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# Insertion of a Vinylidene Unit into a Ru–O Bond: Synthesis and Molecular Structure of $[C_5H_5(PPh_3)RuC({=}CHCO_2Me)OC(Me)O]^1$

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*Summary: The cyclopentadienyl ruthenium acetate* $[C_5H_5Ru(\eta^2\text{-}O_2CMe)(PPh_3)]$ *(**2**) which is obtained on treatment of* $[C_5H_5Ru(\eta^3\text{-}2\text{-}MeC_3H_4)(PPh_3)]$ *(**1**) with acetic acid reacts with CO to give the carbonyl complex* $[C_5H_5Ru(CO)(PPh_3)(\eta^1\text{-}O_2CMe)]$ *(**3**). In contrast, with* $HC{\equiv}CCO_2Me$ *the cyclic vinyl ester ruthenium compound* $[C_5H_5(PPh_3)RuC({=}CHCO_2Me)OC(Me)O]$ *(**4**) instead of the expected vinylidene complex is formed. The X-ray crystal structure analysis (monoclinic space group C2c (No. 15) with a = 21.123(8) Å, b = 22.541(4) Å, c = 12.435(6) Å, and β = 115.83(1)°) reveals that the* $RuC({=}CHCO_2Me)OC(Me)O$ *unit represents an intermediate state between a five-membered chelate ring and a separated* $Ru({=}C{=}CHCO_2Me)(\eta^1\text{-}O_2CMe)$ *moiety. From NMR measurements at various temperatures, it can be concluded that in solution a rapid Z/E isomerization at the exocyclic C=C bond of the chelate ligand of **4** takes place.*

Following the discovery that complexes of the general type $[C_5H_5Ru({=}C{=}CRR')L_2]^+$ (L = $PPh_3$, $PMe_3$; $L_2$ = dppm, dppe) can be easily prepared by addition of an electrophile to the β-carbon atom of the alkynyl ligand in $[C_5H_5Ru(C{\equiv}CR)L_2]$,[2] a large variety of cationic vinylideneruthenium derivatives has been reported.[3] There is, however, no single neutral compound of composition $[C_5H_5Ru({=}C{=}CRR')(L)X]$ (X = anionic ligand) known although the corresponding carbonyls $[C_5H_5Ru(CO)(L)X]$ represent a well-established class of cyclopentadienylruthenium complexes.[4]

We have recently observed[5] that the rhodium acetate $[Rh(\eta^2\text{-}O_2CMe)(P\mathit{i}Pr_3)_2]$ which in the crystalline state contains a four-coordinate metal center,[6] smoothly reacts with $HC{\equiv}CCO_2Me$ to give the vinylidene complex *trans*-$[Rh(\eta^1\text{-}O_2CMe)({=}C{=}CHCO_2Me)(P\mathit{i}Pr_3)_2]$. The fact that during this reaction, a $\eta^2$ to $\eta^1$ conversion of the acetato ligand takes place, prompted the preparation of the phosphine-substituted cyclopentadienyl ruthenium acetate **2** (Scheme I) with the hope that it would be an appropriate precursor for the target compound $[C_5H_5Ru({=}C{=}CHCO_2Me)(PPh_3)X]$ (X = OAc).

Like the 2-methallylrhodium derivative $[Rh(\eta^3\text{-}2\text{-}MeC_3H_4)(P\mathit{i}Pr_3)_2]$,[6a] the related ruthenium complex **1**[7] reacts with acetic acid at room temperature in toluene to afford compound **2** in 91% yield. The small difference in wave numbers between the symmetrical and the unsymmetrical OCO stretching frequencies in the IR spectrum indicates that the acetato ligand in **2** is *dihapto* bonded.[8] We note that complexes of the type $[C_5H_5Ru(\eta^2\text{-}X_2CR)(PPh_3)]$ with X = S are known,[9] whereas the corresponding compounds with X = O, to the best of our knowledge, have not been described in the literature.

By passing a slow stream of carbon monoxide through a toluene solution of **2**, a spontaneous color change from red to yellow occurs and the carbonyl complex **3** is quantitatively formed. The expected change from the $\eta^2$ to the $\eta^1$ bonding mode of the acetate ligand is evident from the IR spectrum which displays only one intense C=O absorption at 1610 $cm^{-1}$ (besides the $Ru(C{\equiv}O)$ band at 1945 $cm^{-1}$). Compound **3** is a yellow solid which under argon does not eliminate CO to regenerate **2**.

The reaction of **2** with $HC{\equiv}CCO_2Me$ seems to proceed in a similar way as that with CO. Again a characteristic color change from red to yellow takes place and a yellow crystalline compound analyzed as $\mathbf{2}\cdot HC_2CO_2Me$ is isolated. The spectroscopic data, however, leave serious doubts whether the product **4** is the expected vinylidene complex $[C_5H_5Ru({=}C{=}CHCO_2Me)(PPh_3)(\eta^1\text{-}O_2CMe)]$ because in the 1500–1700 $cm^{-1}$ region of the IR spectrum three bands at 1525, 1625, and 1700 $cm^{-1}$ are observed while in the $^{13}C$ NMR spectrum no signal at very low field (δ ca. 350)[3,10] assigned to a Ru=C carbon atom appears.

The X-ray structural analysis indeed confirms that **4** is not a vinylidene but a cyclic vinyl ester ruthenium compound. As shown in Figure 1, there is a pseudooctahedral arrangement of the ligands around the metal center with the cyclopentadienyl unit occupying three coordination sites. The chelating five-membered ring is virtually planar whereas the exocyclic $CHCO_2Me$ group is slightly twisted by 7.7(1.9)° out of the [Ru,C1,O4,C5,-

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**Scheme I**

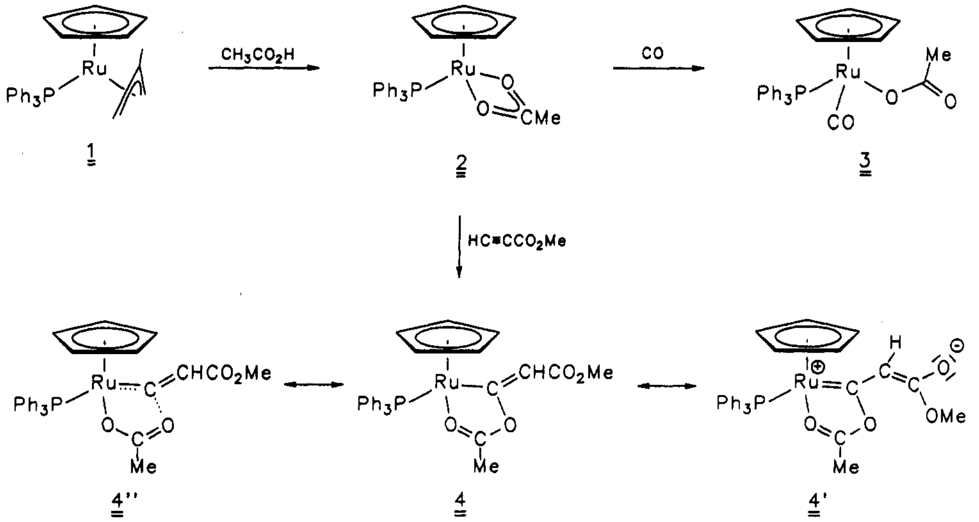


**Table I. Selected Bond Distances and Angles with Esd's for Compound 4**

Bond Distances (Å)

| | | | | | |
|---|---|---|---|---|---|
| Ru–M[a] | 1.8509(2) | Ru–P | 2.2925(5) | Ru–O3 | 2.132(1) |
| Ru–C1 | 2.002(2) | O1–C3 | 1.202(2) | O2–C3 | 1.358(3) |
| O2–C4 | 1.437(3) | O3–C5 | 1.227(3) | O4–C1 | 1.493(2) |
| O4–C5 | 1.311(3) | C1–C2 | 1.351(3) | C2–C3 | 1.443(3) |
| C2–H2 | 0.92(2) | C5–C6 | 1.501(3) | | |

Bond Angles (deg)

| | | | |
|---|---|---|---|
| P–Ru–O3 | 89.39(4) | P–Ru–C1 | 93.07(6) |
| O3–Ru–C1 | 78.21(7) | C3–O2–C4 | 116.1(2) |
| Ru–O3–C5 | 113.4(1) | C1–O4–C5 | 114.7(2) |
| Ru–C1–O4 | 111.4(1) | Ru–C1–C2 | 143.6(2) |
| O4–C1–C2 | 104.9(2) | C1–C2–C3 | 125.4(2) |
| C1–C2–H2 | 123.(1) | C3–C2–H2 | 112.(1) |
| O1–C3–O2 | 120.8(2) | O1–C3–C2 | 129.5(2) |
| O2–C3–C2 | 109.7(2) | O3–C5–O4 | 122.2(2) |
| O3–C5–C6 | 123.0(2) | O4–C5–C6 | 114.8(2) |

[a] M represents the center of the cyclopentadienyl ring.

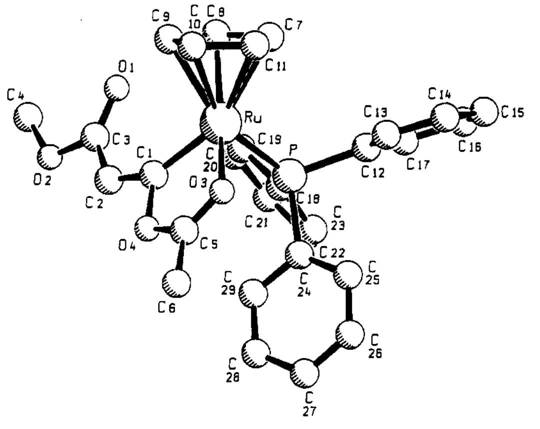
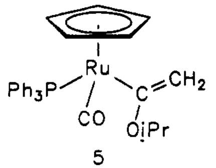


**Figure 1.** Molecular structure of $[C_5H_5(PPh_3)\overline{RuC({=}CHCO_2Me)OC(Me)O}]$ (4).

O3] plane. The Ru–C1 distance (2.002(2) Å) is significantly shorter than would be expected for a Ru–C(sp$^2$) single bond (cf. (5): Ru–C = 2.103(6) Å)[11] which indicates that for an adequate description of the bonding situation in 4 a second zwitterionic resonance form such as 4′ should be considered.

The most characteristic structural features of the chelate complex, however, are the C1–O4 bond length and the angles around the vinyl carbon atom. The C1–O4 distance (1.493(2) Å) is ca. 0.1 Å longer than the C–O single bond of the vinyl ligand in 5 and is thus consistent with the assumption that the $\overline{RuC({=}CHCO_2Me)OC(Me){=}O}$ unit represents an intermediate state between a "normal" chelate ring and a Ru(=C=CHCO$_2$Me)($\eta^1$-O$_2$CMe) moiety 4″ in which the carbonyl oxygen of the acetate is on the way to nucleophilic attack at the C$_\alpha$ carbon of the vinylidene ligand. This proposal is also supported by the size of the Ru–C1–C2 and O4–C1–C2 angles of which the first one is widened to 143.6(2)° and the second one compressed to 104.9(2)° compared with the 120° value for a sp$^2$-carbon center. A related situation has been found by Roper et al.[12] for the (chlorocarbene)ruthenium complex 6 where the angle Ru–C–C amounts to 139.2(1)° and the C–Cl distance (1.826(13) Å) is considerably longer than in other chlorocarbene metal derivatives.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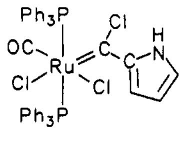
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The weakening of the C1–O4 bond together with the contribution of the zwitterionic resonance form 4′ to the structure of the vinylester complex probably also explains why in solution a rapid *Z*/*E* isomerization at the exocyclic C=C bond takes place. Whereas at 308 K in CD$_2$Cl$_2$ the $^{13}$C NMR spectrum of 4 displays one broad signal at $\delta$ 227.9 for the metal-bound carbon atom, at 233 K two doublets at $\delta$ 232.75 and 224.43 are observed. A similar change of the splitting pattern occurs for the resonance of the CO$_2$Me carbon of the noncoordinated ester group. In both cases the two signals coalesce at ca. 298 K, and thus a $\Delta G^{\ddagger}$ value of 54 kJ/mol can be calculated.[13] The observed phenomenon is reversible and also reflected in the $^{31}$P NMR spectrum where at 298 K one singlet and at 198 K two singlets appears. Again with the coalescence

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at 256 K, a free energy of activation $\Delta G^{\ddagger}$ = 51.5 kJ/mol can be determined which is in good agreement with the value obtained from the $^{13}C$ NMR measurements. It should be pointed out that the two isomers of 4 observed at low temperatures are not present in a 50:50 but in an approximate 60:40 ratio. On the basis of the slightly different P–H coupling of the $CHCO_2Me$ signal in the $^1H$ NMR spectrum (at 203 K), we assume that the major species is the *Z* isomer also found in the crystal lattice. We finally note that a similar situation with regard to *Z*/*E* isomerization at the exocyclic C=C bond has been observed for the rhodium chelate $[C_5H_5(P\mathit{i}Pr_3)RhC(=CHMe)N=C(Ph)O]$ where the *Z* form also is thermodynamically favored.[14]

## Experimental Section

All experiments were carried out under an atmosphere of argon by using Schlenk tube techniques. The starting material 1 was prepared as described in the literature.[7] Melting points were determined by DTA.

**Preparation of $[C_5H_5Ru(\eta^2\text{-}O_2CMe)(PPh_3)]$ (2).** A solution of 1 (226 mg, 0.46 mmol) in 3 mL of toluene was treated with neat acetic acid (50 μL, 0.87 mmol) and stirred for 30 min at room temperature. The solvent was removed in vacuo and the oily residue treated with 5 mL of pentane at 0 °C. An orange-red crystalline solid was formed which was filtered off and dried: yield 203 mg (91%); mp 135 °C dec; IR ($C_6H_6$) $\nu(OCO_{asym})$ 1520, $\nu(OCO_{sym})$ 1460 cm$^{-1}$; $^1H$ NMR (60 MHz, $C_6D_6$) δ 7.60 and 7.05 (both m, $C_6H_5$), 3.97 (s, $C_5H_5$), 1.33 (s, $O_2CCH_3$); $^{31}P$ NMR (36.2 MHz, $C_6D_6$) δ 46.10 (s). Anal. Calcd for $C_{25}H_{23}O_2PRu$: C, 61.59; H, 4.76. Found: C, 61.33; H, 4.67.

**Preparation of $[C_5H_5Ru(CO)(PPh_3)(\eta^1\text{-}O_2CMe)]$ (3).** CO was passed for 1 min through a solution of 2 (76 mg, 0.16 mmol) in 5 mL of toluene at room temperature. Then 10 mL of pentane were added and the solution was cooled to −78 °C. After some hours, yellow crystals precipitated which were filtered off, washed with pentane, and dried in vacuo: yield 76 mg (93%); mp 144 °C; IR (KBr) $\nu(C{\equiv}O)$ 1945, $\nu(C{=}O)$ 1610 cm$^{-1}$; $^1H$ NMR (60 MHz, $CDCl_3$) δ 7.38 (m, $C_6H_5$), 4.92 (s, $C_5H_5$), 1.52 (s, $O_2CCH_3$); $^{31}P$ NMR (36.2 MHz, $CDCl_3$) δ 54.31 (s). Anal. Calcd for $C_{26}H_{23}O_3PRu$: C, 60.58; H, 4.50. Found: C, 60.14; H, 4.50.

**Preparation of $[C_5H_5(PPh_3)RuC(=CHCO_2Me)OC(Me)O]$ (4).** A solution of 2 (153 mg, 0.31 mmol) in 3 mL of toluene was treated with $HC{\equiv}CCO_2Me$ and stirred for 5 min at room temperature. After the solvent was removed, the residue was washed twice with 5 mL of pentane. A yellow microcrystalline solid was obtained: yield 159 mg (90%); mp 152 °C dec; MS (70 eV): *m*/*z* 572 (0.4; M$^+$); IR (KBr) $\nu(C{=}O_{uncoord})$ 1700, $\nu(C{=}O_{coord})$ 1625, $\nu(C{=}C)$ 1525 cm$^{-1}$; $^1H$ NMR (90 MHz, $CD_2Cl_2$, 203 K); major isomer δ 7.34 (m, $C_6H_5$), 6.17 (d, *J*(PH) = 2.4 Hz, C=CH), 4.57 (s, $C_5H_5$), 3.59 (s, $CO_2CH_3$), 1.48 (s, chelate-$CCH_3$); minor isomer δ 7.34 (m, $C_6H_5$), 5.60 (d, *J*(PH) = 1.6 Hz, C=CH), 4.42 (s, $C_5H_5$), 3.46 (s, $CO_2CH_3$), 1.61 (s, chelate-$CCH_3$); $^{31}P$ NMR (36.2 MHz, $CD_2Cl_2$, 198 K); major isomer δ 58.85 (s); minor isomer δ 60.95 (s); $^{13}C$ NMR (100.6 MHz, $CD_2Cl_2$, 233 K); major isomer δ 232.75 (d, *J*(PC) = 18.6 Hz, RuC), 178.86 (s, chelate-$CCH_3$), 170.60 (s, $CO_2CH_3$), 134.59 (d, *J*(PC) = 41.1 Hz, ipso-C of $PC_6H_5$), 133.83 (d, *J*(PC) = 11.6 Hz, *o*-C of $PC_6H_5$), 129.23 (s, *p*-C of $PC_6H_5$), 127.47 (d, *J*(PC) = 9.6 Hz, *m*-C of $PC_6H_5$), 111.24 (d, *J*(PC) = 2.1 Hz, C=CH), 78.64 (s, $C_5H_5$), 50.24 (s, $CO_2CH_3$), 17.33 (s, chelate-$CCH_3$); minor isomer δ 224.43 (d, *J*(PC) = 19.6 Hz, RuC), 179.72 (s, chelate-$CCH_3$), 160.96 (s, $CO_2CH_3$), 134.41 (d, *J*(PC) = 41.6 Hz, ipso-C of $PC_6H_5$), 133.62 (d, *J*(PC) = 11.2 Hz, *o*-C of $PC_6H_5$), 129.37 (s, *p*-C of $PC_6H_5$), 127.73 (d, *J*(PC) = 9.5 Hz, *m*-C of $PC_6H_5$), 108.32 (d, *J*(PC) = 1.6 Hz, C=CH), 77.81 (s, $C_5H_5$), 49.75 (s, $CO_2CH_3$), 16.93 (s, chelate-$CCH_3$). Anal. Calcd for $C_{29}H_{27}O_4PRu$: C, 60.94; H, 4.76. Found: C, 60.48; H, 4.81.

**Crystal Structure Analysis of 4.** Single crystals were grown by slow diffusion of pentane into a saturated solution of 4 in toluene. Crystal data (from 23 reflections, 12° < θ < 13°): monoclinic space group *C*2*c* (No. 15), *a* = 21.123(8) Å, *b* = 22.541(4) Å, *c* = 12.435(6) Å, β = 115.83(1)°, *V* = 5076(3) Å$^3$, *Z* = 8, $D_{calcd}$ = 1.496 g cm$^{-3}$, μ(Mo Kα) = 7.0 cm$^{-1}$. Crystal size: 0.25 × 0.2 × 0.1 mm. Enraf-Nonius CAD4 diffractometer, Mo Kα radiation (0.70930 Å), graphite monochromator, zirkon filter (factor 15.41), *T* = 293 K, ω/2θ-scan, max. 2θ = 48°; 4096 independent reflections measured, 3091 regarded as being observed [$F_o > 3\sigma(F_o)$]; intensity data corrected for Lorentz and polarization effects, empirical absorption correction (ψ-scan method) applied, min transmission 94.57%; structure solved by direct methods (SHELXS-86); atomic coordinates and anisotropic thermal parameters of the non-hydrogen atoms refined by full-matrix least-squares (unit weights, Enraf-Nonius SDP);[15] hydrogen atom H2 refined isotropically; positions of all other hydrogen atoms calculated according to ideal geometry and refined using the riding method; *R* = 0.023, $R_w$ = 0.025; reflex/parameter ratio 8.93; residual electron density 0.239 e Å$^{-3}$.

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**Supplementary Material Available:** Tables of bond lengths and angles, positional and thermal parameters, and least-squares planes for 4 (10 pages). Ordering information is given on any current masthead page.

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