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Preliminary communication

ORGANIC CHEMISTRY OF THE IRON–RUTHENIUM CENTRE

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Summary

The dynamic behaviour (*cis/trans* isomerisation via CO migration) of $[\mathrm{FeRu(CO)_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2}]$ in solution, the determination of the molecular structure of *trans*-$[\mathrm{FeRu(CO)_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2}]$ by X-ray diffraction, and the developing organic chemistry of the iron–ruthenium centre are described.

The complexes $[\mathrm{M_2(CO)_4(\eta\text{-}C_5H_5)_2}]$ (M = Fe or Ru) provide an excellent entry into the organic chemistry of di-iron and diruthenium centres [1]. In comparison with such homonuclear systems relatively little is known of the organic chemistry of heterodinuclear metal centres, but it is clearly important to determine what influence this character has on the structure and reactivity of co-ordinated hydrocarbons. We have therefore prepared $[\mathrm{FeRu(CO)_4(\eta\text{-}C_5H_5)_2}]$, structurally characterised the complex by X-ray diffraction, and are employing it to develop the organic chemistry of the iron–ruthenium centre. The preliminary results of these studies are described here; while the work was in progress the synthesis of $[\mathrm{FeRu(CO)_4(\eta\text{-}C_5H_5)_2}]$ was reported independently [2].

Dark red crystalline $[\mathrm{FeRu(CO)_4(\eta\text{-}C_5H_5)_2}]$ (I) is formed in ca. 80% yield when $[\mathrm{RuI(CO)_2(\eta\text{-}C_5H_5)}]$ is treated with $\mathrm{Na[Fe(CO)_2(\eta\text{-}C_5H_5)]}$ in tetrahydrofuran, and in ca. 40% yield from $[\mathrm{FeI(CO)_2(\eta\text{-}C_5H_5)}]$ and the less nucleophilic $[\mathrm{Ru(CO)_2(\eta\text{-}C_5H_5)}]^-$ anion. Although the solid complex is stable in air, solutions in common organic solvents decompose within hours unless held under an inert atmosphere. Crystals suitable for X-ray diffraction were obtained from dichloromethane/hexane.

Crystal data: $\mathrm{C_{14}H_{10}O_4FeRu}$, $M = 399$, monoclinic, space group $P2_1/c$ (No. 14), a 7.064(2), b 12.518(3), c 8.011(2) Å, β 106.23(2)°, U 680.2(3) Å^3, $Z = 2$, D_m 1.92 g cm^{-3}, D_c 1.95 g cm^{-3}, $F(000) = 392$, $\mu(\text{Mo-}K_\alpha)$ 21.6 cm^{-1};

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R 0.028 for 1532 independent reflections (at 298 K in range $4 \leqslant 2\theta \leqslant 60°$ with $I > 2\sigma(I)$, Nicolet $P3$ diffractometer, Mo-K_α X-radiation, λ 0.71069 Å).

The structure determination revealed (Fig. 1) that I is present in the crystal as the carbonyl-bridged form with a *trans* arrangement of the terminal CO and η-C_5H_5 ligands. The molecule is disordered about a centre of inversion at the mid-point of the metal—metal bond, the length of which (2.626(1) Å) is approximately mid-way between the Fe—Fe (2.534(2) Å) and Ru—Ru (2.735(2) Å) single bond distances in *trans*-$[M_2(CO)_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$ (M = Fe [3], M = Ru [4]). Other molecular dimensions (Fig. 1 caption) are averaged due to the disorder*.

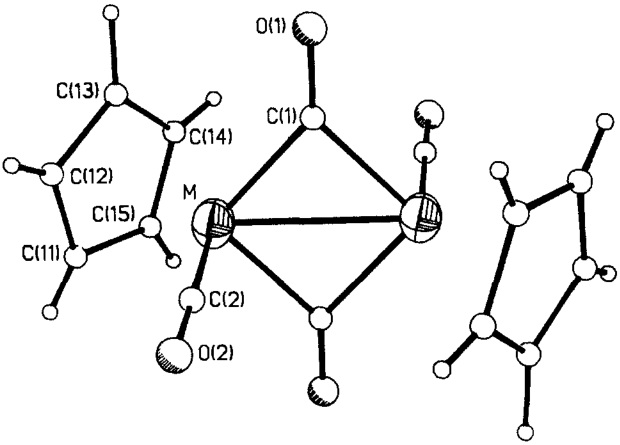

Fig. 1. The molecular structure of *trans*-$[FeRu(CO)_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$ (I). Bond lengths (M = 50% Fe, 50% Ru): M—M 2.626(1), M—C(1) 1.974(4), M—C(2) 1.788(4), C(1)—O(1) 1.179(5), C(2)—O(2) 1.148(5) Å.

The IR spectrum** of I shows that one carbonyl-bridged isomer of the complex is dominant in CH_2Cl_2 at 25°C. This is also the case at −80°C in CD_2Cl_2, when the ^{13}C NMR spectrum contains an intense set of ^{13}CO signals at δ 199.5 (RuCO), 211.5 (FeCO), and 261.5 (μ-CO), with an additional weak broad signal at 233.2 ppm. On warming to −60°C the latter sharpens while the others collapse, but at −30°C all four signals have coalesced into a very broad resonance which on further warming to 25°C evolves into a sharp singlet at δ 231.6 ppm. These observations are strikingly similar to those reported for $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ by Gansow et al. [5], and in accordance with their analysis we assign the major CO

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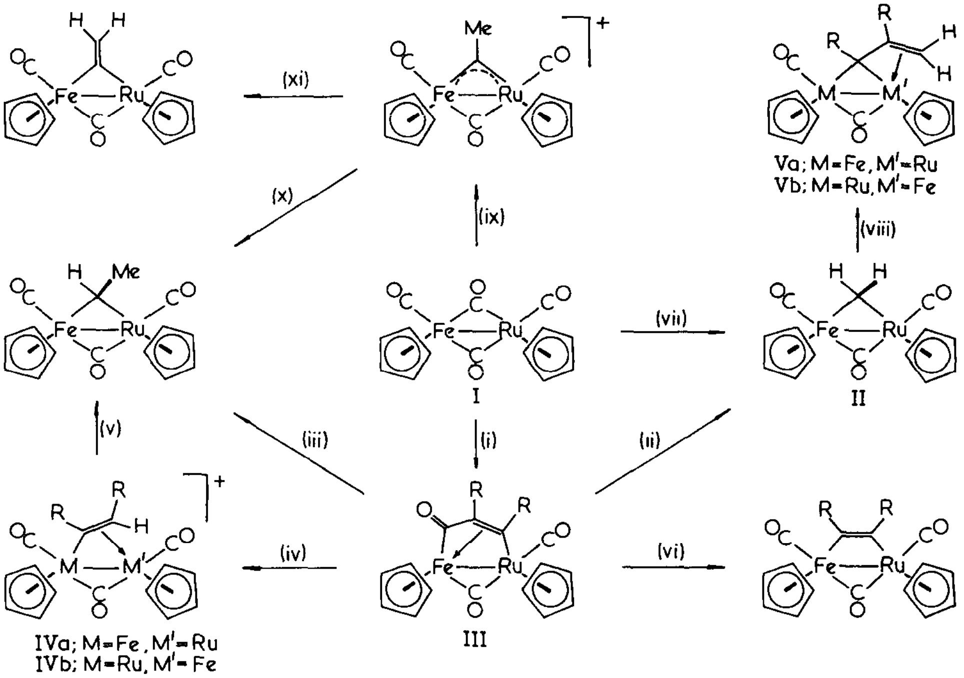
*The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain).

**Selected spectroscopic data (IR in CH_2Cl_2, NMR in $CDCl_3$, coupling constants in Hz): I, dark red crystals, ν(CO) at 1998s, 1957m, 1773s cm^{-1}, ^1H NMR (at 25°C) δ 4.68 (s, 5H, C_5H_5), 5.18 ppm (s, 5H, C_5H_5), ^{13}C NMR, see text; II, orange-red crystals, ν(CO) at 1983s, 1943m, 1780w cm^{-1}, ^1H NMR (*cis* isomer) δ 4.73 (s, 5H, C_5H_5), 5.26 (s, 5H, C_5H_5), 7.95 (s, 1H, μ-CH), 9.75 ppm (s, 1H, μ-CH); ^{13}C NMR (*cis* isomer) δ 124.5 (μ-CH_2); III (R = Ph) dark green crystals, ν(CO) 1979s, 1802s, 1755m (C=O) cm^{-1}, ^1H NMR δ 4.81 (s, 5H, C_5H_5), 5.16 (s, 5H, C_5H_5), 7.09 ppm (m, 10H, 2Ph); IVa (R = H), dark red crystals as BF_4^- salt, ν(CO) 2037s, 2014m, 1863m cm^{-1}, ^1H NMR δ 3.43 (d, 1H, J 12), 5.06 (d, 1H, J 7), 5.70 (s, 5H, C_5H_5), 5.94 (s, 5H, C_5H_5), 11.66 ppm (dd, 1H, J 7 and 12), ^{13}C NMR δ 59.8 (CH_2), 175.6 ppm (μ-CH); Va (R = H), brown-red crystals, ν(CO) 1946s, 1773s cm^{-1}, ^1H NMR δ −0.44 (dd, 1H, J 2 and 7), 2.44 (dd, 1H, J 2 and 4), 4.54 (m, 1H), 4.75 (s, 5H, C_5H_5), 4.98 (s, 5H, C_5H_5), 10.82 ppm (d, 1H, J 6, μ-CH).

signals at −80°C to a static *cis* carbonyl-bridged isomer and the weak signal to the carbonyls of a *trans* carbonyl-bridged isomer which is undergoing bridge ⇌ terminal CO site exchange. At higher temperatures the onset of CO exchange within the *cis* isomer and *cis* ⇌ *trans* isomerisation results eventually in complete averaging of CO environments. The energy barrier to CO scrambling in I appears to be similar to that in $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ and, as expected, higher than that in $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$, which even at −80°C contains a single CO resonance, albeit broad, in the ^{13}C NMR spectrum.



SCHEME 1. Reagents: (i) RC_2R, u.v.; (ii) $Ph_3P{=}CH_2$, boiling toluene, R = Ph; (iii) $Ph_3P{=}CHMe$, boiling toluene, R = Ph; (iv) $HBF_4\cdot OEt_2$; (v) $NaBH_4$, R = H; (vi) boiling toluene, R = CO_2Me; (vii) $LiBHEt_3$, H_2O [8]; (viii) RC_2R, u.v.; (ix) MeLi, $HBF_4\cdot OEt_2$; (x) $NaBH_4$; (xi) H_2O.

Complex I is a precursor of a variety of organo—iron—ruthenium species as laid out in Scheme 1. The products are mildly air-sensitive, generally formed in good yield, and were readily characterised by IR, ^1H and ^{13}C NMR, mass spectra, and elemental analyses (see footnote). There are several noteworthy features of this chemistry:

(a) The pattern of reactions parallels those of the di-iron and diruthenium systems [1], showing that no significant restrictions are imposed by the heteronuclear character of the dimetal centre. In particular, carbon—carbon bond-making and -breaking processes are again observed.

(b) Heteronuclear I and II react faster with alkynes than either the Fe_2 or Ru_2 analogues. For example, dimer $[M_2(CO)_4(\eta\text{-}C_5H_5)_2]$ is consumed by diphenylacetylene [6] under UV irradiation in the order: FeRu (16 h) > Ru_2 (2 d) > Fe_2 (28 d). Likewise, the μ-CH_2 complex II reacts to completion with ethyne within 1 h whereas $[Ru_2(CO)_3(\mu\text{-}CH_2)(\eta\text{-}C_5H_5)_2]$ requires ca. 17 h.

(c) The photochemical reactions of I yield no Fe_2- or Ru_2-based products, establishing that the reactions do not proceed via homolytic Fe—Ru bond fission.

(d) The complexes III—V contain organic ligands bound asymmetrically to the Fe—Ru centre and therefore allow the possibility of isomers in which the metal atom sites are exchanged. This situation is not observed for III, when the species illustrated is formed exclusively, but arises for both IV and V. The isomers **a** and **b** are inseparable and the **a**/**b** ratio is strongly dependent on the nature of R. Thus, for V the **a**/**b** ratio varies from 100% **a** when R = H to 5/1 when R = Me, 1/3 when R = Ph, and 1/7 for R = CO_2Me.

Isomerism such as that in IV and V introduces the possibility of stereo- and regio-specific organic synthesis at a dinuclear metal centre. A preliminary indication of this comes from hydride attack upon the μ-vinyl cations IV. When one of R is Me and one is H the product is exclusively a μ-CHEt iron—ruthenium complex, whereas the corresponding Fe_2 and Ru_2 μ-vinyl cations each afford a mixture of μ-CHEt and μ-CMe_2 complexes [7].

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