square procedure using SHELXL97[20] on the Crystal Structure ver.3.8 package program.[21] A Psi-Scan was applied for absorption collections. In the differential Fourier map, C(12) was found to be disordered, where the alternative methyl group C(25) was connecting to O(2). The occupancy of C(12)/C(25) was refined [$C(12)_{occ}$ + $C(25)_{occ}$ = 1.00] and the final population was estimated to be 0.500/0.500. Although O(2) and O(3) must also disorder around O(3) and O(2) positions, respectively, they cannot be found from the differential Fourier-map and they were treated as virtually ordered oxygen atoms. All non-hydrogen atoms except C(12) and C(25) were refined with anisotropic displacement parameters. All hydrogen atoms were added theoretically, riding on the concerned atoms and were not refined. The crystallographic data is summarized in Table 3.

Single crystals of **6** were also obtained from recrystallisation of **6** from a cold CH_2Cl_2/hexane solution. A selected single crystal of **6** was mounted on the top of glass capillary by use of Paraton N oil. The reflection data were collected at 200 K under a cold nitrogen stream. The collected data were solved by Direct methods (SIR92), and refined by a full-matrix least-square procedure using SHELXL97[20] on the Crystal Structure ver. 3.8 package program.[21] The solved crystal belonged to a chiral space group ($Pna2_1$) and the absolute structure of **6** was determined on the basis of the anomalous dispersion effect of Friedel pairs.[22] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were added theoretically, riding on the concerned atoms and were not refined.

Table 3 Crystallographic data and refinement details for **3** and **6**

	3·CH_2Cl_2	**6**·CH_2Cl_2
Formula	$C_{24}H_{43}Cl_2O_5P_3Ru$	$C_{24}H_{43}Cl_2O_5P_3Ru$
Formula weight	676.50	676.50
Crystal system	*monoclinic*	*orthorhombic*
Space group	$P2_1/n$ (*No.*14)	$Pna2_1$ (*No.*33)
Unit cell dimensions		
a (Å)	22.265(8)	17.068(3)
b (Å)	15.629(14)	13.970(3)
c (Å)	9.049(3)	13.023(3)
β (deg)	91.11(3)	
V (Å^3)	3143(3)	3105.1(10)
D_{calcd} (g cm^{-1})	1.427	1.447
Temp (K)	298.1	200.0
$F(000)$	1400.00	1400.00
μ (mm^{-1})	0.850	0.862
Unique reflections	7233	4281
No. of observed reflections $[F^2>2\sigma(F^2)]$	2968	3035
Crystal size (mm)	0.40 × 0.20 × 0.10	0.35 × 0.20 × 0.10
No. of variables in LS	315	329
Flack parameter		-0.06(3)
Goodness of fit	0.946	1.025
$R_1(wR_2)$	0.0502 (0.1539)	0.0318(0.0810)

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