Synthesis, X-Ray Crystal Structure, and Fluxional Behaviour of *fac*-$[Ru(CH_3CO_2)_2(PPh_3)_3] \cdot 2\,CH_3CO_2H$

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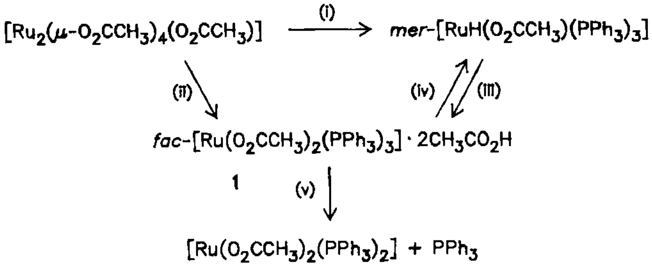
$[Ru_2(\mu\text{-}O_2CCH_3)_4(O_2CCH_3)]$ reacts with excess triphenylphosphane in acetic acid to give *fac*-$[Ru(O_2CCH_3)_2(PPh_3)_3] \cdot 2\,CH_3CO_2H$ (**1**), which crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$. The three phosphane ligands are in the sterically congested facial configuration, and the distorted octahedral geometry around the metal is completed by a unidentate and chelating acetate. A variable temperature $^{31}P\{^1H\}$-NMR study of the complex in CH_2Cl_2 showed the three phosphanes to be inequivalent at low temperature. On raising the temperature two separate coalescence processes are observed, ultimately making all of the phosphanes equivalent at room temperature. Complex **1** shows slight catalytic activity for the ring-opening polymerization of bicyclo[2.2.1]hept-2-ene (norbornene).

Because of their importance as catalysts triphenylphosphane ruthenium(II) carboxylates have been the subject of intense study for the last twenty years. For example, one of the most important complexes of this kind is *mer*-$[RuH(O_2CCH_3)(PPh_3)_3]$ which has been shown to be an efficient hydrogenation catalyst[1,2]. As with the above mentioned hydride most tris(triphenylphosphane)ruthenium(II) complexes have been found to be meridional with respect to phosphane[3,4]. To our knowledge the anionic complex *fac*-$[Ru(H)_3(PPh_3)_3]^-$ is the only structurally characterized facial tris(triphenylphosphane)ruthenium(II) complex[5] although many facial complexes containing less bulky or polyfunctional phosphanes have been reported[3,6]. The synthesis of *fac*-$[Ru(O_2CCF_3)_2(PPh_3)_3]$ has been reported[7] but the complex was not structurally characterized. Following our preparation of the bis(acetato)ether-phosphane complex *fac*-$[Ru(O_2CCH_3)_2(Ph_2PCH_2CH_2OCH_3)_3]$[6] by way of the dinuclear species $[Ru_2(\mu\text{-}O_2CCH_3)_4(O_2CCH_3)]$ we have used a similar method to prepare the title compound *fac*-$[Ru(O_2CCH_3)_2(PPh_3)_3] \cdot 2\,CH_3CO_2H$ (**1**). The complex has been characterized by IR and $^{31}P\{^1H\}$-NMR spectroscopy, and also by X-ray crystallography. The only previous mention in the literature[8] of a complex of formula $[Ru(O_2CCH_3)_2(PPh_3)_3]$ appears, in fact, to be an erroneous reference to the well-known bis(triphenylphosphane) complex $[Ru(O_2CCH_3)_2(PPh_3)_2]$[9].

Results and Discussion

It is known that upon refluxing a solution of $[Ru_2(\mu\text{-}O_2CCH_3)_4(O_2CCH_3)]$ with excess triphenylphosphane in oxygen-free methanol for ca. 2 hours, hydride is abstracted from the alcohol to give *mer*-$[RuH(O_2CCH_3)(PPh_3)_3]$[6,10]. However, when this reaction is carried out at room temperature for 24 hours a yellow powder precipitates, the IR spectrum of which does not show hydride bands. Recrystallisation of the powder from glacial acetic acid gives **1**. Complex **1** can be made more directly, and in higher yield, by treating $[Ru_2(\mu\text{-}O_2CCH_3)_4(O_2CCH_3)]$ with a solution of triphenylphosphane in glacial acetic acid (Scheme 1). Furthermore, prolonged reflux of the hydride *mer*-$[RuH(O_2CCH_3)(PPh_3)_3]$ in glacial acetic acid also afford **1**. Complex **1** can itself be converted to the above hydride by refluxing for ca. 1 hour in a methanolic solution of triphenylphosphane.

Scheme 1. (i) MeOH + PPH_3 (reflux). – (ii) CH_3CO_2H + PPh_3 (90°C). – (iii) CH_3CO_2H + PPh_3 (reflux). – (iv) MeOH (reflux). – (v) CH_2Cl_2 (20°C)



Conductivity measurements show that **1** behaves as a non-electrolyte in dichloromethane and is partially ionically dissociated in methanol. On storing a solution of **1** in dichloromethane at room temperature for 48 hours, almost complete dissociation into $[Ru(O_2CCH_3)_2(PPh_3)_2]$ and free PPh_3 occurs. Moreover, we were unable to prepare **1** by treating $[Ru(O_2CCH_3)_2(PPh_3)_2]$ with excess PPh_3.

X-ray Crystal Structure of Complex 1

Figure 1 shows the molecular structure of **1**, and selected bond distances and angles are listed in the caption. The central metal atom has a distorted octahedral coordination geometry in which the three triphenylphosphane ligands are facial, and there is one monodentate and one bidentate acetate. Two acetic acid molecules are associated with each molecule of the complex. The first acid molecule is hydrogen-bonded to the uncoordinated oxygen atom of the monodentate acetate (O4 – O5), and the second acid molecule, in turn, is hydrogen-bonded to the carbonyl oxygen atom of the first acid (O6 – O7). There are no other bonding interactions in the lattice. For the chelating acetate there is a significant difference between the bond lengths Ru – O1 [2.116(2) Å] and Ru – O2 [2.207(2) Å]. The mean Ru – P bond length (2.345 Å) is longer than usual for P *trans* to carboxylate oxygen[1,11]. In addition, the longest metal-to-phosphane bond, Ru – P3 [2.374(1) Å], is *trans* to the shorter Ru – O1 bond. As expected, the mean of the P – Ru – P angles in **1** (101.3°) is considerably less than that in *fac*-$[Ru(H)_3(PPh_3)_3]^-$ (106.1°)[5] confirming the greater steric demands of the carboxylate compared to hydride. Furthermore, the mean of the P – Ru – P angles in **1** is only slightly larger than the *cis* P – Ru – P angles observed in a range of meridional tris(triphenylphosphane)ruthenium(II) complexes[1,12–14]. The angle between a pair of *cis* phosphanes in the latter complexes is in the region 98 – 101° (in the presence of only one *cis* neighbour). The large degree of steric crowding indicated by the similarly small P – Ru – P angles in **1** (in the presence of two *cis* neighbours) is reflected in the spontaneous and irreversible loss of one PPh_3 molecule in dichloromethane (see Scheme 1). Together with the above, the fact that the P2 – Ru – O1 angle (90.49°) is smaller than the P3 – Ru – O2 angle (104.97°) indicates that P3 and P2 are effectively skewed into an off-central position relative to the bidentate acetate opposite to them. Since there is no apparent electronic explanation for this asymmetry in the central coordination sphere of the metal it must thus arise from the sterically congested environment of the three interlocking triphenylphosphanes.

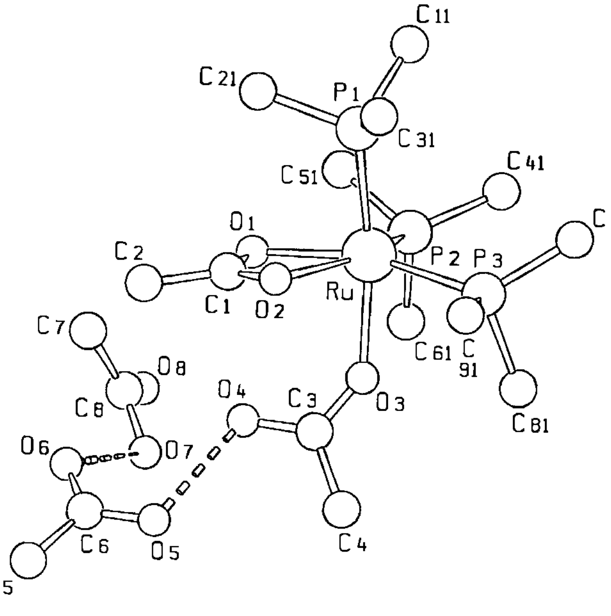


Figure 1. Structure of complex **1** (the phenyl rings of triphenylphosphane are omitted for clarity). Selected bond lengths [Å] and bond angles [°] with estimated standard deviations in parentheses: Ru – P1 2.331(1), Ru – P2 2.332(1), Ru – P3 2.374(1), Ru – O1 2.116(2), Ru – O2 2.207(2), Ru – O3 2.142(2), O4 – O5 2.473(5), O6 – O7 2.817(8). – P1 – Ru – P2 100.28(4), P1 – Ru – P3 100.57(3), P1 – Ru – O1 90.03(7), P1 – Ru – O2 83.99(7), P1 – Ru – O3 164.41(7), P2 – Ru – P3 103.07(3), P2 – Ru – O1 90.49(7), P2 – Ru – O2 150.34(7), P2 – Ru – O3 94.98(7), P3 – Ru – O1 160.87(7), P3 – Ru – O2 104.97(7), P3 – Ru – O3 78.84(7), O1 – Ru – O2 60.0(1), O1 – Ru – O3 86.7(1), O2 – Ru – O3 81.2(1)

Variable-Temperature $^{31}P\{^1H\}$-NMR Study of Complex 1

The $^{31}P\{^1H\}$-NMR spectrum of **1** measured at 203 K in dichloromethane solution (Figure 2) closely reflects the solid state structure. It consists of three doublets of doublets with very similar *cis* coupling constants (ca. 30 Hz) between the three components, reflecting the close similarity of the three P – Ru – P bond angles as measured in the solid state. The magnitude of the coupling constants is typical for *cis* PPh_3 on ruthenium(II)[15]. The difference in bond lengths and angles between the P2 – Ru – O1 and P3 – Ru – O2 axes are also reflected in the $^{31}P\{^1H\}$-NMR spectrum: if the phosphanes were positioned symmetrically *trans* to the bidentate acetate and the bond lengths in the latter were equal, we would expect a doublet and a triplet, with P2 and P3 magnetically equivalent. The analogous complex *fac*-$[Ru(O_2CCH_3)_2(Ph_2PCH_2CH_2OCH_3)_3]$, in which the phosphanes are less bulky, does in fact give a doublet and a triplet[6]. On raising the temperature, the highest and lowest field components of the pattern broaden and collapse to a broad coalesced signal at ca. 253 K. At this temperature the middle component, although slightly broadened, has not coalesced. On further raising the temperature, all three components coalesce to give a sharp singlet at 308 K ($\delta = 48.56$ relative to external H_3PO_4).

We propose that the first coalescence (estimated free energy of activation $\Delta G^{+} = 48.7\ kJ\ mol^{-1}$)[16] is due to a rapid interchange in solution of the molecular constraints which give rise to the inequivalent P2 – Ru – O1 and P3 – Ru – O2 bond lengths and angles. This interchange allows P2 and P3 to become equivalent on the NMR timescale, while P1 (*trans* to monodentate acetate) remains inequivalent. The second coalesence, which makes all three phosphanes equivalent on the NMR timescale[17] arises from a dynamic process by which the two acetates interchange between monodentate and bidentate coordination modes[18]. This type of interchange has been directly observed in the $^{13}C\{^1H\}$-NMR spectrum of the carboxylate carbons of the analogous complex *fac*-$[Ru(O_2CCH_3)_2(Ph_2PCH_2CH_2OCH_3)_3]$[6].

Polymerization of Bicyclo[2.2.1]hept-2-ene (Norbornene)

Whereas some mononuclear ruthenium(II) phosphane complexes are known to be moderately active catalysts for the ring-opening polymerization of bicyclo[2.2.1]hept-2-ene[19] we have found catalytic activity of **1** for this polymerization to be quite low, even at elevated temperatures (polymer yield = 4%).

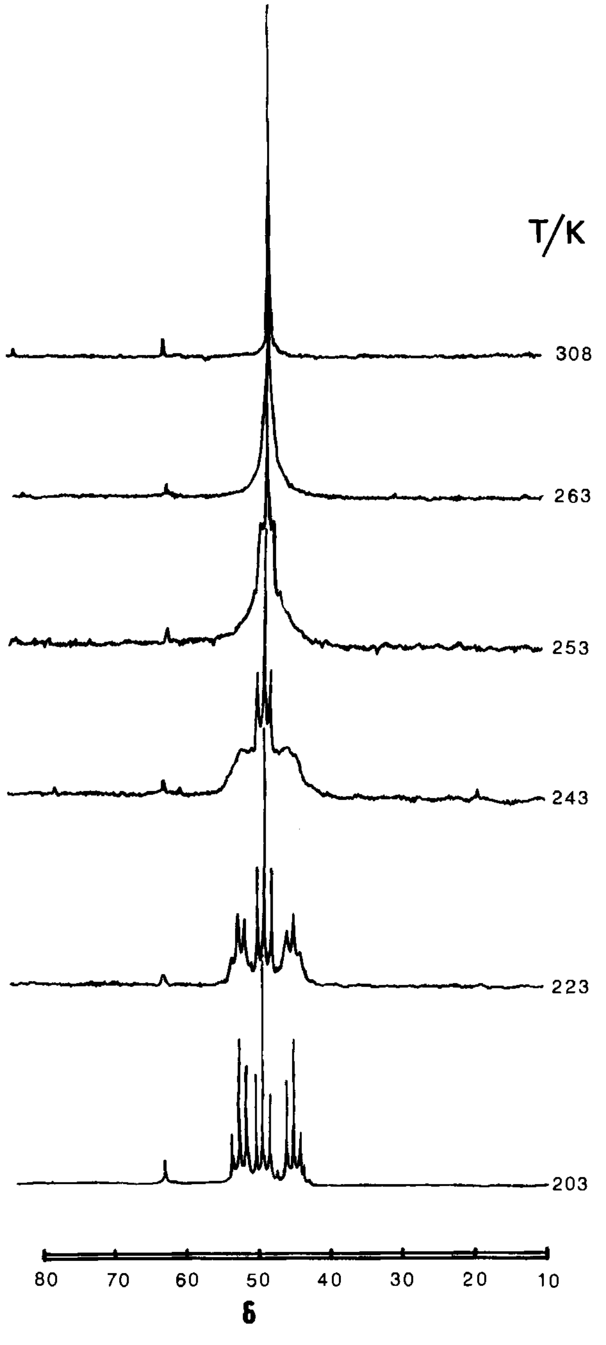
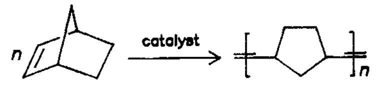


Figure 2. Variable-temperature $^{31}P\{^1H\}$-NMR study of complex **1** in dichloromethane

From the $^{13}C\{^1H\}$-NMR spectrum of the polynorbornene obtained using **1** the *cis* content (σ_c) (i.e. fraction of double bonds in the polymer chain with *cis* character) was evaluated as 0.32[19,20].



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Experimental

[Ru$_2$(μ-O$_2$CCH$_3$)$_4$Cl] was prepared by the literature method[9]. – IR: KBr disc, Bruker IFS 48 spectrophotometer. – $^{31}P\{^1H\}$ NMR: 32.39 MHz, Bruker WP 80 spectrometer [δ values downfield from 1% H$_3$PO$_4$ in (CD$_3$)$_2$CO external standard; values uncorrected]. – $^{13}C\{^1H\}$ NMR of polynorbornene: Bruker AC 80 spectrometer, 20.15 MHz, solution in CDCl$_3$, TMS as reference. – Conductivity readings: 1.0×10^{-3} M in dichloromethane and in methanol, AGB Scientific Ltd. model 10 conductivity meter. – Elemental analyses: Carlo Erba 1106 analyser.

fac-Bis(acetato-O;O,O′)tris(triphenylphosphane)ruthenium(II) · 2 CH$_3$CO$_2$H (**1**): A mixture comprising [Ru$_2$(μ-O$_2$CCH$_3$)$_4$Cl] (0.475 g, 1.0 mmol), silver acetate (0.165 g, 1.0 mmol), glacial acetic acid (50 ml), and methanol (30 ml) was stirred (in air) with gentle heating for 0.5 h. AgCl was removed by filtration (P4) and the dark brown filtrate (containing [Ru$_2$(μ-O$_2$CCH$_3$)$_4$(O$_2$CCH$_3$)]) was reduced to ca. 35 ml under vacuum in order to remove all of the methanol. The remaining solution was purged with nitrogen and triphenylphosphane (2.62 g, 10 mmol) added. The mixture was then stirred at 90°C for 72 h under nitrogen, during which time the initial deep red-brown color changed to deep yellow. Upon cooling, and with constant stirring, complex **1** precipitate as a bright yellow microcrystalline solid. The solid was removed by filtration, washed with ether (3 × 5 ml) and dried under vacuum. Yield: 1.55 g (69%). On evaporation of the mother liquors to low volume a further crop of impure **1** was recovered. Recrystallization of **1** from glacial acetic acid containing triphenylphosphane gave orange-yellow single crystals. – $^{31}P\{^1H\}$ NMR (CH$_2$Cl$_2$, 203 K): δ = 52.9, 49.6, 45.3 (3 dd, $^2J_{P1P2} \approx {}^2J_{P2P3} \approx {}^2J_{P3P1} = 30 \pm 1$ Hz); (308 K): δ = 48.6 (s). – IR (KBr, cm^{-1}): 1765, 1727, 1256 (CH$_3$CO$_2$H); 1542, 1412 CH$_3$CO$_2^-$); 1482, 1434, 1087 (PPh$_3$). – Λ_M (CH$_2$Cl$_2$) = 1.2 S cm^2 mol^{-1}; (MeOH) = 29.5 S cm^2 mol^{-1}.

$C_{62}H_{59}O_8P_3Ru$ (1126.15) Calcd. C 66.13 H 5.28
Found C 66.31 H 5.40

Polymerization of Bicyclo[2.2.1]hept-2-ene (Norbornene): The procedure used was similar to that reported previously[20]. A solution comprising complex **1** (0.01 g, 8.8×10^{-6} mol), norbornene (0.5 g, 5.3×10^{-3} mol), and dry chlorobenzene (1 ml) was placed in a glass tube. The tube was flame-sealed and heated to 135°C for 15 h. As polymerization progressed there was a noted increase in the viscosity of the solution. After cooling to room temp. the tube was opened and the dark yellow viscous solution was poured into CH$_2$Cl$_2$ (10 ml). MeOH (10 ml) was added, and the CH$_2$Cl$_2$ was then evaporated off under vacuum. On adding one drop of conc. HCl the polynorbornene immediately precipitated as a white solid and was recovered by filtration. The solid was washed with MeOH and dried under vacuum. Yield: 0.02 g (4%).

Crystallography[21]: Crystal data for $C_{62}H_{59}O_8P_3Ru$, M_r = 1126.15, space group $P\bar{1}$, lattice constants a = 1260.6(2), b = 1295.6(2), c = 1965.6(4) pm, α = 107.25(2), β = 97.36(2), γ = 111.73(2)°, $V = 2743.9 \times 10^6$ pm^3, Z = 2, d calcd. = 1.363 g cm^{-3}, μ(Mo-K_α) = 4.18 cm^{-1}, Θ limits 3–25°, scan type ω/Θ, 10094 reflections were measured. No. of observed data with $I \geq 3\sigma(I)$ = 7720, No. of variables = 667, R = 0.051 and R_w = 0.060. A single crystal with approximate dimensions 0.2 × 0.2 × 0.3 mm was mounted on a glass fibre and then transferred to an Enraf-Nonius CAD 4 diffractometer. Automatic peak search and indexing pro-

Table 1. Fractional atomic coordinates of **1** with equivalent isotropic thermal parameters U_{eq} [Å^2]

Atom	x	y	z	U_{eq}
Ru	0.23024(3)	0.02679(3)	0.23868(2)	0.028(1)
P1	0.3510(1)	0.0241(1)	0.15836(7)	0.032(1)
P2	0.3491(1)	0.0309(1)	0.34158(7)	0.034(1)
P3	0.2545(1)	0.2276(1)	0.27350(7)	0.032(1)
O1	0.1491(3)	-0.1627(3)	0.1967(2)	0.037(2)
O2	0.0845(3)	-0.0737(3)	0.1359(2)	0.037(2)
O3	0.0844(3)	0.0177(3)	0.2857(2)	0.038(2)
O4	-0.0689(4)	-0.1611(4)	0.2348(3)	0.064(3)
O5	-0.2865(4)	-0.2651(4)	0.1829(3)	0.072(4)
O6	-0.2656(5)	-0.4309(5)	0.1617(4)	0.102(4)
O7	-0.1204(5)	-0.3761(6)	0.3008(4)	0.118(5)
O8	0.000(1)	-0.4294(8)	0.3515(6)	0.224(9)
C1	0.0748(4)	-0.1698(4)	0.1428(3)	0.035(2)
C2	-0.0189(6)	-0.2906(5)	0.0897(3)	0.046(3)
C3	-0.0238(4)	-0.0507(5)	0.2712(3)	0.041(2)
C4	-0.1030(5)	0.0025(6)	0.3022(4)	0.071(5)
C5	-0.4559(8)	-0.4424(8)	0.1092(5)	0.081(6)
C6	-0.3287(6)	-0.3778(6)	0.1522(4)	0.067(4)
C7	-0.028(1)	-0.467(1)	0.2249(7)	0.193(8)
C8	-0.050(1)	-0.4265(8)	0.2930(6)	0.122(7)
C11	0.5130(4)	0.0782(4)	0.1884(3)	0.036(2)
C12	0.5725(5)	0.0221(5)	0.1471(3)	0.052(3)
C13	0.6956(5)	0.0692(6)	0.1706(4)	0.065(4)
C14	0.7600(6)	0.1736(6)	0.2332(4)	0.080(4)
C15	0.7002(5)	0.2292(6)	0.2746(4)	0.056(4)
C16	0.5769(5)	0.1803(5)	0.2519(3)	0.042(3)
C21	0.3088(4)	-0.1276(4)	0.0894(3)	0.035(2)
C22	0.2898(5)	-0.1504(5)	0.0137(3)	0.045(3)
C23	0.2643(5)	-0.2647(6)	-0.0368(4)	0.053(3)
C24	0.2592(5)	-0.3552(5)	-0.0113(4)	0.056(4)
C25	0.2797(5)	-0.3322(5)	0.0646(4)	0.057(4)
C26	0.3048(5)	-0.2190(5)	0.1150(3)	0.049(3)
C31	0.3377(4)	0.1015(4)	0.0947(3)	0.036(2)
C32	0.4364(5)	0.1676(5)	0.0752(3)	0.048(3)
C33	0.4210(6)	0.2163(5)	0.0223(3)	0.063(3)
C34	0.3078(6)	0.1992(5)	-0.0119(3)	0.069(3)
C35	0.2096(5)	0.1337(5)	0.0086(3)	0.057(3)
C36	0.2248(5)	0.0850(5)	0.0610(3)	0.045(2)
C41	0.4928(4)	0.1484(4)	0.4047(3)	0.038(2)
C42	0.5225(5)	0.2665(5)	0.4157(3)	0.043(3)
C43	0.6320(6)	0.3573(5)	0.4656(4)	0.053(3)
C44	0.7076(6)	0.3270(6)	0.5041(4)	0.057(4)
C45	0.6767(6)	0.2080(6)	0.4951(4)	0.061(4)
C46	0.5689(5)	0.1182(5)	0.4454(3)	0.052(3)
C51	0.3854(5)	-0.0984(4)	0.3149(3)	0.042(2)
C52	0.3112(6)	-0.2087(5)	0.3141(4)	0.059(4)
C53	0.3422(7)	-0.3053(5)	0.2942(5)	0.080(5)
C54	0.4475(6)	-0.2906(6)	0.2737(4)	0.079(4)
C55	0.5208(6)	-0.1814(5)	0.2733(4)	0.070(4)
C56	0.4911(5)	-0.0846(5)	0.2936(3)	0.056(3)
C61	0.2643(5)	0.0023(4)	0.4092(3)	0.045(2)
C62	0.3117(5)	0.0717(5)	0.4852(3)	0.055(3)
C63	0.2410(6)	0.0484(6)	0.5339(4)	0.074(4)
C64	0.1256(6)	-0.0415(6)	0.5070(4)	0.080(4)
C65	0.0784(6)	-0.1113(6)	0.4314(4)	0.070(3)
C66	0.1469(5)	-0.0902(5)	0.3820(3)	0.057(3)
C71	0.3945(4)	0.3642(4)	0.3023(3)	0.036(2)
C72	0.4692(5)	0.3701(5)	0.2558(3)	0.047(3)
C73	0.5789(5)	0.4697(5)	0.2767(4)	0.054(3)
C74	0.6120(6)	0.5644(5)	0.3441(4)	0.056(4)
C75	0.5367(6)	0.5601(5)	0.3902(4)	0.053(4)
C76	0.4270(5)	0.4605(5)	0.3902(4)	0.044(3)
C81	0.1865(4)	0.2707(4)	0.3488(3)	0.034(2)
C82	0.1135(5)	0.3610(5)	0.3443(3)	0.048(3)
C83	0.0647(5)	0.3610(5)	0.4033(4)	0.058(3)
C84	0.0878(6)	0.3347(5)	0.4659(4)	0.057(3)
C85	0.1612(6)	0.2769(5)	0.4700(3)	0.051(3)
C86	0.2106(5)	0.2454(5)	0.4118(3)	0.043(3)
C91	0.1676(4)	0.2471(4)	0.1999(3)	0.038(2)
C92	0.0518(5)	0.1601(5)	0.1645(3)	0.043(3)
C93	-0.0209(5)	0.1765(5)	0.1117(3)	0.052(3)
C94	0.0222(5)	0.2777(6)	0.0948(3)	0.069(3)
C95	0.1383(6)	0.3641(6)	0.1299(4)	0.074(3)
C96	0.2116(5)	0.3498(5)	0.1830(3)	0.056(3)

cedure yielded a triclinic reduced primitive cell, and there were no conventional cells of higher symmetry. No correction for crystal decomposition was necessary. The structure was solved by direct methods[22] and difference Fourier syntheses[23] were used to locate the remaining non-hydrogen atoms. An empirical correction for absorption (DIFABS[24]) was applied to the intensities. Calculated positions of the hydrogen atoms were included in the structure factor calculation but were not refined. The fractional atomic coordinates of **1** with equivalent isotropic thermal parameters U_{eq} are summarized in Table 1.

CAS Registry Numbers

1: 136489-54-8 / $[Ru_2(\mu\text{-}O_2CCH_3)_4Cl]$: 38833-34-0 / Norbornene: 498-66-8

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