Pentamethylcyclopentadienyl Diruthenium Chemistry

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The chemistry of the diruthenium centre, when stabilised by η-C_5Me_5 ligands, provides examples of new organic transformations (*e.g.* isomerisation of ethylene to ethylidene, addition of ethylene to vinylidene) and new species {*e.g.* $[Ru_2(CO)_2(\mu\text{-}H)_2(\eta\text{-}C_5Me_5)_2]$}.

In recent years we have shown that there exists an extensive organic chemistry of the diruthenium centre stabilised by CO and η-C_5H_5 ligands.[1] The ease with which carbon–carbon bond formation processes occur at the dimetal centre is particularly notable, and implications for Fischer–Tropsch synthesis and alkyne oligomerisation have been drawn. The pentamethylcyclopentadienyl ligand has substantially different steric and electronic properties compared with cyclopentadienyl, and it was therefore of interest to investigate the effect on organo-diruthenium chemistry of changing from η-C_5H_5 to η-C_5Me_5. In this communication we report the preliminary results of these studies. They show that the effect is considerable, with new organic transformations and new species of diruthenium complex being observed (see Scheme 1).

Unlike $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$, u.v. irradiation (250 W mercury lamp, silica flask, 3 days) of a toluene solution of $[Ru_2(CO)_4(\eta\text{-}C_5Me_5)_2]$ (**1**) while purging with ethylene yields the yellow-orange air-stable complexes $[Ru_2(CO)(C_2H_4)(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ (**2**) (22%), $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHMe)(\eta\text{-}C_5Me_5)_2]$ (**3**) (6%), and $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(Me)CHCH_2\}(\eta\text{-}C_5Me_5)_2]$ (**4**) (28%).† Further experiments

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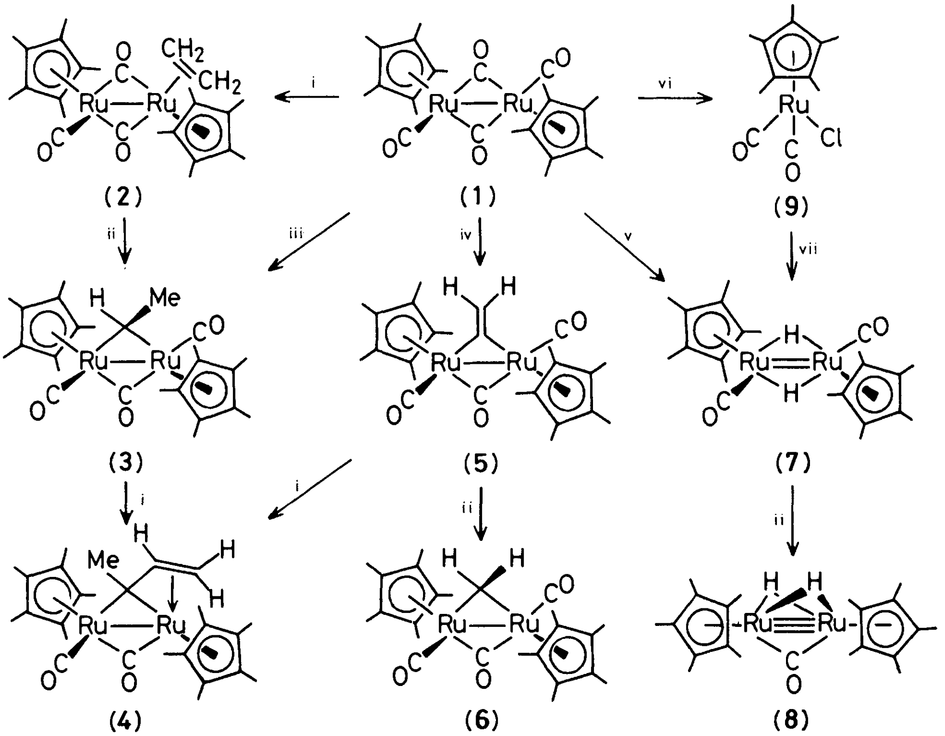
† The new complexes (**2**)—(**9**) were characterised by elemental analyses, and mass, i.r., and n.m.r. (^1H and ^{13}C) spectroscopy. Selected spectroscopic data (i.r. in CH_2Cl_2, n.m.r. in CD_2Cl_2, coupling constants in Hz): (**2**), $\nu(CO)$ at 1 931m and 1 726s cm^{-1}, ^1H n.m.r., δ 0.98 (s, br., 4 H, C_2H_4). (**3**), $\nu(CO)$ at 1 910s and 1 764m cm^{-1}, ^1H n.m.r., δ 8.45 (q, *J* 7, 1 H, C*H*Me) and 2.94 (d, *J* 7, 3 H, CH*Me*), ^{13}C n.m.r., δ 169.7 p.p.m. (μ-*C*HMe). (**4**), $\nu(CO)$ at 1 908s and 1 754m cm^{-1}, ^1H n.m.r., δ 3.20 (dd, *J* 7 and 9, 1 H, CH), 2.68 (s, 3 H, Me), 1.35 (dd, *J* 2 and 7, 1 H, CH_2), and −0.34 (dd, *J* 2 and 9, 1 H, CH_2), ^{13}C n.m.r. δ 171.9 (μ-*C*Me), 87.8 (CH), and 35.1 p.p.m. (CH_2). (**5**), $\nu(CO)$ at 1 923s and 1 775m cm^{-1}, ^1H n.m.r., δ 6.15 (s, 2 H, CH_2), ^{13}C n.m.r., δ 269.6 (*C*CH_2) and 111.7 p.p.m. (CH_2). (**6**), $\nu(CO)$ at 1 910s and 1 767m cm^{-1}, ^1H n.m.r., δ 7.40 (s, 2 H, CH_2), ^{13}C n.m.r., δ 129.5 p.p.m. (CH_2). (**7**), $\nu(CO)$ at 1 890 cm^{-1}, ^1H n.m.r., δ −17.44 (s, 2 μ-H). (**8**), $\nu(CO)$ at 1 794 cm^{-1}, ^1H n.m.r., δ −13.76 (s, 2 μ-H).



Scheme 1. *Reagents:* i, C_2H_4 (1 atm), u.v.; ii, u.v.; iii, MeLi, HBF_4, $NaBH_4$; iv, MeLi, HBF_4, NEt_3; v, H_2 (1 atm), u.v.; vi, $CHCl_3$, u.v.; vii, $LiAlH_4$.

reveal that these products are formed in the sequence (**2**) → (**3**) → (**4**). Thus (**3**) is formed slowly (7% yield) upon u.v. irradiation of (**2**), and (**4**) (35%) upon u.v. irradiation of (**3**) while purging with ethylene.

The ethylene to ethylidene transformation in the isomerisation of (**2**) to (**3**) is of interest in relation to the origin of the alkylidene which initiates alkene metathesis.[2] In metal complex chemistry both the alkene to alkylidene transformation[3,4] and its reverse[3,5,6] are known, but the former was previously brought about by the intervention of another reagent. The nature of the (**2**) to (**3**) isomerisation is unknown. However, there is an indication from tetrafluoroethylene chemistry that both metal centres may be required; at 35 °C the complex $[FeCF_2CF_2Fe(CO)_6(\mu\text{-}SMe)_2]$, which can be viewed as having C_2F_4 in a bridging site, isomerises to $[Fe\{CF(CF_3)\}Fe(CO)_6(\mu\text{-}SMe)_2]$, and evidence for an intermediate μ-alkenyl complex was obtained.[7] The $\eta\text{-}C_5H_5$ analogue of (**2**) is known,[8] but no C_2H_4 to CHMe transformation occurs for that system, perhaps because there is less steric pressure for ethylene to rearrange to the smaller ethylidene ligand.

We suggest that complex (**4**) is formed through initial substitution of a CO in (**3**) by ethylene, followed by the formation of a dimetallacyclopentane ring which then undergoes β-elimination processes. Previously, $\mu\text{-}CH_2$ complexes have been observed to react with ethylene to give propene, and the homologation was proposed to follow such a path.[9] It appears that in this diruthenium system the influence of $\eta\text{-}C_5Me_5$ in stabilising M–C bonds causes the C_4 fragment to be retained and not eliminated as a butene. Only upon heating at 200 °C are butenes generated from (**4**).

These observations indicate how ethylene could be homologated on a metal surface. However, the framework of another possible pathway is illustrated by the reactivity of the μ-vinylidene complex (**5**)[†] towards ethylene (1 atm, u.v. irradiation, toluene solution, 20 h), when (**4**) is obtained in 60% yield. Similar reaction of ethylene with (**5**) containing $\mu\text{-}^{13}C{=}CH_2$ gave a $\mu\text{-}^{13}C(Me)CHCH_2$ ligand in (**4**), showing that the $CHCH_2$ fragment derives from the olefin, probably *via* initial co-ordination to ruthenium before C–C bond formation and H transfer.

U.v. irradiation of (**5**) in toluene over several days surprisingly gave the μ-methylene complex (**6**)[†] in 20% yield. This does not appear to be the result of cleaving the vinylidene C=C bond in that photolysis of the $\mu\text{-}C{=}C(^2H)_2$ and $\mu\text{-}^{13}C{=}CH_2$ derivatives of (**5**) afforded (**6**) containing no label; further experiments to elucidate the nature of the process are in hand. The ability of the pentamethylcyclopentadienylruthenium system to activate hydrocarbons is seen in the formation of μ-alkylidyne complexes $[Ru_3(\mu\text{-}CO)_3(\mu_3\text{-}CR)(\eta\text{-}C_5Me_5)_3]$ (R = H and Me) when (**1**) is refluxed in diglyme.

Treatment of (**1**) or (**3**) with hydrogen under u.v. irradiation produces red crystalline $[Ru_2(CO)_2(\mu\text{-}H)_2(\eta\text{-}C_5Me_5)_2]$ (**7**)[†] and yellow crystalline $[Ru_2(\mu\text{-}CO)(\mu\text{-}H)_2(\eta\text{-}C_5Me_5)_2]$ (**8**),[†] each in *ca.* 10% yield. These interesting species, whose osmium analogues are known,[10] are better obtained from reduction of $[RuCl(CO)_2(\eta\text{-}C_5Me_5)]$ (**9**) with lithium aluminium hydride. This gives (**7**) in 25% yield, which can be converted quantitatively into (**8**) under u.v. irradiation as required. Complex (**7**) is a dimer of the $RuH(CO)(\eta\text{-}C_5R_5)$ unit, which in the cyclopentadienylruthenium system is seen as the trimer $[Ru_3(CO)_3(\mu\text{-}H)_3(\eta\text{-}C_5H_5)_3]$.[11] The latter is highly reactive towards unsaturated hydrocarbons, as is $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ which contains the $M_2(\mu\text{-}H)_2$ unit present in (**7**), and we therefore anticipate an extensive organodiruthenium chemistry based on (**7**).

We are grateful to the S.E.R.C. for the award of a Research Studentship (N. J. F.) and for support, and to Johnson Matthey for a loan of ruthenium trichloride.

Received, 13th February 1984; Com. 191

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