

Cluster chemistry

XCIV. * Preparation and characterisation of some Ru₅ clusters containing vinylidene ligands **

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Abstract

Reactions of the open Ru₅C₂ cluster complex, Ru₅(μ₅-C₂)(μ-SMe)₂(μ-PPh₂)₂(CO)₁₁ (1), with hydrogen or olefins afforded electron-rich vinylidene complexes Ru₅(μ₃-CCHR)(μ₃-SMe)₂(μ-PPh₂)₂(CO)₁₀ [2; R = H and 3; R = CH=CHR' (R' = H, Me, Ph and CO₂Et)]. X-ray structural determinations have been carried out on 2 and 3 (R' = H, Me and Ph). These complexes contain an Ru₅ core consisting of three edge-sharing triangles; the vinylidene ligand, which spans one of the Ru₃ faces, is fluxional, with concomitant changes occurring in the orientations of the SMe, PPh₂ and CO groups. The clusters have 80 cluster valence electrons, the Ru–Ru separations being elongated (av. 3.03 Å) as a result of occupation of Ru–Ru anti-bonding orbitals.

Key words: Ruthenium; Cluster; Vinylidene; Fluxionality; Crystal structure; X-ray diffraction; Dicarbon

1. Introduction

The complex Ru₅(μ₅-C₂)(μ-SMe)₂(μ-PPh₂)₂(CO)₁₁ (1; Scheme 1) [1] contains a C₂ ligand situated on top of a pentagonal Ru₅ skeleton; in this position, this ligand is sterically readily accessible and the cluster is unusually reactive. We have carried out Extended Hückel MO calculations on the model complex Ru₅(μ₅-C₂)(μ-SH)₂(μ-PH₂)₂(CO)₁₁, described elsewhere [2], and confirm, as experimentally observed that electrophilic attack can occur on C_β and one or both of the bridging sulfur atoms and nucleophilic attack on C_α. Characteristic reactions include the insertion of C_β into HX (X = H, C) bonds in, for example, H₂ and olefins to give the novel electron-rich vinylidene clus-

ters 2 and 3. This paper gives a full account of this chemistry, some of which has appeared in a preliminary report [2].

2. Results

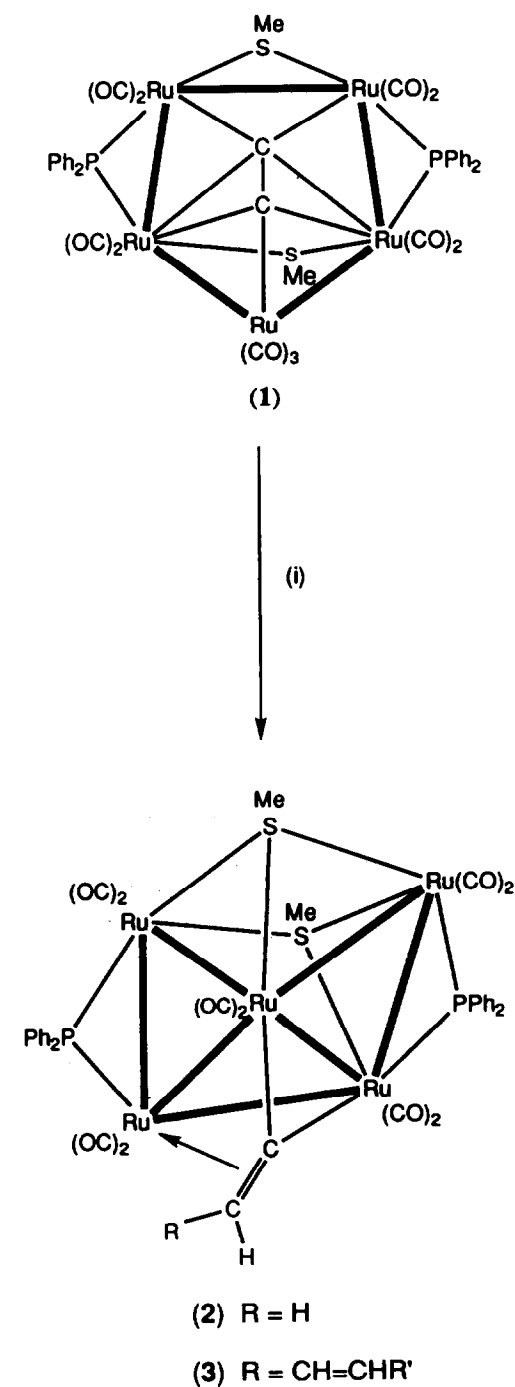
The parent vinylidene cluster was obtained from reactions between 1 and dihydrogen in refluxing toluene, which gave 2 in virtually quantitative yield. The black crystalline product was characterised by a single-crystal X-ray structural determination, which was reported earlier [2], as the μ₃-vinylidene complex Ru₅(μ₃-CCH₂)(μ₃-SMe)₂(μ-PPh₂)₂(CO)₁₀. This structure will not be discussed in detail here, but appropriate comparisons with the structures of the olefin addition products 3 are made below.

The FAB mass spectrum of 2 contains a molecular ion at *m/z* 1277, together with ions formed by loss of up to ten CO groups between *m/z* 1249 and 997. The IR spectrum contains only terminal ν(CO) absorptions.

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* For Part XCIII, see reference [19].

** Dedicated to Helmut Werner in recognition of his many pioneering contributions to organometallic chemistry.



Reagents: (i) For R = H, H₂

For R = CH=CHR', CH₂=CHR'
(R' = H, Me, Ph, CO₂Et)

Scheme 1.

The NMR spectra contain resonances which are also generally consistent with the solid-state structure. In particular, the two inequivalent SMe singlets are found

in the ¹H NMR spectrum at δ -0.22 and 3.17, and the protons of the CCH₂ group resonate at δ 5.12 and 5.22; the chemical shifts of the latter are similar to those found for the trinuclear complex Fe₃(μ₃-CCH₂)(μ-CO)(CO)₉ (δ 5.23) [3]. The ¹³C NMR spectrum contains signals at δ 20.09 and 22.63 for the SMe groups, several signals between δ 190.8 and 204.5 for the CO ligands, and two doublets at δ 70.22 and 285.43, which we assign to the C_β and C_α carbons, respectively (cf. δ 75.12 and 250.12 for the Fe₃ complex mentioned above). The resonance for C_α has the characteristic down-field shift found for other carbons of this type [4]. The ³¹P NMR spectrum consists of two singlets at δ 86.9 and 101.0. As a result of the fluxionality found for complexes 3, to be discussed below, we examined the variable temperature ³¹P NMR spectra of 2. At room temperature a fully resolved low-temperature limiting spectrum is found with some broadening of the two resonances occurring at 80°C.

The reactions between 1 and ethene, propene, styrene and ethyl acrylate were all carried out in the same way, involving heating of the reactants together in a Carius tube at 110°C for about 20 h. The black products were obtained in yields ranging between 78 (R' = H) and 36% (R' = Ph). Single-crystal X-ray structural determinations were carried out on the clusters obtained from the first three olefins, and showed that the complexes were similar to 2, but contained the novel μ₃-vinylrinylidene ligands CCHCH=CHR' (R' = H, Me, Ph or CO₂Et) in place of the μ₃-CCH₂ ligand found in 2. The structure of 3 (R' = H) was described in the preliminary account of this work [2]; all of these structures are now fully discussed below.

In all cases, the FAB mass spectra contained molecular ions which fragmented by loss of up to ten CO groups. The IR spectra were similar to that of 2, containing ν(CO) bands only in the terminal region. The ¹H NMR spectra were also similar to that found for 2, with the two inequivalent SMe signals being found around δ -0.2 and 3.2 and the vinylidene CH resonances occurring at δ ca. 6.6. The vinyl CH signals occurred between δ 6.2–7.5; the coupling constants (ca. 15 Hz) found for the olefinic protons were consistent with the *trans* stereochemistry of the vinyl groups found in the solid-state structures and allow the same stereochemistry to be assigned to 3 (R' = CO₂Et). Other resonances characteristic of the R' substituents are listed in the Experimental section.

The ¹³C NMR spectra were also easily assigned. The two SMe carbons were found between δ 18.5 and 22.7, while C_β resonated between δ 90–98. The Ru-bonded C_α appeared as a singlet between δ 270–290. Detailed examination of the resonances assigned to the P–Ph groups and to the CO ligands indicated that some were

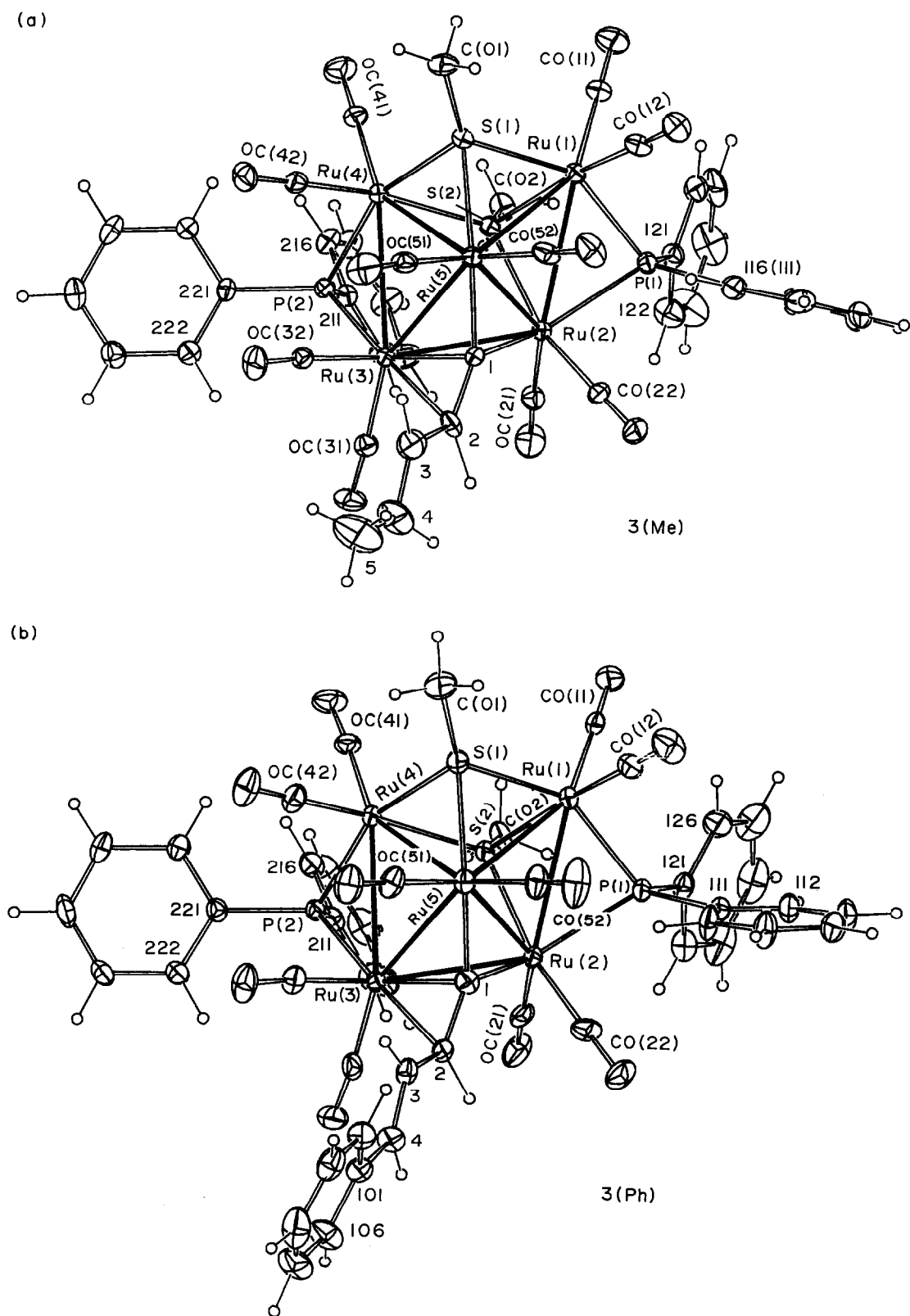


Fig. 1. Plots of molecules of $[\text{Ru}_5(\mu_3\text{-CCH}(\text{CH}=\text{CHR}'))(\mu_3\text{-SMe})_2(\mu\text{-PPh}_2)_2(\text{CO})_{10}]\mathbf{3}$; (a) $\text{R}' = \text{Me}$, (b) $\text{R}' = \text{Ph}$, showing the atom-numbering schemes. Non-hydrogen atoms are shown as 20% thermal ellipsoids; hydrogen atoms have arbitrary radii of 0.1 Å.

broadened, possibly by a fluxional process; at room temperature these were not observed, being broadened sufficiently to merge with the baseline. The ³¹P NMR spectra also gave unequivocal evidence of a fluxional process involving these atoms, two broadened resonances appearing at δ 86.3 and 100.0 (R' = H), 88.0 and 99.0 (R' = Me), 88.7 and 100.7 (R' = Ph) and 89.1 and 103.4 (R' = CO₂Et).

The ³¹P resonances in the NMR spectrum of **3** (R' = H) coalesced at 65°C and sharp low-temperature limiting spectra were obtained at -20°C. These data enabled a value for ΔG[‡] for the fluxional process of 60.3(3) kJ mol⁻¹ to be calculated. We estimate that ΔG[‡] for the similar process occurring in **2** is about 10 kJ mol⁻¹ greater.

3. X-ray structural studies

Figure 1(a) and (b) are plots of single molecules of **3** (R' = Me and Ph, respectively) and Table 1 summarises significant bond parameters for the four complexes **2** and **3** (R' = H, Me and Ph). The main structural features of all four complexes are similar, the structures being based on an open Ru₅ framework consisting of three edge-sharing triangles. The two SMe ligands each bridge three of the five Ru atoms: both sulfur atoms are attached to Ru(1) and Ru(4), S(1) also being bonded to Ru(5), while S(2) is attached to Ru(2). Except for Ru(5)-S(1), which is short at between 2.335-2.356(2) Å, all the Ru-S distances fall in the range 2.378(4)-2.420(2) Å, the longest being the Ru(2)-S(2) vectors.

TABLE 1. Some bond parameters for complexes **2** and **3** (R' = H, Me and Ph)

R	H ^a	CH=CH ₂	CH=CHMe	CH=CHPh
<i>Distances (Å)</i>				
Ru(1)-Ru(2)	3.095(1)	3.053(3)	3.0455(9)	3.083(2)
Ru(1)-Ru(5)	2.992(1)	2.993(1)	3.046(1)	3.046(2)
Ru(2)-Ru(3)	2.9802(9)	2.948(1)	2.976(1)	2.974(2)
Ru(2)-Ru(5)	2.937(2)	2.983(1)	2.929(1)	2.944(2)
Ru(3)-Ru(4)	3.139(1)	3.162(3)	3.113(1)	3.130(1)
Ru(3)-Ru(5)	3.080(1)	3.062(2)	3.056(1)	3.045(3)
Ru(4)-Ru(5)	3.039(1)	3.024(2)	3.074(1)	3.076(2)
av.	3.037	3.032	3.034	3.043
Ru(1)···Ru(4)	3.729(1)	3.723(2)	3.709(1)	3.701(2)
Ru(1)-S(1)	2.396(2)	2.384(3)	2.401(3)	2.378(4)
Ru(4)-S(1)	2.409(2)	2.395(2)	2.386(2)	2.386(3)
Ru(5)-S(1)	2.356(2)	2.351(3)	2.335(2)	2.350(2)
Ru(1)-S(2)	2.391(2)	2.394(2)	2.384(2)	2.373(3)
Ru(2)-S(2)	2.417(2)	2.419(3)	2.420(2)	2.407(2)
Ru(4)-S(2)	2.391(2)	2.406(3)	2.401(3)	2.403(4)
Ru(1)-P(1)	2.313(2)	2.313(3)	2.317(3)	2.308(4)
Ru(2)-P(1)	2.373(2)	2.377(2)	2.376(2)	2.389(3)
Ru(3)-P(2)	2.319(2)	2.316(3)	2.320(2)	2.318(3)
Ru(4)-P(2)	2.303(2)	2.300(2)	2.297(2)	2.289(3)
Ru(2)-C(1)	2.144(6)	2.164(8)	2.142(8)	2.15(1)
Ru(3)-C(1)	2.052(6)	2.063(8)	2.063(8)	2.07(1)
Ru(5)-C(1)	1.964(6)	1.975(8)	1.957(7)	1.958(9)
Ru(3)-C(2)	2.308(7)	2.39(1)	2.358(8)	2.363(9)
C(1)-C(2)	1.37(1)	1.38(1)	1.397(9)	1.40(1)
<i>In C(3)H=C(4)HR</i>				
C(2)-C(3)	-	1.47(1)	1.45(1)	1.45(2)
C(3)-C(4)	-	1.31(2)	1.43(1)	1.34(1)
<i>Angles (°)</i>				
Ru(1)-Ru(5)-Ru(3)	110.36(5)	109.51(4)	107.92(3)	108.56(4)
Ru(1)-Ru(5)-Ru(4)	76.39(3)	76.45(3)	74.62(2)	74.38(4)
Ru(2)-Ru(5)-Ru(4)	83.17(4)	82.12(4)	82.89(3)	82.86(5)
Ru(1)-S(1)-Ru(4)	101.81(6)	102.34(8)	101.59(8)	101.9(1)
Ru(1)-S(2)-Ru(4)	102.49(6)	101.74(7)	101.64(8)	101.6(1)
<i>Dihedrals (°)</i>				
Ru(1,2,5)/Ru(2,3,5)	139.25(4)	141.40(4)	136.80(4)	137.10(4)
Ru(2,3,5)/Ru(3,4,5)	99.32(4)	97.93(4)	99.26(4)	98.94(4)

^a Unsolvated phase.

The Ru–P bridges are asymmetric; in general, P(2) forms shorter bonds to Ru(3) and Ru(4) [2.316–2.318(3), 2.289–2.303(3) Å] than does P(1) to Ru(1) and Ru(2) [2.308–2.317(3), 2.373–2.389(3) Å].

The organic ligands in these complexes have been formed by insertion of one of the carbons of the C₂ ligand present in **1** into the H–H bond of dihydrogen or one of the C–H bonds of the olefinic CH₂ group. The resulting vinylidene ligand bridges the Ru(2)–Ru(3)–Ru(5) triangle in the commonly found η^1, η^2 bonding mode, the π bond being coordinated to Ru(3). Atom C(1) is bonded to all three Ru atoms [C(1)–Ru(2,3,5) range between 2.142(8)–2.164(8), 2.052(6)–2.07(1) and 1.957(7)–1.975(8) Å, respectively], while Ru(3)–C(2) is 2.308(7) Å for **2** and between 2.358(8)–2.39(1) Å for **3**. These values may be compared with those found in Ru₃(μ_3 -CCMe(OMe))(μ_3 -CO)(CO)₉, where C _{α} –Ru(1,2,3) are 2.056(2), 2.066(2) and 2.161(2) Å, respectively, but C _{β} is outside a bonding distance from Ru(3) [2.782(2) Å] [5]. In Co₂Ru(μ_3 -CCH^tBu)(CO)₉, in which the vinylidene ligand has a stronger π interaction with the Ru atom, C(1,2)–Ru are 2.099(8) and 2.405(8) Å, respectively [3].

Of most interest in these structures are the Ru–Ru separations. Most of these are considerably longer than “normal” Ru–Ru distances found in electron-precise clusters where, for example, in Ru₃(CO)₁₂ the average Ru–Ru separation is 2.854 Å [6], while in Ru₅(μ_5 -C₂PPh₂)(μ -PPh₂)(CO)₁₃ (**4**), the immediate precursor of **1** [1], which has the same Ru₅ skeleton as **2** and **3**, the Ru–Ru separations average 2.869 Å [7]. The average Ru–Ru distances in **2** and **3** are essentially constant at 3.032–3.043 Å; the shortest bonds are Ru(2)–Ru(5) [2.929–2.983(1) Å] and Ru(2)–Ru(3) [2.948(1)–2.983(1) Å] (there is a curious anomaly in the Ru(2)–Ru(3,5) distances in **3** (R = CH=CH₂) compared with the other complexes), the other five bonded Ru–Ru vectors being between 2.992(1)–3.162(3) Å. The S(1)- and S(2)-bridged Ru(1)···Ru(4) vector is 3.701(2)–3.729(1) Å.

4. Discussion

The experiments described herein demonstrate a particular aspect of the reactivity of the C₂ molecule in **1**, namely the proclivity for one carbon of the C₂ ligand to insert into the H–H bond of dihydrogen or into a C–H bond of an olefinic substrate. The resulting complexes contain new examples of cluster-bound vinylidenes, which in the case of the olefin reaction products, are novel vinylvinylidenes. These are the first examples of cluster-bound ligands of this type, although the dedicatee of this paper has recently described some mononuclear rhodium complexes con-

taining related ligands, obtained either from enynes or by elimination of HX (X = Cl, HO, NH₂) from γ -functionalised vinylidenes [8].

Concomitant with the formation of the vinylidene ligand is the condensation of the pentagonal Ru₅ skeleton in **1** (with five Ru–Ru bonds) to the three triangle skeleton in **2** or **3** with seven Ru–Ru bonds. Unusually, only one CO ligand is lost, even though the SMe groups become 5-e μ_3 -bridging ligands. Consequently, the clusters are electron-rich. The normal cluster valence electron (CVE) count predicted for M₅ clusters with the geometry found here (three edge-sharing triangles with seven Ru–Ru bonds) is 76 [9]. In the present cases, the electron count is 80. They join the increasing number of Ru₄ and Ru₅ clusters which are being found with more than the normal numbers of electrons. Some examples include the planar (rhombohedral) clusters MRu₃(μ -PR₂)₂(CO)₁₃ (M = Ru [10], Fe [11]), Ru₄(μ -PR₂)₄(CO)₁₀ [10] and Ru₄(μ -PPh₂)(μ -C^tBu)(CO)₁₃ [12], and the butterfly clusters Ru₄(μ -NCy=CHCH=NCy)₂(CO)₈ [13] and Os₄(μ_3 -S)₂(CO)₁₂ [14]. All these complexes contain one or more M–M bonds which are longer than normal.

The explanation for the lengthening of these bonds may be found by considering the electron count for these clusters. Theoretical calculations have been carried out on several M₄ clusters of this type [15]. The response of the cluster to the extra electrons seems to be two-fold, and is dependent on the HOMO–LUMO separation: (a) lengthening of one (or more) of the Ru–Ru vectors to the point where there is no significant bonding interaction between the atoms, or (b) a general lengthening of the Ru–Ru vectors so that the cluster geometry is preserved, but the cluster core is expanded. The present case falls into class (b).

It is to be expected that these complexes would exhibit reactivity patterns consistent with the presence of excess electron density on the cluster. This has been demonstrated in the reaction between **2** and Fe₂(CO)₉, which afforded an FeRu₅ cluster **5** with unusual geometry, in which the vinylidene ligand assumed the unprecedented μ_4 -mode [16].

As described above, variable temperature NMR studies revealed that these complexes are fluxional, this process having $\Delta G^\ddagger = 60.3(3)$ kJ mol⁻¹ for **3** (R' = H). The dynamic process observed with complexes **3** and studied in detail with the vinylvinylidene complex only affects the resonances of the aryl protons, the aryl and CO carbons and the two phosphorus atoms. At temperatures below –20°C all resonances that are affected sharpen except those for the aryl protons (which may be due to lack of resolution of overlapping resonances). Neither the SMe nor the olefinic protons show any changes with temperature.

The simplest explanation for these results is a switching of the vinylidene ligand across the Ru(2)–Ru(3)–Ru(5) face of the cluster, with concomitant shifts in bonding of S(2) from Ru(2) to Ru(3) and a reorientation of the two μ -PPh₂ groups and the CO groups (Scheme 2). That the SMe resonances are not affected by these changes may be explained by the similarity in chemical surroundings of these groups in the two isomers. A possible explanation for the smaller barriers to isomerisation found for **3** is that in these complexes, the π basicity of the vinylidene C=C bond is decreased by conjugation with the olefinic π bond. The two shorter Ru–Ru bonds are found in the Ru₃ moiety capped by the vinylidene ligand. Both involve Ru(2), which has the longest Ru–C distance. In contrast, the shortest Ru(5)–C(1) distance involves a ruthenium atom with three long Ru–Ru bonds. This suggests that strong π back-bonding to the vinylidene occurs from the electron-rich central Ru(5). A similar pattern is found for the bonding of the SMe groups, where the shortest Ru–S bonds are to Ru(5). A weaker Ru–C(1)–C(2) interaction would facilitate the flipping of the vinylidene ligand. Intuitively, one would expect that the ligand could use Ru(5) as an anchor point, with the electron rearrangement consequent upon the flipping process occurring over the Ru(2,3)–C(1,2) moiety.

Detailed analysis of the ¹H and low temperature ³¹P NMR spectra of all complexes **3** reveal that a second isomer is present in small amount (about 10%). These isomers have slightly different chemical shifts for the SMe resonances as well as for the olefinic protons. A full analysis of the NMR spectra for these minor isomers was not possible on account of the low signal intensities and overlapping of several resonances. The

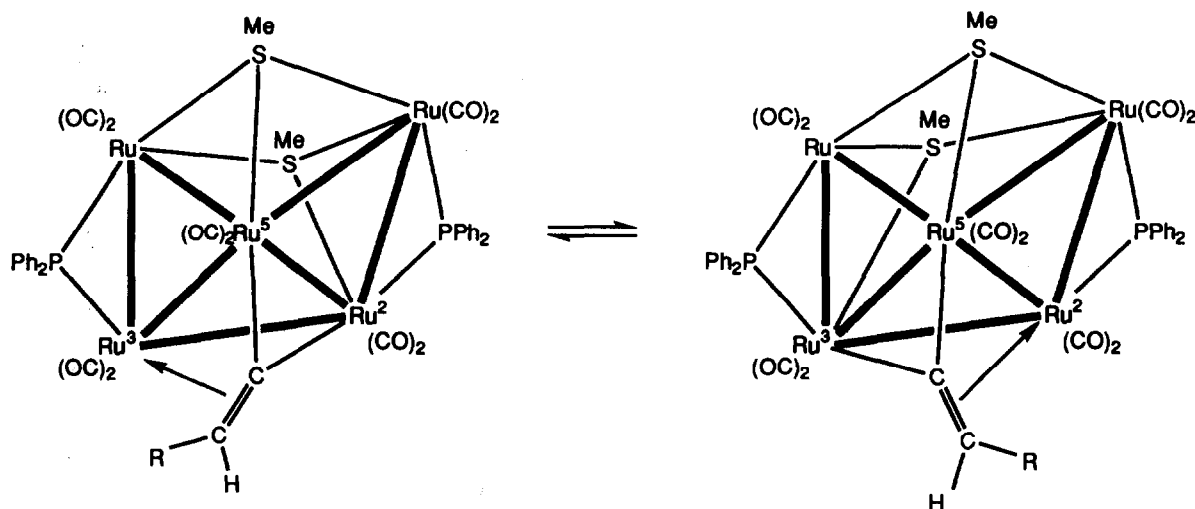
formation of a second isomer in the case of **3** (R' = H) rules out *cis/trans* isomerism about the olefinic C=C bond as the reason for the presence of the second isomer. Analysis of the solid-state structures also ruled out any possibility of hindered rotation about the C(2)–C(3) bond. The most likely explanation appears to be the formation of the second isomer by virtue of a 180° rotation of the vinyl ligand in these complexes, as a result of formal rotation of the vinylidene about the M=C=C axis. Such an isomer would experience severe steric congestion, consistent with its being the minor isomer.

5. Conclusion

This work has demonstrated the high reactivity of a cluster-bound C₂ ligand towards dihydrogen or olefins. During these reactions, one carbon of the ligand is drawn into a close association with the metal cluster while the other inserts into the H–H or C–H bonds to give vinylidene ligands which bridge three atoms of an open Ru₅ cluster. These clusters are electron-rich, the extra electron density being accommodated in Ru–Ru anti-bonding orbitals with consequent elongation of the Ru–Ru vectors to about 3 Å.

6. Experimental details

General experimental conditions and techniques were similar to those described earlier [17]. Complex **1** was made as described previously [1]. Hydrogen, ethene and propene were purchased from CIG Ltd. and used as received. Styrene and ethyl acrylate were Aldrich products.



Scheme 2.

6.1. Reaction of Ru₅(μ₅-C₂)(μ-SMe)₂(μ-PPh₂)₂(CO)₁₁ with H₂

A solution of Ru₅(μ₅-C₂)(μ-SMe)₂(μ-PPh₂)₂(CO)₁₁ (80 mg, 0.061 mmol) in toluene (20 cm³) was heated under reflux with a H₂ purge for 7 h. The solvent was removed and the residue purified by preparative TLC (light petroleum/acetone 10:3). The main dark brown band (R_f 0.6) was recrystallised from CH₂Cl₂/MeOH to yield black crystals of Ru₅(μ₃-CCH₂)(μ₃-SMe)₂(μ-PPh₂)₂(CO)₁₀ (**2**) (73 mg, 94%), m.p. 228–229°C (decomp.). Found: C, 35.55; H, 2.28%; M⁺ 1277. C₃₈H₂₈O₁₀P₂Ru₅S₂ requires C, 35.76; H, 2.21%; M 1277. IR (cyclohexane): ν(CO) 2050m, 2045m, 2026vs, 2023vs, 2008m, 1992m, 1970m, 1957m, 1948w, 1936m cm⁻¹. ¹H NMR: δ(CDCl₃) -0.22 (3H, s, SMe), 3.17 (3H, s, SMe), 5.12, 5.22 [2 × 1H, s (br), CH₂], 6.78–8.03 (20H, m, Ph). ¹³C NMR: δ(CDCl₃) 20.09, 22.63 (2 × s, SMe), 70.22 (d, J_{CP} 9.8 Hz, C_β), 127.61–135.85 (m, Ph), 137.93–142.86 (m, *ipso* C), 190.79–204.47 (CO), 285.43 (d, J_{CP} 10.6 Hz, C_α). ³¹P NMR: δ(CDCl₃) 86.94 (s), 100.96 (s). FAB mass spectrum (*m/z*): 1277, M⁺; 1249–997, [M - *n*CO]⁺ (*n* = 1–10). Some starting material was recovered (R_f 0.55; 2.5 mg, 3%). One other trace band (R_f 0.65; 1.9 mg) has not been identified.

6.2. Reaction of Ru₅(μ₅-C₂)(μ-SMe)₂(μ-PPh₂)₂(CO)₁₁ with ethene

A solution of Ru₅(μ₅-C₂)(μ-SMe)₂(μ-PPh₂)₂(CO)₁₁ (80 mg, 0.061 mmol) in toluene (40 cm³) was pressurised to 25 atm with C₂H₄ and heated at 90°C for 20 h. The solvent was removed and the residue purified by preparative TLC (light petroleum/acetone 10:3) to yield four bands. The major brown band (R_f 0.45) was recrystallised from CH₂Cl₂/MeOH to yield black crystals of Ru₅(μ₃-CCH(CH=CH₂))(μ₃-SMe)₂(μ-PPh₂)₂(CO)₁₀ (**3**; R' = H) (62 mg, 78%), m.p. 222–224°C (decomp.). Found: C, 35.75; H, 2.40%; M⁺ 1302. C₄₀H₃₀O₁₀P₂Ru₅S₂ · 0.5CH₂Cl₂ requires C, 36.18; H, 2.32%; M 1302. IR (cyclohexane): ν(CO) 2043m, 2026vs, 2023(sh), 2006m, 1988s, 1971s, 1966m, 1946w, 1943m cm⁻¹. ¹H NMR: δ(CDCl₃) -0.24 (3H, s, SMe), 3.40 (3H, t, J_{HP} 2.0 Hz, SMe), 5.31 (1H, d, J_{HH} 10.8 Hz, CH), 5.61 (1H, d, J_{HH} 16.2 Hz, =CH₂), 6.48 (1H, dt, J_{HH} 9.6, 16.5 Hz, =CH), 6.58 (1H, d, J_{HH} 9.3 Hz, =CH₂), 6.8–7.95 (20H, m, Ph). ¹³C NMR: δ(CDCl₃) 20.69, 23.18 (2 × s, SMe), 96.22 (t, J_{PC} 5.0 Hz, Ru=C=C), 116.34 (s, CH=CH₂), 126.7–143.8 [m (br), Ph], 145.3 (s, CH=CH₂), 191–206 (m, br, CO), 278.68 (s, Ru=C). ³¹P NMR: δ(CDCl₃) (at room temperature) 86.31 (s, br), 100.00 (s, br); (at -20°C) 88.00 (s), 99.86 (s). FAB mass spectrum (*m/z*): 1303, M⁺; 1275–1023, [M - *n*CO]⁺ (*n* = 1–10). Some starting material

was recovered (R_f 0.55; 7 mg, 9%). Two other trace bands have not been identified.

6.3. Preparation of the μ₃-vinylidene clusters Ru₅{μ₃-C=CH-(E)-CH=CHR'}(μ₃-SMe)₂(μ-PPh₂)₂(CO)₁₀ (**3**; R' = Me, Ph, CO₂Et)

General procedure: A solution of Ru₅(μ₅-C₂)(μ-PPh₂)₂(μ-SMe)₂(CO)₁₁ (52 mg, 0.04 mmol) and the olefin [propene(1 atm), styrene (0.5 ml) or ethyl acrylate (0.5 ml)] was heated in a Carius tube under N₂ to 110°C for 20 h. After removal of the solvent *in vacuo* the residue was purified by preparative TLC (light petroleum/acetone 10:3). The major brown band (R_f ≈ 0.5) was chromatographed again (light petroleum/CH₂Cl₂ 7:3) to yield the black crystalline complexes **3** [R' = Me (21 mg, 40%), Ph (10 mg, 36%) and CO₂Me (28 mg, 51%), respectively]. Crystals for X-ray structural determinations and elemental analyses were grown by solvent diffusion of pentane into a CH₂Cl₂ solution (R' = Me) or of hexane into toluene solutions (R' = Ph or CO₂Et).

For **3** (R' = Me), m.p. 196°C (decomp.): Found: C, 37.11; H, 2.43%; M⁺, 1317. C₄₁H₃₂O₁₀P₂Ru₅S₂ requires C, 37.42; H, 2.45%; M, 1317. IR (cyclohexane): ν(CO) 2042m, 2025vs, 2020s, 2004m, 1987s, 1979w, 1970m, 1962m, 1944w, 1933m cm⁻¹. ¹H NMR δ(CDCl₃) -0.24 (s, SCH₃), 1.89 (d, J_{HH} = 5.7 Hz, CH₃), 3.15 (s, SCH₃), 6.23 (m, CH=C HCH₃), 6.65 (d, J_{HH} = 8.5 Hz, Ru=C=CH), 6.7–7.9 [m (br), C₆H₅]. ¹³C NMR δ(CDCl₃): 18.49 (s, CH=CHCH₃), 20.04 (s, SCH₃), 22.51 (s, SCH₃), 97.26 (t, J_{PC} = 5.2 Hz, Ru=C=C), 126.0–143.0 [m (br), C₆H₅ and CH=CHCH₃], 191.0–206.0 (m, vbr, CO), 269.57 (s, Ru=C=C). ³¹P NMR: δ(CDCl₃) δ 88.0 (s, br), 99.0 (s, br). FAB mass spectrum (*m/z*): 1317, M⁺; 1289–1037, [M - *n*CO]⁺ (*n* = 1–10).

For **3** (R' = Ph), m.p. 172°C (decomp.): Found: C, 43.78; H, 3.01%; M⁺, 1379s. C₄₆H₃₄O₁₀P₂Ru₅S₂ · C₇H₈ requires C, 43.29; H, 2.88%; M, 1379 (unsolvated). IR (cyclohexane): ν(CO) 2042m, 2026vs, 2021s, 2005m, 1987s, 1978w, 1971m, 1963m, 1945w, 1933m, cm⁻¹. ¹H NMR δ(CDCl₃): -0.22 (s, SCH₃), 3.19 (s, SCH₃), 6.7–8.0 (m br, C₆H₅ and CH=CH Ph). ¹³C NMR δ(CDCl₃): 20.04 (s, SCH₃), 22.55 (s, SCH₃), 96.73 (t, J_{PC} = 5.0 Hz, Ru=C=C), 126.2–142.9 [m (br), C₆H₅ and CH=CHCH₃], 191.0–204.0 (m, vbr, CO), 277.93 (s, Ru=C=C). ³¹P NMR: δ(CDCl₃) δ 88.7 (s, br), 100.7 (s, br). FAB mass spectrum (*m/z*): 1379, M⁺; 1351–1099, [M - *n*CO]⁺ (*n* = 1–10).

For **3** (R' = CO₂Et), m.p. 157°C (decomp.): Found: C, 41.05; H, 2.99%; M, 1374. C₄₃H₃₄O₁₂P₂Ru₅S₂ · C₇H₈ requires C, 40.96; H, 2.89%; M, 1374 (unsolvated). IR (cyclohexane): ν(CO) 2045m, 2028vs, 2023s, 2009m, 1991s, 1974m, 1966m, 1949w, 1938m

(CO) 1701s (C=O) cm⁻¹. ¹H NMR: δ(CDCl₃) -0.20 (s, SCH₃), 1.31 (t, *J*_{HH} = 7.1 Hz, OCH₂CH₃), 3.23 (s, SCH₃), 4.25 (m, OCH₂CH₃), 6.27 (d, *J*_{HH} = 15.2 Hz, CH=CHCO₂Et), 6.55 (d, *J*_{HH} = 10.3 Hz, Ru=C=CH), 7.52 (dd, *J*_{HH} = 15.2 a. 10.3 Hz, CH=CHCO₂Et), 6.7–8.0 [m (br), C₆H₅]. ¹³C NMR δ(CDCl₃): 14.03 (s, OCH₂CH₃), 19.89 (s, SCH₃), 22.65 (s, SCH₃), 60.16 (s, OCH₂CH₃), 89.85 (t, *J*_{PC} = 5.4 Hz, Ru=C=C), 118.67 (s, CH=CHCO₂Et), 128.3–142.6 [m (br), C₆H₅], 153.35 (s, CH=CHCO₂Et), 191.0–204.0 (m, vbr, CO), 287.01 (s, Ru=C=C). ³¹P NMR δ(CDCl₃): 89.1 (s, br), 103.4 (s, br). FAB mass spectrum (*m/z*): 1374, M⁺; 1346–1094, [M - *n*CO]⁺ (*n* = 1–10).

7. Crystallography

Unique room temperature diffractometer data sets (*T* ca 295 K; 2θ/θ scan mode; monochromatic Mo Kα radiation, λ 0.7107₃ Å) yielded *N* independent reflections, *N*_o with *I* > 3σ(*I*) being considered 'observed' and used in the large block/full matrix least squares refinement after gaussian absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; (*x*, *y*, *z*, *U*_{iso})_H were constrained at estimated values. Conventional residuals *R*, *R*_w on |*F*| at convergence are quoted; statistical weights derivative of σ²(*I*) = σ²(*I*_{diff}) + 0.0004σ⁴(*I*_{diff}) were used. Neutral atom complex scattering factors were em-

TABLE 2. Crystal data and refinement details for complexes 3 (R' = Me and Ph)

	3 (R' = Me)	3 (R' = Ph)
Formula	C ₄₁ H ₃₂ O ₁₀ P ₂ Ru ₅ S ₂	C ₄₆ H ₃₄ O ₁₀ P ₂ Ru ₅ S ₂ ·C ₇ H ₈
<i>M</i>	1316.1	1470.3
Crystal system	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>P</i> $\bar{1}$ (No. 2)
<i>a</i> , Å	10.356(3)	16.867(14)
<i>b</i> , Å	19.124(6)	14.493(5)
<i>c</i> , Å	25.623(7)	14.348(6)
α, °		118.47(3)
β, °	113.35(2)	90.34(5)
γ, °		111.02(4)
<i>U</i> , Å ³	4659	2810
<i>Z</i>	4	2
<i>D</i> _c , g cm ⁻³	1.88	1.74
<i>F</i> (000)	2560	1444
Crystal size, mm	0.42 × 0.17 × 0.15	0.16 × 0.10 × 0.32
<i>A</i> * (min, max)	1.21, 1.35 (Gaussian)	1.11, 1.64 (Gaussian)
μ, cm ⁻¹	17.9	15.0
2θ _{max}	55	50
<i>N</i>	10331	9855
<i>N</i> _o	6296	6790
<i>R</i>	0.045	0.052
<i>R</i> _w	0.043	0.057

TABLE 3. Non-hydrogen positional and isotropic displacement parameters for 3 (R' = Me)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} (Å ²)
Ru(1)	0.65639(7)	0.32655(3)	0.60594(3)	0.0363(2)
Ru(2)	0.91602(6)	0.25465(3)	0.69187(2)	0.0330(2)
Ru(3)	0.88181(6)	0.23245(3)	0.80063(2)	0.0321(2)
Ru(4)	0.56643(6)	0.25199(3)	0.72092(2)	0.0325(2)
Ru(5)	0.78345(7)	0.36654(3)	0.73124(3)	0.0360(2)
C(11)	0.5020(9)	0.3069(5)	0.5396(4)	0.054(4)
O(11)	0.4058(7)	0.2948(4)	0.4993(3)	0.088(4)
C(12)	0.6711(9)	0.4162(5)	0.5785(3)	0.049(4)
O(12)	0.6784(7)	0.4703(3)	0.5610(3)	0.068(3)
C(21)	1.0089(9)	0.1689(5)	0.7081(3)	0.048(4)
O(21)	1.0702(8)	0.1174(4)	0.7171(3)	0.090(4)
C(22)	1.0856(8)	0.2985(5)	0.7039(3)	0.047(4)
O(22)	1.1887(6)	0.3249(3)	0.7099(3)	0.065(3)
C(31)	1.0161(9)	0.1644(4)	0.8406(3)	0.045(3)
O(31)	1.0982(7)	0.1260(3)	0.8686(3)	0.068(3)
C(32)	0.8552(8)	0.2644(4)	0.8646(3)	0.041(3)
O(32)	0.8497(7)	0.2866(4)	0.9046(3)	0.076(4)
C(41)	0.3917(8)	0.2136(5)	0.6815(3)	0.048(4)
O(41)	0.2829(7)	0.1874(4)	0.6571(3)	0.079(3)
C(42)	0.5193(8)	0.2887(4)	0.7792(4)	0.042(3)
O(42)	0.4909(7)	0.3082(3)	0.8153(3)	0.069(3)
C(51)	0.7804(9)	0.4158(5)	0.7937(4)	0.050(4)
O(51)	0.7853(8)	0.4455(4)	0.8325(3)	0.092(4)
C(52)	0.8459(9)	0.4456(5)	0.7065(4)	0.055(4)
O(52)	0.8823(8)	0.4953(3)	0.6917(3)	0.079(4)
S(1)	0.5471(2)	0.3582(1)	0.66950(8)	0.0379(8)
C(01)	0.4224(9)	0.4261(5)	0.6628(4)	0.063(4)
S(2)	0.6715(2)	0.2198(1)	0.65602(8)	0.0344(7)
C(02)	0.6088(9)	0.1421(4)	0.6129(3)	0.050(4)
P(1)	0.8451(2)	0.2761(1)	0.59307(8)	0.0382(8)
C(111)	0.9552(8)	0.3291(5)	0.5680(3)	0.046(3)
C(112)	1.0052(9)	0.3043(5)	0.5288(3)	0.058(4)
C(113)	1.084(1)	0.3467(7)	0.5089(4)	0.080(6)
C(114)	1.111(1)	0.4142(7)	0.5269(5)	0.081(6)
C(115)	1.064(1)	0.4398(5)	0.5666(5)	0.072(5)
C(116)	0.9874(9)	0.3977(5)	0.5881(4)	0.056(4)
C(121)	0.8125(9)	0.1996(4)	0.5479(3)	0.046(4)
C(122)	0.899(1)	0.1428(6)	0.5640(4)	0.075(5)
C(123)	0.874(2)	0.0829(6)	0.5300(6)	0.111(8)
C(124)	0.759(2)	0.0795(7)	0.4793(6)	0.107(8)
C(125)	0.675(1)	0.1355(7)	0.4626(4)	0.081(6)
C(126)	0.695(1)	0.1970(5)	0.4951(4)	0.062(4)
P(2)	0.6858(2)	0.1613(1)	0.77869(8)	0.0337(8)
C(211)	0.6774(8)	0.0783(4)	0.7425(3)	0.035(3)
C(212)	0.7959(9)	0.0478(4)	0.7413(4)	0.051(4)
C(213)	0.788(1)	-0.0136(5)	0.7103(5)	0.071(5)
C(214)	0.660(1)	-0.0437(4)	0.6816(4)	0.062(5)
C(215)	0.539(1)	-0.0162(5)	0.6834(4)	0.059(4)
C(216)	0.5488(9)	0.0446(4)	0.7138(4)	0.048(4)
C(221)	0.6297(8)	0.1350(4)	0.8348(3)	0.037(3)
C(222)	0.7270(9)	0.1170(4)	0.8884(3)	0.047(4)
C(223)	0.685(1)	0.0962(5)	0.9309(4)	0.057(4)
C(224)	0.546(1)	0.0930(5)	0.9205(4)	0.061(5)
C(225)	0.446(1)	0.1092(5)	0.8673(4)	0.060(5)
C(226)	0.4883(9)	0.1311(5)	0.8253(3)	0.050(4)
C(1)	0.9580(7)	0.3136(4)	0.7680(3)	0.036(3)
C(2)	1.0767(9)	0.3067(4)	0.8187(3)	0.046(3)
C(3)	1.113(1)	0.3493(5)	0.8692(5)	0.078(6)
C(4)	1.244(1)	0.3406(6)	0.9171(5)	0.098(6)
C(5)	1.275(2)	0.385(1)	0.9644(6)	0.17(1)

TABLE 4. Non-hydrogen positional and isotropic displacement parameters for **3** (R' = Ph)

Atom	x	y	z	U _{eq} (Å ²)
Ru(1)	0.40920(5)	0.84722(7)	0.70878(6)	0.0413(4)
Ru(2)	0.22415(5)	0.65726(7)	0.59220(6)	0.0373(4)
Ru(3)	0.17472(5)	0.51112(6)	0.69160(6)	0.0381(4)
Ru(4)	0.32283(5)	0.72957(7)	0.88396(6)	0.0392(4)
Ru(5)	0.35829(5)	0.60115(7)	0.65711(7)	0.0441(5)
C(11)	0.4514(6)	1.0043(9)	0.7990(7)	0.047(6)
O(11)	0.4730(5)	1.1027(6)	0.8579(6)	0.072(5)
C(12)	0.5041(7)	0.8553(9)	0.6384(9)	0.058(6)
O(12)	0.5614(5)	0.8639(8)	0.5981(7)	0.093(6)
C(21)	0.1127(7)	0.6506(9)	0.5915(8)	0.055(6)
O(21)	0.0435(5)	0.6500(8)	0.5918(6)	0.086(7)
C(22)	0.1933(7)	0.5632(9)	0.4402(8)	0.061(6)
O(22)	0.1722(6)	0.5091(7)	0.3482(6)	0.082(5)
C(31)	0.0533(7)	0.4369(9)	0.6545(8)	0.058(6)
O(31)	-0.0211(5)	0.3871(7)	0.6354(6)	0.080(5)
C(32)	0.1910(7)	0.4131(9)	0.7311(8)	0.057(6)
O(32)	0.1984(6)	0.3471(7)	0.7483(7)	0.091(6)
C(41)	0.3467(7)	0.8568(8)	1.0196(8)	0.053(6)
O(41)	0.3572(5)	0.9334(6)	1.1058(6)	0.077(5)
C(42)	0.3579(7)	0.652(1)	0.9347(8)	0.061(7)
O(42)	0.3807(6)	0.6025(8)	0.9644(7)	0.094(7)
C(51)	0.3824(8)	0.496(1)	0.6777(9)	0.066(8)
O(51)	0.3964(6)	0.4291(8)	0.6871(7)	0.093(7)
C(52)	0.4217(7)	0.582(1)	0.5468(9)	0.065(8)
O(52)	0.4593(7)	0.566(1)	0.4823(8)	0.115(9)
S(1)	0.4489(2)	0.7762(2)	0.8123(2)	0.047(1)
C(01)	0.5560(7)	0.806(1)	0.870(1)	0.08(1)
S(2)	0.2838(2)	0.8034(2)	0.7808(2)	0.037(1)
C(02)	0.2439(7)	0.9146(8)	0.8424(8)	0.051(6)
P(1)	0.3114(2)	0.8152(2)	0.5722(2)	0.041(1)
C(111)	0.3495(6)	0.7878(8)	0.4465(8)	0.049(6)
C(112)	0.3530(7)	0.8533(9)	0.4003(9)	0.061(7)
C(113)	0.3910(8)	0.838(1)	0.311(1)	0.074(8)
C(114)	0.4207(8)	0.752(1)	0.2655(9)	0.072(8)
C(115)	0.4156(9)	0.686(1)	0.3091(9)	0.075(9)
C(116)	0.3779(8)	0.702(1)	0.3975(9)	0.068(8)
C(121)	0.2702(7)	0.9231(9)	0.5956(8)	0.050(6)
C(122)	0.1837(7)	0.889(1)	0.5595(9)	0.063(7)
C(123)	0.153(1)	0.971(1)	0.570(1)	0.10(1)
C(124)	0.212(1)	1.086(1)	0.620(1)	0.11(1)
C(125)	0.298(1)	1.119(1)	0.655(1)	0.11(1)
C(126)	0.3278(8)	1.0378(9)	0.644(1)	0.075(7)
P(2)	0.1786(2)	0.6325(2)	0.8720(2)	0.039(1)
C(211)	0.1145(6)	0.7176(8)	0.9061(8)	0.043(5)
C(212)	0.0474(7)	0.6945(9)	0.8308(9)	0.055(7)
C(213)	0.0010(8)	0.761(1)	0.859(1)	0.072(8)
C(214)	0.0215(8)	0.854(1)	0.963(1)	0.081(9)
C(215)	0.0849(8)	0.8745(9)	1.0387(9)	0.069(7)
C(216)	0.1329(7)	0.8106(9)	1.0127(8)	0.055(6)
C(221)	0.1533(6)	0.5722(8)	0.9592(7)	0.043(5)
C(222)	0.0853(7)	0.4662(9)	0.9239(8)	0.057(6)
C(223)	0.0671(7)	0.4202(9)	0.9887(9)	0.069(7)
C(224)	0.1166(8)	0.476(1)	1.089(1)	0.080(9)
C(225)	0.1833(8)	0.584(1)	1.1305(9)	0.076(8)
C(226)	0.2027(7)	0.630(1)	1.0625(8)	0.063(7)
C(1)	0.2397(6)	0.5075(8)	0.5686(8)	0.047(6)
C(2)	0.1752(6)	0.3950(8)	0.5074(7)	0.044(5)
C(3)	0.1868(7)	0.2906(8)	0.4765(7)	0.047(6)
C(4)	0.1225(7)	0.1865(8)	0.4102(8)	0.056(6)
C(101)	0.1239(7)	0.0733(9)	0.3656(8)	0.057(6)

TABLE 4 (continued)

Atom	x	y	z	U _{eq} (Å ²)
C(102)	0.2009(8)	0.0593(9)	0.3590(9)	0.066(7)
C(103)	0.2025(9)	-0.048(1)	0.3177(9)	0.076(8)
C(104)	0.126(1)	-0.142(1)	0.285(1)	0.10(1)
C(105)	0.049(1)	-0.130(1)	0.288(1)	0.098(9)
C(106)	0.0483(8)	-0.0228(9)	0.330(1)	0.079(7)
C(11s)	0.219(2)	0.208(3)	0.895(1)	0.64(4)
C(1s)	0.2389(9)	0.241(2)	1.012(1)	0.29(2)
C(2s)	0.2011(9)	0.160(1)	1.043(2)	0.187(9)
C(3s)	0.220(1)	0.191(2)	1.151(2)	0.19(1)
C(4s)	0.276(1)	0.304(2)	1.230(1)	0.24(1)
C(5s)	0.314(1)	0.385(2)	1.199(2)	0.35(2)
C(6s)	0.295(1)	0.354(1)	1.090(2)	0.34(2)

ployed; computation used the XTAL 3.2 program system [18] implemented by S.R. Hall. Pertinent results are given in the Figures and Tables. Material deposited with the Cambridge Crystallographic Data Centre comprises hydrogen and thermal parameters and full molecular non-hydrogen geometries.

7.1. Abnormal features / variations in procedure

The toluene solvent molecule in **3** (R' = Ph) exhibited very high thermal motion but had a population refining to approximately unity, at which value it was constrained in conjunction with its refinement as a rigid body.

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