Methyl Group Mobility and Conversion into Methyne at a Diruthenium Centre

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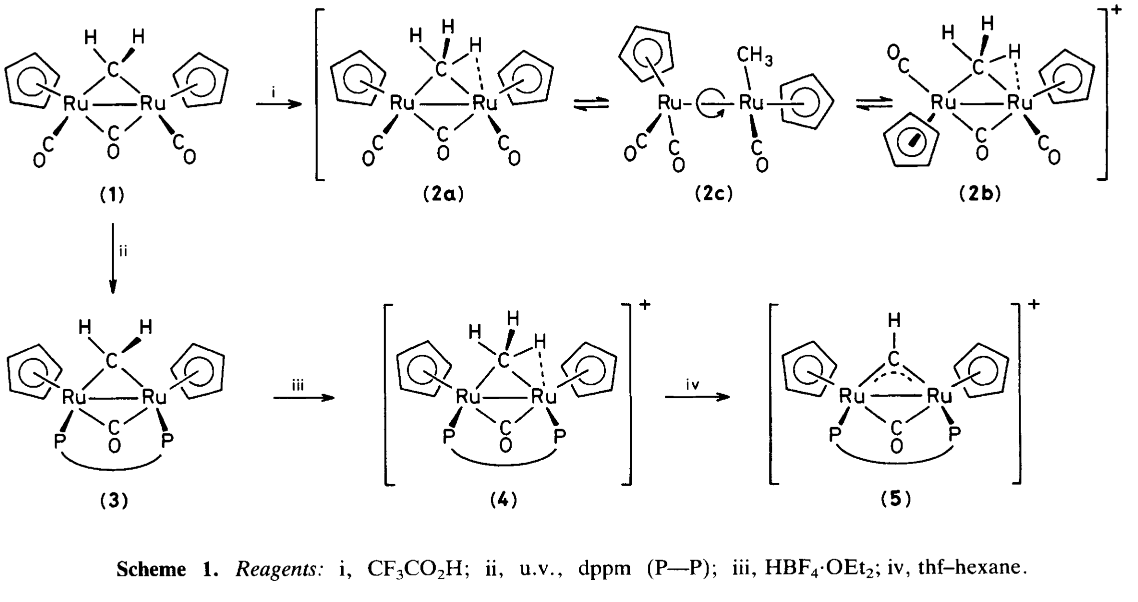
Protonation of $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)(\eta\text{-}C_5H_5)_2]$ yields the μ-methyl complex $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_3)(\eta\text{-}C_5H_5)_2]^+$ as *cis* and *trans* isomers which interconvert ($\Delta G^\ddagger$ *ca.* 55 kJ mol^{-1}) on the n.m.r. time scale, proposed to occur *via* an intermediate with a terminally bound methyl group; protonation of $[Ru_2(\mu\text{-}dppm)(\mu\text{-}CO)(\mu\text{-}CH_2)(\eta\text{-}C_5H_5)_2]$ [dppm = bis(diphenylphosphino)methane] gives $[Ru_2(\mu\text{-}dppm)(\mu\text{-}CO)(\mu\text{-}CH_3)(\eta\text{-}C_5H_5)_2]^+$ similarly, but in solution this converts into the μ-methyne cation $[Ru_2(\mu\text{-}dppm)(\mu\text{-}CO)(\mu\text{-}CH)(\eta\text{-}C_5H_5)_2]^+$, whose structure has been established by *X*-ray diffraction.

The mobility of hydrocarbon species over metal centres and the ways in which they interconvert are important aspects of catalysis by metal surfaces, aspects which may be better understood through the study of metal complexes.[1] In this communication we describe the protonation of μ-methylene diruthenium complexes, leading to the observation of methyl group migration over the dimetal unit and the conversion of μ-methyl into μ-methyne, completing the transformation $CH_2 \rightarrow CH_3 \rightarrow CH$ at a diruthenium centre (Scheme 1).

Treatment of a dichlormethane solution of the μ-methylene complex $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)(\eta\text{-}C_5H_5)_2]$ (**1**)[2] with an excess of CF_3CO_2H gives orange crystalline $[Ru_2(CO)_2(\mu\text{-}$



Scheme 1. *Reagents:* i, CF_3CO_2H; ii, u.v., dppm (P—P); iii, $HBF_4{\cdot}OEt_2$; iv, thf–hexane.

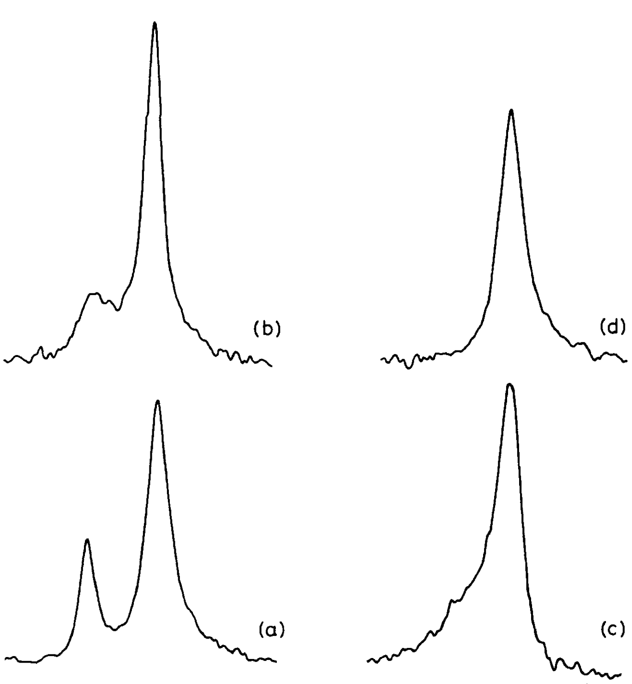


Figure 1. ^{1}H N.m.r. spectrum (μ-CH_3 signals) of (**2**) at (a) −55, (b) −20, (c) −10, and (d) 0 °C in CD_2Cl_2 solution.

$CO)(\mu\text{-}CH_3)(\eta\text{-}C_5H_5)_2][CO_2CF_3]$ (**2**)† in 80% yield. Although the solid is stable in air for several hours, deprotonation occurs in organic solvents and (**1**) can be observed in equilibrium with (**2**). However, when this dissociation is repressed by addition of CF_3CO_2H both *cis* (**2a**) and *trans* (**2b**) isomers of the μ-methyl cation are detected in the ^{1}H n.m.r. spectrum at −55 °C (Figure 1). The i.r. spectrum† indicates that the *cis* form is dominant and consequently the more intense μ-CH_3 signal at δ −1.09 is assigned to this isomer and the one at δ −0.98 to the *trans* isomer. In CD_2Cl_2 at −55 °C the *cis* : *trans* ratio is *ca.* 3 : 1. The high field shift of the μ-methyl group signals of (**2a**) and (**2b**) is typical of this ligand when co-ordinated in the agostic mode.[3—5]

On warming above −55 °C the signals for the methyl groups of (**2a**) and (**2b**) broaden and coalesce at −10 °C before appearing as a singlet at room temperature (see Figure 1). Similar behaviour is observed for the η-C_5H_5 signals, which coalesce near −30 °C. We attribute these changes, which are reversible, to *cis* $\rightleftharpoons$ *trans* isomerisation occurring on the n.m.r. time scale and propose that this proceeds *via* the transient terminal methyl species (**2c**), which will permit exchange of ligand environments through rotation about the unbridged Ru–Ru bond. In this way the methyl group is provided with a means of migrating from one metal atom to the other. An analogous mechanism has been established for the rapid *cis* $\rightleftharpoons$ *trans* isomerisation of the related complex $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CMe_2)(\eta\text{-}C_5H_5)_2]$.[6] The possibility that deprotonation of (**2**) and subsequent μ-CH_2 mobility in (**1**) is responsible for the time-averaging of the signals is ruled out by the free energy of activation of the (**2a**) $\rightleftharpoons$ (**2b**) process, calculated as *ca.* 55 kJ mol^{-1} from the coalescence temperature. This is much less than that for *cis* $\rightleftharpoons$ *trans* isomerisation in (**1**) [>85 kJ mol^{-1} (ref. 2)]. Moreover, it has recently been reported that terminal methyl groups migrate from one metal atom to another in a dirhodium complex.[7] The expectation was that a μ-methyl intermediate is involved and this is strengthened by our observations. The Ru_2 and Rh_2 systems complement one another in having, respectively, bridging or terminal methyl as the ground state.

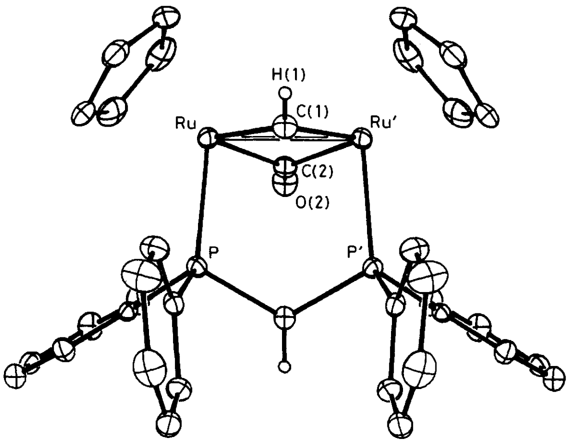


Figure 2. Molecular structure of the cation of (**5**) viewed along its crystallographic and molecular mirror plane. Phenyl and cyclopentadienyl hydrogen atoms are omitted for clarity; the second methylene hydrogen of dppm is obscured. Selected distances: Ru–Ru' 2.716(1), Ru–P 2.300(1), Ru–C(1) 1.937(7), Ru–C(2) 2.028(6), C(1)–H(1) 0.98(8) Å; angles: Ru–C(1)–Ru' 89.1(4), Ru–C(2)–Ru' 84.1(3)°.

Under u.v. irradiation in the presence of bis(diphenylphosphino)methane (dppm) the complex $[Ru_2(\mu\text{-}dppm)(\mu\text{-}CO)(\mu\text{-}CH_2)(\eta\text{-}C_5H_5)_2]$ (**3**)† is obtained in good yield from (**1**). Protonation of (**3**) with $HBF_4{\cdot}OEt_2$ gave, quantitatively, the expected μ-methyl complex $[Ru_2(\mu\text{-}dppm)(\mu\text{-}CO)(\mu\text{-}CH_3)(\eta\text{-}C_5H_5)_2][BF_4]$ (**4**),† analogous to (**2**) but restricted to a *cis* geometry. However, upon slow crystallisation of (**4**) from tetrahydrofuran (thf)–hexane orange crystals of the μ-methyne complex $[Ru_2(\mu\text{-}dppm)(\mu\text{-}CO)(\mu\text{-}CH)(\eta\text{-}C_5H_5)_2][BF_4]$ (**5**)† were obtained in low yield. The methyne ligand, the simplest hydrocarbyl moiety, is an important but rarely encountered species in transition metal chemistry. It is known bound at mono-,[8] di-,[4] tri-,[9] and tetra-nuclear[10] metal centres, but no structural characterisation has been achieved for the dinuclear case. We therefore undertook an *X*-ray diffraction study of (**5**).‡

The molecular cation of (**5**) is illustrated in Figure 2. The cation has crystallographic mirror symmetry with the η-C_5H_5 ligands forced to lie mutually *cis* because of the demands of

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† The new complexes (**2**)—(**5**) were characterised by elemental analyses, and i.r. and n.m.r. spectroscopy. Selected spectroscopic data [i.r. in CH_2Cl_2, n.m.r. in CD_2Cl_2 (**2**) or $CDCl_3$, coupling constants in Hz]: (**2**), orange crystals, ν(CO) at 2045s, 2020s, and 1882m cm^{-1}; ^{1}H n.m.r. (−55 °C), δ −1.09 (s, 3 H) and 5.63 (s, 10 H) (**2a**), −0.98 (s, 3 H) and 5.64 (s, 10 H) (**2b**). (**3**), yellow crystals, ν(CO) at 1694 cm^{-1}; ^{1}H n.m.r. δ 5.03 (dt, J_{HH} 1.5, J_{HP} 15.6, 1 H, CH_2) and 8.85 (d, J_{HH} 1.5, 1 H, CH_2); ^{13}C n.m.r. δ 108.3 (t, J_{CP} 9, CH_2). (**4**), orange crystals, ν(CO) at 1779 cm^{-1}; ^{1}H n.m.r. δ −2.10 (br. s, CH_3); ^{13}C n.m.r. δ 19.2 (t, J_{CP} 5, CH_3). (**5**), orange crystals, ν(CO) at 1779 cm^{-1}; ^{1}H n.m.r. δ 20.81 (t, J_{HP} 1.5, CH).

‡ *Crystal data* for (**5**): $C_{37}H_{33}OP_2Ru_2{\cdot}BF_4$, M = 844.57, orthorhombic, space group *Pnma* (by refinement), a = 12.917(4), b = 14.274(5), c = 17.958(6) Å, U = 3311(2) Å^3, Z = 4, D_c = 1.69 g cm^{-3}, $F(000)$ = 1696 electrons, graphite-monochromated Mo-K_α *X*-radiation, λ = 0.71069 Å, μ(Mo-K_α) = 10.4 cm^{-1}. Intensity data were collected at 200 K on a Nicolet P3m diffractometer for a unique octant of reciprocal space in the range $4 < 2\theta < 50°$. The structure was solved by the heavy atom method and refined by least squares to give a current residual index R = 0.043 for 2127 unique, absorption-corrected, observed [$I > 2\sigma(I)$] data. The cation is ordered and lies astride a crystallographic mirror plane which bisects the Ru–Ru vector; the anion is disordered across the mirror. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

μ-dppm co-ordination. The central $Ru_2(\mu\text{-}C)_2$ unit is somewhat puckered, the interplanar (Ru_2C) angle being 12.6(4)°, with the folding bringing C(1) and C(2) towards the μ-dppm ligand. The μ-CH ligand bridges the diruthenium unit symmetrically with $Ru_2(CH)$ being near planar. The Ru(μ-CH) distance is significantly shorter than the Ru(μ-CO) distance [1.937(7) *vs.* 2.028(6) Å], reflecting the superior π-acceptor qualities of CH^+ as compared to CO.

The mechanism by which two hydrogen atoms are lost from the μ-CH_3 group of (**4**) in giving (**5**) is not obvious and studies to differentiate several possibilities are in hand. Preliminary work shows that (**3**) is readily oxidised to its radical cation which loses a hydrogen radical upon treatment with $Ph_3C\cdot$ to yield (**5**), that (**3**) is not converted into (**5**) upon treatment with $[Ph_3C][BF_4]$, and that (**5**) does not revert to (**4**) under 1 atm. of hydrogen.

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