Transformation of Vinylidene to Ketene at a Diruthenium Centre: Crystal Structure of $[Ru_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(O)CH_2\}(\eta\text{-}C_5Me_5)_2]$

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Oxidation of the μ-vinylidene complex $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCH_2)(\eta\text{-}C_5Me_5)_2]$ (**1**) yields the μ-ketene complex $[Ru_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(O)CH_2\}(\eta\text{-}C_5Me_5)_2]$ (**4**), structurally characterised by *X*-ray diffraction, which decarbonylates readily to the μ-methylene complex $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)(\eta\text{-}C_5Me_5)_2]$ (**6**), and is carbonylated to yield $[(\eta\text{-}C_5Me_5)(CO)_2RuC(O)CH_2Ru(CO)_2(\eta\text{-}C_5Me_5)]$ (**8**); upon reduction with BH_3·tetrahydrofuran (**4**) affords the μ-ethylidene complex $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHMe)(\eta\text{-}C_5Me_5)_2]$ (**9**) and the ethylene complex $[Ru_2(CO)(C_2H_4)(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ (**10**).

Interest in ketene as a ligand in both mononuclear[1] and polynuclear[2] transition metal chemistry has been aroused by the possibility of its involvement in both carbon chain growth and C_2-oxygenate production during catalytic hydrogenation of carbon monoxide. Its complexes have previously been obtained either from ketene itself or from combination of methylene with CO at a metal centre. We describe here (a) a new derivation of co-ordinated ketene, achieved by an oxidatively-induced transformation of a μ-vinylidene ligand, (b) the first determination of the molecular structure of a complex in which ketene bridges a dinuclear metal centre, and (c) the preliminary results of a study of its reactivity.

Recently we reported that μ-alkylidene and μ_3-alkylidyne ligands are induced to eject a proton when their di- and tri-ruthenium complexes, respectively, are oxidised to dications.[3,4] This method of activating a hydrocarbon co-ordinated at a polynuclear metal centre is also applicable to the μ-vinylidene complex $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCH_2)(\eta\text{-}C_5Me_5)_2]$ (**1**).[5] The cyclic voltammogram of (**1**) shows a reversible one-electron oxidation wave at 0.57 V and a second, irreversible wave at 0.80 V (scan rate 100 mV s^{-1});† accordingly, addition of 2 mol equiv. of $AgBF_4$ as chemical oxidant to a tetrahydrofuran (THF) solution of (**1**) resulted in a shift of carbonyl stretching absorptions to higher frequencies, compatible with the formation of the μ-ethynyl cation $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCH)(\eta\text{-}C_5Me_5)_2]^+$ (**2**) through proton ejection from the dication of (**1**). We have been unable to isolate (**2**) but its reaction with lithium dimethylcuprate to yield (66%) the μ-methylvinylidene complex $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCHMe)(\eta\text{-}C_5Me_5)_2]$ (**3**) is strong evidence for its identity.

In an attempt to purify (**2**) the complex was chromatographed on an alumina column in hexane. None of (**2**) survived and only the orange crystalline μ-ketene complex $[Ru_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(O)CH_2\}(\eta\text{-}C_5Me_5)_2]$ (**4**)‡ was eluted [63% yield from (**1**)]. One explanation for this surprising outcome is that the alumina provides hydroxide ion to attack the α-carbon of the μ-ethynyl in (**2**), giving the enol (**5**) which tautomerises to the keto form (**4**).[6] In support of this, when (**4**) was prepared from a sample of (**1**) enriched in ^{13}C (*ca.* 18%) at the μ-carbon of the vinylidene, ^{13}C n.m.r. spectroscopy revealed that the label had made the required progression to the carbonyl group of the ketene. Treatment of (**2**) directly

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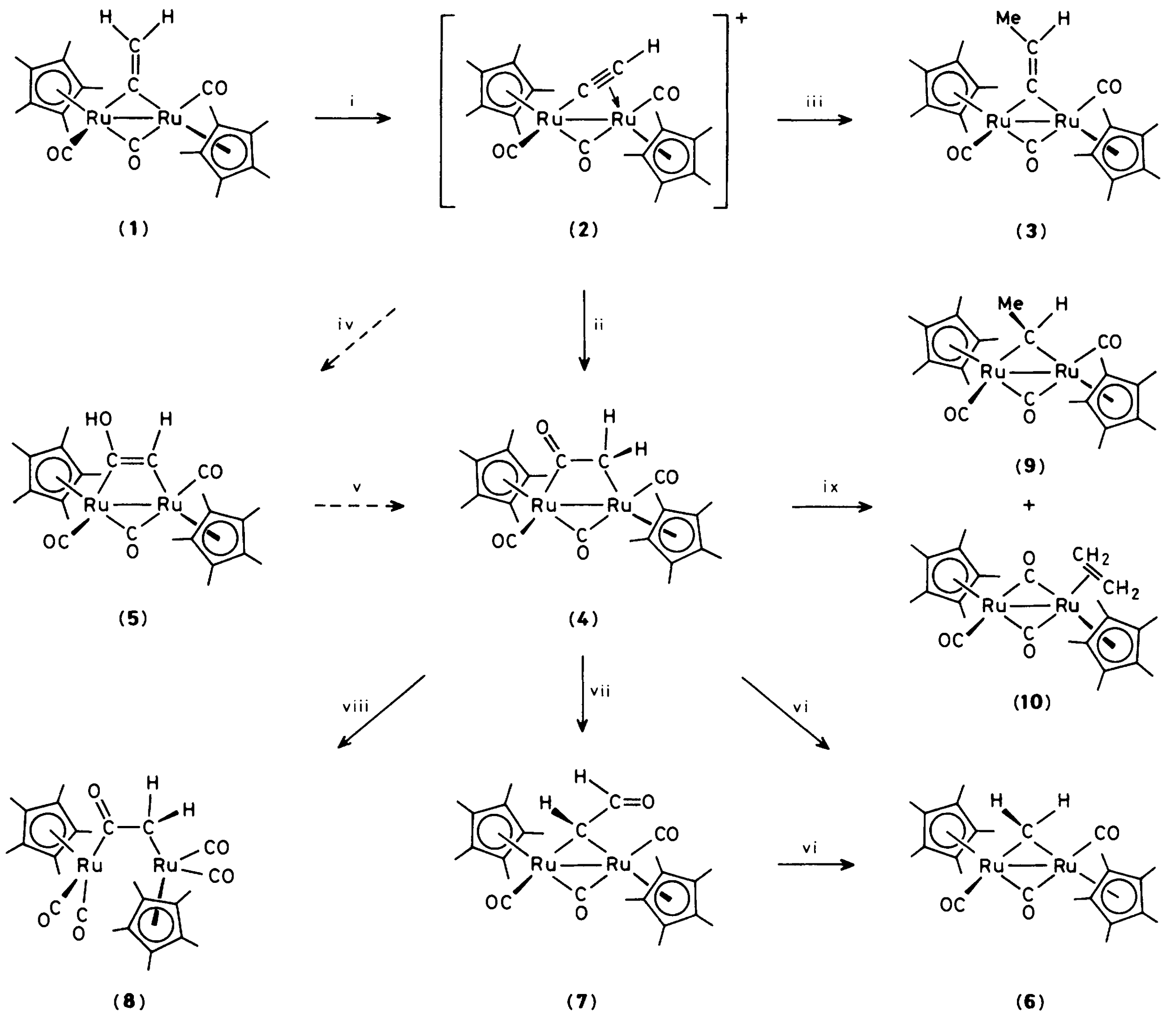
† Carried out at a Pt bead electrode in dichloromethane containing 0.1 mol dm^{-3} $[Bu^n{}_4N][PF_6]$ as supporting electrolyte; potentials are *vs.* the saturated calomel electrode.

‡ The complexes (**4**), (**7**), and (**8**) were characterised by elemental analyses and mass, i.r., and n.m.r. spectroscopy. Selected spectroscopic data (i.r. in CH_2Cl_2, n.m.r. in $CDCl_3$, coupling constants in Hz): (**4**), orange crystals, ν(CO) 1941 s, 1773 m, and 1568 (w, br.) cm^{-1}, ^1H n.m.r. δ 1.92 (d, *J* 5.6, 1 H) and 1.02 (d, *J* 5.6, 1 H), ^{13}C n.m.r. δ 1.0 (CH_2) and 234.3 ($\mathit{C}OCH_2$); (**7**), yellow crystals, ν(CO) 1948 sh, 1927 s, and 1784 m cm^{-1}, ^1H n.m.r. δ 8.90 (d, *J* 9, 1 H) and 7.02 (d, *J* 9, 1 H), ^{13}C n.m.r. δ 134.7 ($\mathit{C}HCHO$) and 198.7 ($CH\mathit{C}HO$); (**8**), yellow crystals, ν(CO) 2008 s, 1994 m, 1946 s, 1940 s, and 1591 (w, br.) cm^{-1}, ^1H n.m.r. δ 2.41 (s, 2 H).



Scheme 1. *Reagents and conditions:* i, $2AgBF_4$; ii, Al_2O_3; iii, $LiCuMe_2$; iv, OH^-; v, H shift; vi, heat; vii, 25 °C; viii, CO (100 atm), 150 °C; ix, $BH_3 \cdot THF$.

with hydroxide, water, or alcohols gives no identifiable products.

The molecular structure of (**4**) was determined by *X*-ray diffraction and is illustrated in Figure 1.§ A ruthenium–ruthenium single bond [2.814(1) Å] is bridged by both carbonyl and ketene ligands, the latter providing a puckered [C(1)–Ru(1)–Ru(2)–C(2) −28.9(1)°] four-membered ring. The C(1)–C(2) distance of 1.450(5) Å indicates that the ketene C–C bond possesses a degree of π-character, although the C–C–O unit is severely bent [C(1)–C(2)–O(2) 127.1(3)°]. In the only other μ-ketene complex to be studied by *X*-ray diffraction, $[Os_3(CO)_{10}\{\mu\text{-}C(O)CH_2\}]$, the ketene spans two well-separated, non-bonded metal atoms and is under no apparent strain [Os–C(H$_2$)–C(O) 112.2(6); Os–C(O)–C(H$_2$) 121.4(6)°].[7] However, the presence of a metal–metal bond in (**4**) clearly imparts considerable ring strain [Ru(1)–C(1)–C(2) 89.0(2); Ru(2)–C(2)–C(1) 107.6(2)°], manifested in the ease with which the complex decarbonylates to yield (**6**), isomerises to yield (**7**), and is carbonylated to give (**8**)[8] (see Scheme 1).

Upon heating in toluene (**4**) rapidly generates the μ-methylene complex $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)(\eta\text{-}C_5Me_5)_2]$ (**6**)[5] in 88% yield, a transformation which is not reversed even under 150 atm of CO at 100 °C. At room temperature (**6**) is formed more slowly (29% after 7 days), and in association with a new μ-formylmethylene complex $[Ru_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(H)\text{-}CHO\}(\eta\text{-}C_5Me_5)_2]$ (**7**)‡ (17%), an isomer of (**4**) which also loses CO to afford (**6**), but too slowly for it to provide the only pathway from (**4**) to (**6**). This μ-CH_2CO to μ-CHCHO isomerisation is unprecedented. It may be noted that in deriving (**6**) from (**1**) *via* the ketene complex (**4**) the C=CH_2 ligand has been cleaved to give CO and CH_2.

The proposed involvement of ketene and related carbonyl-

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§ *Crystal data* for (**4**): $C_{25}H_{32}O_4Ru_2$, $M = 598.7$, triclinic, space group $P\bar{1}$ (No. 2), $a = 8.719(2)$, $b = 9.510(1)$, $c = 15.056(4)$ Å, $\alpha = 99.27(2)$, $\beta = 93.08(2)$, $\gamma = 103.50(2)$°, $U = 1192.7(5)$ Å^3, $Z = 2$, $D_c = 1.71$ g cm^{-3}, $F(000) = 604$, graphite monochromated *X*-radiation, $\lambda = 0.71069$ Å, $\mu(\text{Mo-}K_\alpha)$ 12.7 cm^{-1}. Intensity data were collected at room temperature for a unique hemisphere of reciprocal space in the range $4 < 2\theta < 50°$ on a Nicolet P3m diffractometer. The structure was solved by heavy atom methods and refined by least squares to a final *R* 0.025 for 3731 unique, absorption-corrected, observed [$I > 3\sigma(I)$] data. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

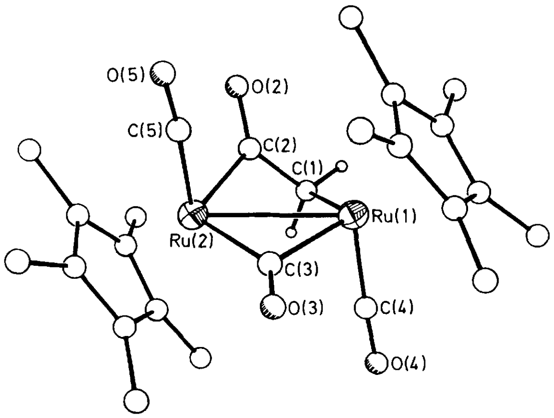

Figure 1. Molecular structure of $[Ru_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(O)CH_2\}(\eta\text{-}C_5Me_5)_2]$ (**4**); methyl group hydrogen atoms have been omitted for clarity. Important molecular parameters include: bond lengths (Å) Ru(1)–Ru(2) 2.814(1), Ru(1)–C(1) 2.194(3), Ru(2)–C(2) 2.105(3), C(1)–C(2) 1.450(5), C(2)–O(2) 1.213(4); bond angles (°) Ru(2)–C(2)–C(1) 107.6(2), Ru(1)–C(1)–C(2) 89.0(2); torsion angle (°) Ru(1)–C(1)–C(2)–Ru(2) −54.5(2).

containing species in hydrocarbon chain growth during the catalytic hydrogenation of CO is based on the carbonyl function being repeatedly added to the chain and then reduced to CH_2. Modelling the reduction stage, treatment of (**4**) in dichloromethane with the BH_3·THF adduct rapidly yields a mixture of the isomeric μ-ethylidene and ethylene complexes $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHMe)(\eta\text{-}C_5Me_5)_2]$ (**9**)[5] (60%) and $[Ru_2(CO)(C_2H_4)(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ (**10**)[5] (3%). Following the observation[9] that BH_3·THF reduces acetyl to ethyl at a mono-iron centre it seems likely that a diruthenacyclobutane ('μ-ethylene') complex is formed initially. Isomerisation to (**9**) can then be seen as a hydrogen shift process which strongly resembles that involved in the transformation of (**4**) to (**7**), *i.e.* $CH_2CH_2 \rightarrow CHCH_3$ *cf.* $CH_2CO \rightarrow CHCHO$, while the isomerisation to (**10**) would comprise a shift from bridging to terminal ethylene co-ordination. Attempts to extend the homologation through carbonylation of (**9**) were unsuccessful; no μ-C(O)CHMe species was obtained by this route.

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