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Preliminary communication

UNUSUAL TETRA- AND PENTA-RUTHENIUM COMPLEXES FROM LINKING OF ETHYLIDYNE AND VINYLIDENE LIGANDS

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Summary

The complexes $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CMe)(\eta\text{-}C_5H_5)_2]^+$ and $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCH_2)(\eta\text{-}C_5H_5)_2]$ react together to give $[\{Ru_2(CO)_3(\eta\text{-}C_5H_5)_2\}_2(\mu\text{-}CMeCHCH)]^+$ and $[\{Ru_3(CO)_3(\eta\text{-}C_5H_5)_3\}(\mu\text{-}CCH_2CHC)\{Ru_2(CO)_3(\eta\text{-}C_5H_5)_2\}]$, each characterised by X-ray diffraction. The former results from ethylidyne-vinylidene linking followed by an alkylidyne to vinyl rearrangement.

The μ-ethylidyne cation $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CMe)(\eta\text{-}C_5H_5)_2]^+$ (I) and the μ-vinylidene complex $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCH_2)(\eta\text{-}C_5H_5)_2]$ (II) are readily interconverted; protonation of II yields I, which upon treatment with triethylamine, methyllithium, or water regenerates II smoothly [1]. The deprotonation of I also gives two minor products, tetraruthenium (III) (9%) and pentaruthenium (IV) (1%), as air-stable red crystals. However, when deprotonation is performed at −78°C rather than at room temperature III becomes the major product (65%) while IV remains in very low yield. (Scheme 1). We were unable to identify these complexes from their IR and NMR spectra and therefore subjected each to an X-ray diffraction study, which revealed them to be of formulation $[\{Ru_2(CO)_3(\eta\text{-}C_5H_5)_2\}_2(\mu\text{-}CMeCHCH)][BF_4]$ (IIIa)* and

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*Selected spectroscopic data (IR in CH_2Cl_2, NMR as stated, coupling constants in Hz): III, red crystals, $\nu(CO)$ at 2002 s, 1970 m, 1931 w, 1852 w-m, 1802 m cm^{-1}, ^1H NMR (at −35°C in C_5D_5N) δ 3.73 (s, Me), 3.95 (s, Me), 5.63 (s, C_5H_5), 5.75 (s, $2C_5H_5$), 5.83 (s, C_5H_5), 5.84, (s, C_5H_5), 6.18 (s, C_5H_5), 6.22 (s, 2 C_5H_5), 10.59 (d, *J* 11, μ-CH), 10.63 (d, *J* 11, μ-CH) (the β-CH proton of each isomer is obscured by the C_5H_5 resonance at δ 6.22); IV, red crystals, $\nu(CO)$ at 1990 s, 1949 w, 1799 s, and 1748 m cm^{-1}, ^1H NMR (in $CDCl_3$) δ 5.23 (s, 3 C_5H_5), 5.33 (s, C_5H_5), 5.43 (s, C_5H_5), 6.08 (dd, *J* 7 and 17, CH), 6.41 (dd, *J* 3 and 17, 1 H of CH_2), 6.82 (dd, *J* 3 and 7, 1 H of CH_2), ^{13}C NMR (in $CDCl_3$) δ 71.8 (CH_2) and 140.8 (CH) ppm; VII, yellow crystals, $\nu(CO)$ at 1977 s, 1939 m, and 1780 m cm^{-1}, ^1H NMR (in $CDCl_3$) δ 1.85 (d, *J* 7, Me), 4.95 (m, CH), 5.24 (s, 2 C_5H_5), 6.91 (dd, *J* 10 and 12, CH), 11.03 (d, *J* 12. μ-CH).

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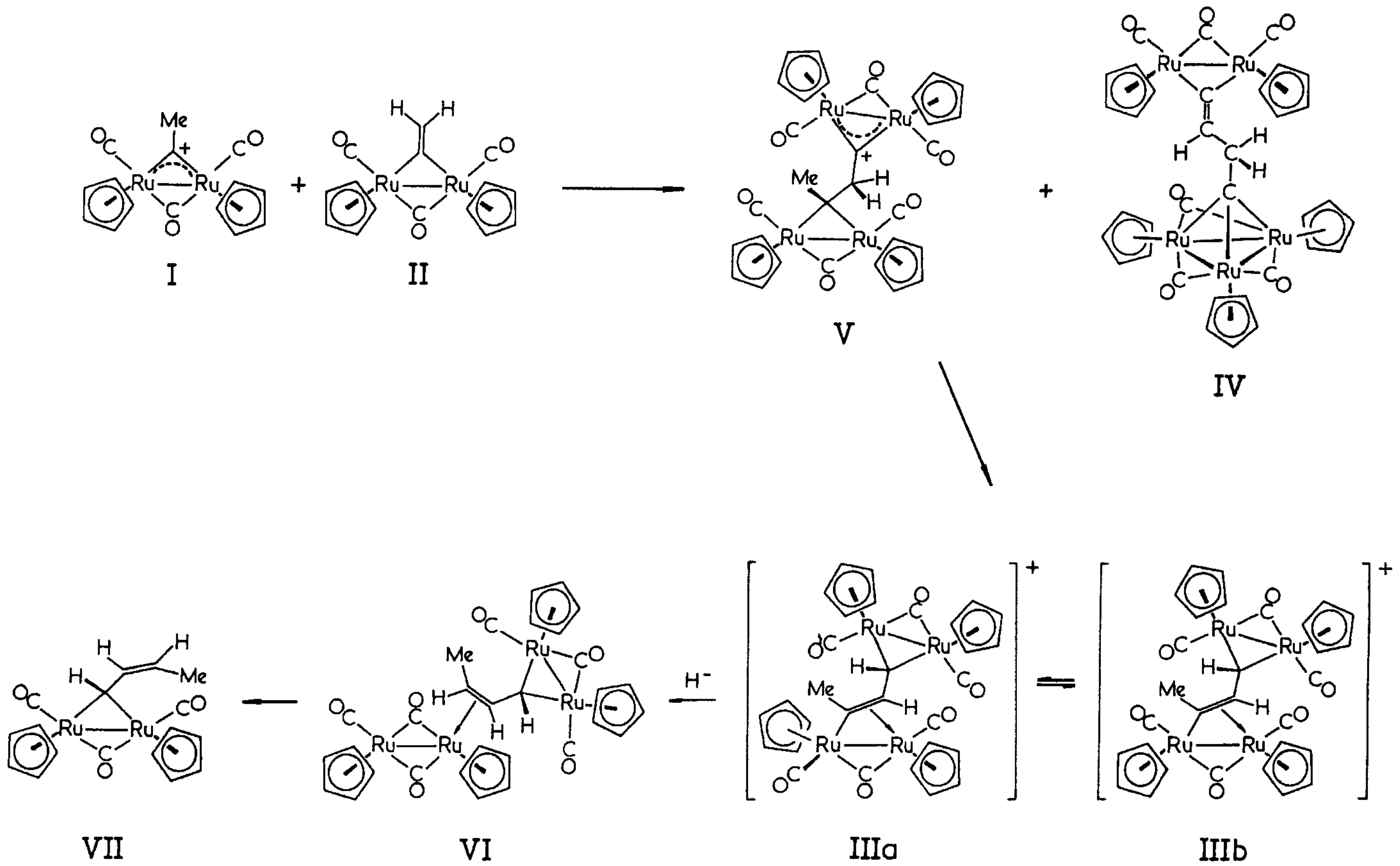

SCHEME 1. (Cations as BF_4^- salts).

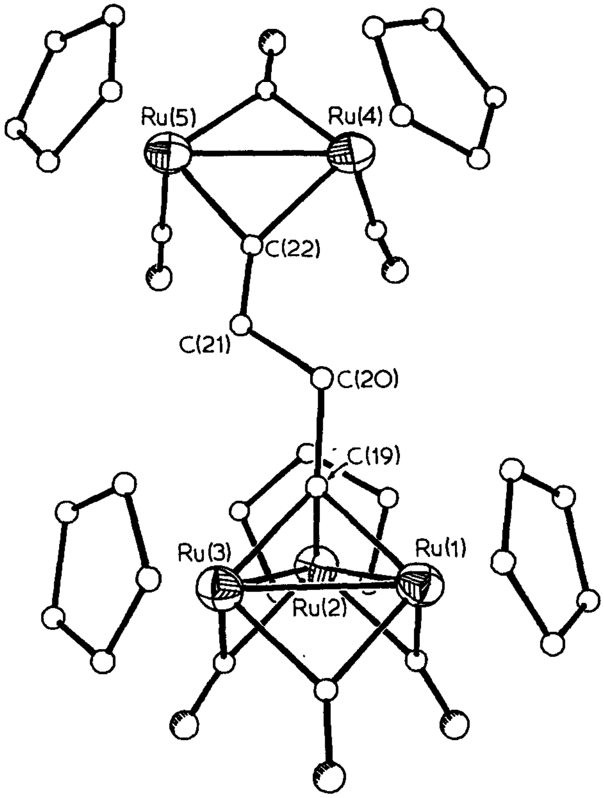

Fig. 1. Molecular structure of IV. Bond distances: Ru(1)—Ru(2) 2.701(1), Ru(1)—Ru(3) 2.683(2), Ru(2)—Ru(3) 2.712(1), Ru(1)—C(19) 2.016(12), Ru(2)—C(19) 2.008(12), Ru(3)—C(19) 2.044(12), Ru(4)—Ru(5) 2.703(2), Ru(4)—C(22) 2.038(13), Ru(5)—C(22) 2.011(13), C(19)—C(20) 1.51(2), C(20)—C(21) 1.52(2), C(21)—C(22) 1.34(2) Å.

$[\{Ru_3(CO)_3(\eta\text{-}C_5H_5)_3\}(\mu\text{-}CCH_2CHC)\{Ru_2(CO)_3(\eta\text{-}C_5H_5)_2\}]$ (IV)*.

Crystal data for IIIa (acetone solvate). $C_{33}H_{31}BF_4O_7Ru_4$, $M = 1\,030.8$, triclinic, space group $P\bar{1}$ (No. 2), a 12.186(4), b 12.385(3), c 13.033(4) Å, α 114.05(3), β 97.79(3), γ 84.76(3)°, U 1778.2(9) Å^3, $F(000) = 1\,004$, D_c 1.93 g cm^{-3} ; $Z = 2$, μ(Mo-K_α) 17.0 cm^{-1} ; $R = 0.06$ for 1954 independent reflections (at 293 K in range $2.9 \leqslant \theta \leqslant 45°$ with $I \geqslant 2.5\sigma(I)$, Nicolet P3 diffractometer, Mo-K_α X-radiation, λ 0.71069 Å).

Crystal data for IV (dichloromethane solvate). $C_{36}H_{30}Cl_2O_6Ru_5$, $M = 1\,147.0$, orthorhombic, space group *Pbca* (No. 61), a 18.124(2), b 24.320(3), c 16.587(3) Å, U 7311(2) Å^3, $F(000) = 4384$, D_c 2.09 g cm^{-3}, $Z = 8$, μ(Mo-K_α) 21.7 cm^{-1} ; $R = 0.048$ for 3012 independent reflections (at 298 K in range $2.9 \leqslant \theta \leqslant 50°$ with $I \geqslant 3.0\sigma(I)$, Nicolet P3 diffractometer, Mo-K_α X-radiation, λ 0.71069 Å).

The molecular structure of IV (Fig. 1) consists of $Ru_3(\mu\text{-}CO)_3(\eta\text{-}C_5H_5)_3$ and $Ru_2(CO)_2(\mu\text{-}CO)(\eta\text{-}C_5H_5)_2$ fragments linked by a $CCH_2CH{=}C$ chain which at one end caps the Ru_3 triangle as a μ_3-alkylidyne ligand and at the other bridges the Ru_2 unit as a μ-vinylidene. The other complex is ionic and the cation IIIa (Fig. 2) also contains a C_4 ligand, of the form $C(Me){=}CHCH$,

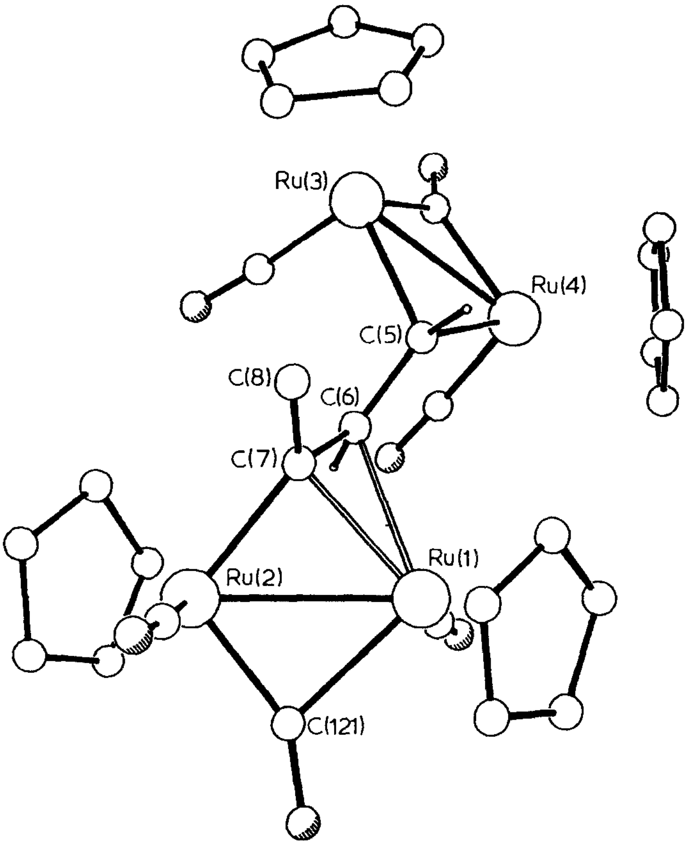

Fig. 2. Molecular structure of the cation IIIa. Bond distances: Ru(1)—Ru(2) 2.767(3), Ru(1)—C(7) 2.17(2), Ru(2)—C(7) 2.08(3), Ru(1)—C(6) 2.40(2), Ru(1)—C(121) 2.19(3), Ru(2)—C(121) 1.89(3), Ru(3)—Ru(4) 2.716(3), Ru(3)—C(5) 2.08(2), Ru(4)—C(5) 2.09(2), C(5)—C(6) 1.44(4), C(6)—C(7) 1.38(3) Å.

but this now links two $Ru_2(CO)_2(\mu\text{-}CO)(\eta\text{-}C_5H_5)_2$ fragments such that one is bridged in a μ-vinyl fashion and the other by a μ-alkylidene. All four of the modes of hydrocarbon coordination seen in III and IV are known [2], but this pair of complexes is unique in having two modes present simultaneously.

It is difficult to envisage a pathway for the formation of IV, but for III a likely mechanism is apparent. The μ-vinylidene complex II is protonated to afford I, as discussed earlier, and if I itself acts as an electrophile towards II then initial formation of cation V is to be expected. Casey et al. have shown [3] that μ-alkylidyne cations with alkyl substituents on the carbon α to the μ-carbon isomerise readily, via a hydrogen shift, to give a μ-vinyl cation; such a process for V yields the observed product III. The production of III in high yield when I is deprotonated at —78° C is now explicable; at this temperature deprotonation is evidently slow enough that appreciable concentrations of I and II are present simultaneously, allowing the reaction with one another to become significant. Confirmation of this was obtained by mixing samples of

I and II in CH_2Cl_2 at 25° C, when III was isolated in 42% yield. The best yield (80%) of III is achieved by adding an excess of CF_3CO_2H to II; presumably because CF_3CO_2H is a much weaker acid than HBF_4 an equilibrium is set up between I and II, and their interreaction can then proceed nearly to completion.

In the crystal of III the alkylidene-bridged diruthenium unit adopts a configuration with the η-C_5H_5 ligands mutually *cis*, while the vinyl-bridged diruthenium unit is *trans* (the "*cis-trans*" isomer IIIa). The ^1H NMR spectrum clearly shows, however, that in solution there are two isomers present in almost equal concentration. Below −10° C these do not interconvert, at ambient temperatures exchange on the NMR time scale results in broadened signals, and above 100° C a time-averaged spectrum is seen. A full description of these observations will be given elsewhere; they are consistent with the existence of both the "*cis-trans*" isomer IIIa and a "*cis-cis*" isomer IIIb in solution, interconverting via *cis*$\rightleftharpoons$*trans* isomerisation of the vinyl-bridged diruthenium unit, and superimposed on this a μ-vinyl group oscillation. Both these processes have been identified in diruthenium complexes [4].

We can view III as a vinyl-bridged diruthenium cation with a rather exotic diruthenium-based substituent on the β-carbon of the μ-vinyl. Such cations normally suffer hydride attack at this β-carbon to give μ-alkylidene complexes [4]. However, treatment of III with $NaBH_4$ gave only VII*, which can be traced to hydride attack upon the α-carbon of the μ-vinyl. In this event "alkene" complex VI would be formed and, on the basis of previous work [5], would be unstable, releasing the bulky "alkene" VII from complexation. The ^1H NMR spectrum of VII indicates that the complex retains the *cis* orientation of the vinyl substituents in III. Presumably attack is directed to the α- rather than β-carbon by the evident crowding (see Fig. 2) about the latter.

The possibility that electrophilic attack of transition metal carbo-cations upon μ-vinylidene will provide a general route to complexes in which polynuclear metal units are bridged by hydrocarbons is under investigation.

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