Reduction–Oxidation Properties of Organotransition-metal Complexes. Part 24.[1] The Oxidative Dimerisation of $[Ru(CO)_2L(\eta^4\text{-cot})]$ ($L = CO$ or PPh_3, cot = cyclo-octatetraene)

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Electrochemical studies show that $[Ru(CO)_3L(\eta^4\text{-cot})]$ (**1**, $L = CO$ or PPh_3, cot = cyclo-octatetraene) undergoes a diffusion-controlled, but irreversible, one-electron oxidation at a platinum-bead electrode in CH_2Cl_2. The reaction of $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ with (**1**, $L = PPh_3$) in CH_2Cl_2 gives $[Ru_2(CO)_4(PPh_3)_2(\eta^2,\eta^3:\eta'^2,\eta'^3\text{-}C_{16}H_{16})][PF_6]_2$ *via* the C–C bond coupling of the radical cation $[Ru(CO)_2(PPh_3)(C_8H_8)]^+$.

We have previously shown[2] that the one-electron oxidation of $[Fe(CO)_3(\eta^4\text{-cot})]$ (cot = cyclo-octatetraene) gives the bi(bicyclo[5.1.0]octadienyl) complex $[Fe_2(CO)_6(\eta^5:\eta'^5\text{-}C_{16}H_{16})]^{2+}$ which is the precursor to a range of polycyclic hydrocarbon derivatives formed by regio- and stereo-selective, redox-based, C–C bond-linking and -cleavage reactions.[3,4] We now describe the one-electron oxidation of $[Ru(CO)_2L(\eta^4\text{-cot})]$ (1, $L = CO$ or PPh_3) which also results in dimerisation but gives an isomer of the iron dication, namely $[Ru_2(CO)_4L_2(\eta^2,\eta^3:\eta'^2,\eta'^3\text{-}C_{16}H_{16})]^{2+}$ in which each of the two, linked, monocyclic cyclo-octatrienyl rings is η^2,η^3-bonded to a ruthenium atom.

Results and Discussion

Cyclic voltammetry shows that $[Ru(CO)_2L(\eta^4\text{-cot})]$ (1, $L = CO$), prepared by a modification of the published procedure,[5] undergoes a diffusion-controlled ($i_{ox}/v^{\frac{1}{2}}$ is constant for scan rates, v, between 50 and 200 mV s^{-1}) but irreversible, one-electron oxidation ($E_{ox} = 0.76$ V, $v = 200$ mV s^{-1}) in CH_2Cl_2 at a platinum-bead electrode; a product wave is observed at −0.44 V on the return sweep of the voltammogram.

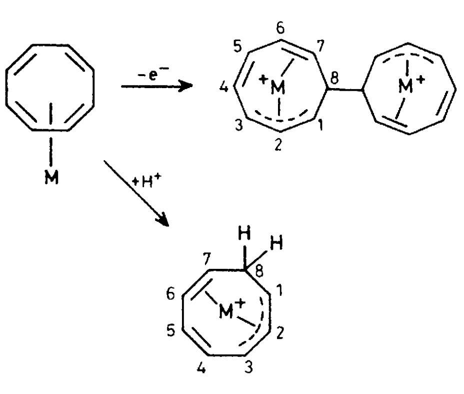
The E_{ox} value of (1, $L = CO$) is such that oxidation to $[Ru(CO)_3(cot)]^+$ should be readily achieved by $[N(C_6H_4\text{-}Br\text{-}p)_3]^+$ ($E^\circ = 1.25$ V) and, indeed, the reaction results in the immediate discharge of the intense blue colour of the oxidant and the appearance of a yellow precipitate {as observed for $[Fe(CO)_3(\eta^4\text{-cot})]^2$}. Surprisingly, however, this precipitate rapidly redissolves and the i.r. spectrum of the resulting solution shows the presence of carbonyl bands indicative of a *neutral* tricarbonyl complex. Attempts to isolate the final product were unsuccessful.

The cyclic voltammogram of $[Ru(CO)_2(PPh_3)(\eta^4\text{-cot})]$ is qualitatively similar to that of the tricarbonyl but the potentials of the irreversible oxidation wave ($E_{ox} = 0.46$ V, $v = 200$ mV s^{-1}) and the product wave ($E_{red} = -1.0$ V) are shifted to more

Table. Analytical and spectroscopic data

Complex	Analysis[a]/(%) C	Analysis[a]/(%) H	$\tilde{\nu}(CO)/cm^{-1}$ [b]	^1H (δ)[c,d]	^{13}C (p.p.m.)[c,e]
$[Ru(CO)_2(PPh_3)(\eta^4\text{-cot})]$	64.2 (64.2)	4.3 (4.4)	2 001, 1 944		
$[Ru_2(CO)_4(PPh_3)_2\text{-}(\eta^2,\eta^3:\eta'^2,\eta'^3\text{-}C_{16}H_{16})][PF_6]_2$	50.4 (50.3)	3.6 (3.5)	2 067, 2 027	3.74 [1 H, ddd, $J(H^3H^2)$ 9, $J(H^3H^4)$ 4, $J(H^3H^1)$ 2, H^3], 4.25 [3 H, m, H^2, H^7, and H^8], 4.95 [1 H, dd, $J(H^1H^2)$ 7, $J(H^1H^8)$ 7, H^1], 5.50 [1 H, dd, $J(H^4H^5)$ 7, $J(H^4H^3)$ 4, H^4], 5.62 [1 H, m, $J(H^5H^4)$ 7, $J(H^5H^6)$ 2, H^5], 6.20 [1 H, d, br, $J(H^6H^7)$ 8, H^6], 7.5 [15 H, m, PPh_3]	44.6 (C^8), 56.6 (C^7), 75.7 (C^1), 75.9 (C^3), 105.4 (C^2), 113.7 [d, J(CP) 8, C^6], 128.6 [d, $J(C^\alpha P)$ 83, $C^\alpha(PPh_3)$], 130.5, 134.9 (C^4, C^5), 130.8 [d, J(CP) 12, PPh_3], 133.8 (PPh_3), 134.5 [d, J(CP) 11, PPh_3], 194.3 [d, J(CP) 12, CO], 200.1 [d, J(CP) 14, CO]
$[Ru(CO)_2(PPh_3)\text{-}(\eta^2,\eta^3\text{-}C_8H_9)][BF_4]$	54.7 (55.0)	4.2 (4.0)	2 064, 2 016	3.53 [1 H, m, $J(H^8H^{8'})$ 15, $J(H^8H^7)$ 7, H^8], 3.70 [1 H, ddd, $J(H^3H^2)$ 9, $J(H^3H^4)$ 4, $J(H^3H^1)$ 2, H^3], 3.85 [1 H, m, $J(H^{8'}H^8)$ 15, $J(H^{8'}H^1)$ 7, $H^{8'}$], 4.13 [1 H, m, $J(H^2H^3)$ 8, $J(H^2H^1)$ 8, $J(H^2H^8)$ 5, H^2], 4.41 [1 H, ddd, $J(H^7H^8)$ 7, $J(H^7H^6)$ 8, $J(H^7H^{8'})$ 3, H^7], 4.81 [1 H, m, $J(H^1H^2)$ 8, $J(H^1H^{8'})$ 7, H^1], 5.46 [1 H, dt, $J(H^5H^4)$ 8, $J(H^5H^6)$ 2, H^5], 5.54 [1 H, dd, $J(H^4H^5)$ 8, $J(H^4H^3)$ 4, H^4], 6.35 [1 H, d, br, $J(H^6H^7)$ 8, H^6], 7.5 [15 H, m, PPh_3]	21.0 (C^8), 49.5 (C^7), 67.8 [d, J(CP) 4, C^1], 74.2 [d, J(CP) 2, C^3], 102.7 (C^2), 109.7 [d, J(CP) 8, C^6], 127.7, 131.8 (C^4, C^5), 130.0 [d, $J(C^\alpha P)$ 90, $C^\alpha(PPh_3)$], 130.7 [d, J(CP) 11, PPh_3], 133.9 (PPh_3), 134.5 [d, J(CP) 11, PPh_3], 195.5 [d, J(CP) 12, CO], 200.7 [d, J(CP) 14, CO]

[a] Calculated values in parentheses. [b] In CH_2Cl_2. [c] The numbering is as in Scheme 1. [d] 200-MHz spectra, in $[^2H_6]$acetone. [e] 50-MHz spectra, in CD_3NO_2.



Scheme 1. M = $Ru(CO)_2(PPh_3)$

negative potentials by the presence of the electron-donating phosphine ligand.

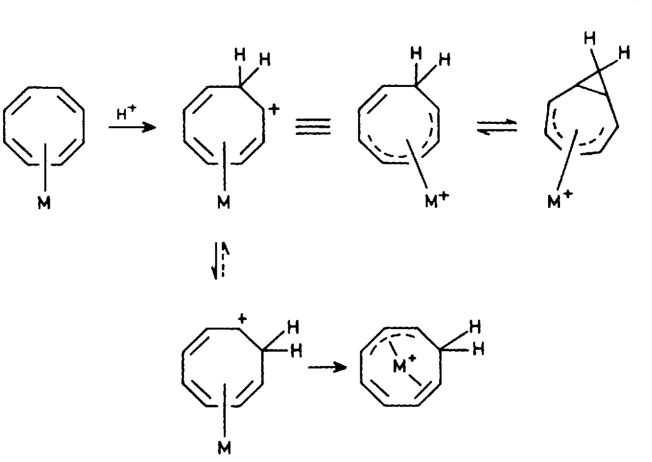
The lowering of E_{ox} on carbonyl substitution allows the use of a milder oxidant in the reaction of (**1**, L = PPh_3). Thus, the dicarbonyl rapidly reacts with $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ (E° = 0.47 V) in CH_2Cl_2 to give a pale yellow solution from which a near-quantitative yield of $[Ru_2(CO)_4(PPh_3)_2(\eta^2,\eta^3:\eta'^2,\eta'^3\text{-}C_{16}H_{16})][PF_6]_2$ (**2**) was isolated. Elemental analysis, and i.r. and n.m.r. spectroscopy (Table) suggested a dimeric structure for (**2**) although the complexity of the ^1H n.m.r. spectrum precluded an immediate assignment of the complete hydrocarbon skeleton. Failure to produce crystals of (**2**), as the $[PF_6]^-$, $[BF_4]^-$, or $[CF_3SO_3]^-$ salt, prevented an *X*-ray crystallographic study, but the structure was finally assigned by comparing the n.m.r. spectra of the dimeric dication with those of $[Ru(CO)_2(PPh_3)(\eta^2,\eta^3\text{-}C_8H_9)]^+$ (**3**).

Complex (**3**), briefly referred to by Cooke *et al.*[6] in 1971, is simply prepared by adding $HBF_4{\cdot}Et_2O$ to (**1**, L = PPh_3) in diethyl ether at room temperature. The pale yellow precipitate was fully characterised by elemental analysis, i.r. and n.m.r. spectroscopy (Table) as the η^2,η^3-bonded cyclo-octatrienyl complex shown in Scheme 1. Thus, the ^{13}C n.m.r. spectrum shows eight resonances, assigned to two free olefinic carbons, two olefinic carbon atoms bonded to ruthenium, three metal-bound allylic carbons, and one *sp*³ carbon atom. Similarly, the ^1H n.m.r. spectrum (including homonuclear decoupling) is fully consistent with the structure shown, and is very similar to those observed for $[Ru(CO)_3(\eta^2,\eta^3\text{-}C_8H_9)]^+$ [6] and the *X*-ray structurally characterised cation $[Ru(\eta^2,\eta^3\text{-}C_8H_9)(\eta\text{-}C_6H_3Me_3)]^+$.[7]

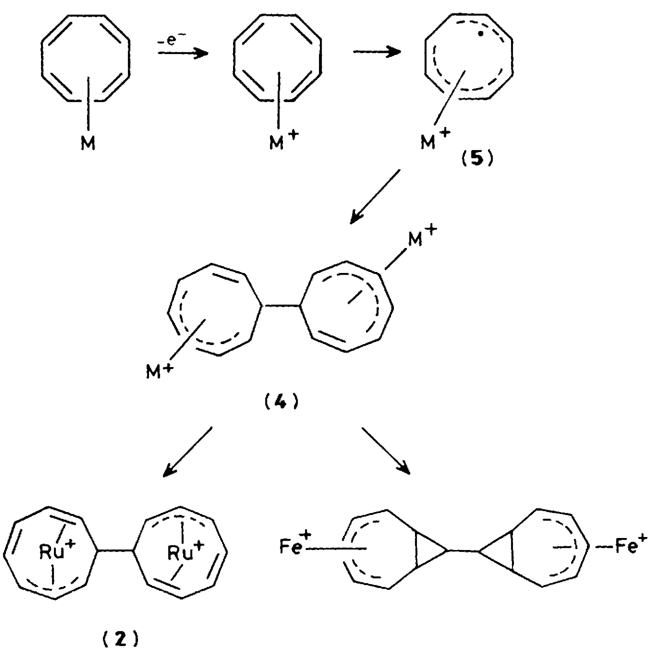
A comparison of the n.m.r. spectra of (**2**) and (**3**) (Table) shows the C_8 hydrocarbon skeletons to be identical. The ^{13}C n.m.r. spectra show similar shifts, and couplings to phosphorus, for all of the analogous carbon atoms except C(8). The resonances for this atom, at 44.6 and 21.0 p.p.m. for (**2**) and (**3**) respectively, reflect the difference between the bridgehead position in the former and the bonding to two hydrogen atoms in the latter.

The proton n.m.r. spectra are also very similar although, of course, one proton signal is absent for (**2**). Unfortunately, it is unclear whether the *exo*- or *endo*-proton on C(8) is replaced although it seems likely that the two halves of the dication (**2**) are linked in an *exo,exo* fashion with, therefore, H(8) in the *endo* position.

The difference between the structures of (**2**) and $[Fe_2(CO)_6(\eta^5:\eta'^5\text{-}C_{16}H_{16})]^{2+}$ is mirrored in the structural preferences of the products of protonation of $[M(CO)_3(\eta^4\text{-cot})]$ (M = Fe or Ru); the thermodynamically stable isomers of $[M(CO)_3(C_8H_9)]^+$ contain the η^5-bicyclo[5.1.0]octadienyl group when M = Fe, but the η^2,η^3-cyclo-octatrienyl ligand for M = Ru.



Scheme 2.



Scheme 3. M = $Ru(CO)_2L$ or $Fe(CO)_2L$, L = CO or PPh_3

A general mechanism for the protonation of η^4-cyclo-octatetraene metal complexes has recently been proposed[7] and is shown in Scheme 2; the initial η^5-cyclo-octatrienyl complex isomerises *via* two competing pathways. The formation of (**2**) and $[Fe_2(CO)_4L_2(\eta^5:\eta'^5\text{-}C_{16}H_{16})]^{2+}$ from the radical cation $[M(CO)_2L(C_8H_8)]^+$ (M = Fe or Ru) (Scheme 3) may also involve a common precursor, namely the $\eta^5:\eta'^5$-bi(cyclo-octatrienyl) complex (**4**). The formation of this species requires that dimerisation of the monomeric allyl radical (**5**) precedes isomerisation; formation of the bicyclo[5.1.0]octadienyl radical from (**5**), and then dimerisation, was previously proposed for iron.[2]

As a precursor to polycyclic hydrocarbon complexes, (**2**) is somewhat disappointing {*cf.* $[Fe_2(CO)_6(\eta^5:\eta'^5\text{-}C_{16}H_{16})]^{2+}$}. The ruthenium dication reacts with 1,8-bis(dimethylamino)-naphthalene ('proton sponge') in CH_2Cl_2 to give an orange-red solution from which a small yield of a red solid (**6**) was isolated. The elemental analysis (C and H) was consistent with the formula $[Ru_2(CO)_4(PPh_3)_2(C_{16}H_{14})]$, and the colour of the complex, reminiscent of that of (**1**), and the i.r. carbonyl spectrum [(**6**), $\tilde{\nu}$(CO) (CH_2Cl_2) = 2 007 and 1 953 cm^{-1}; *cf.* (**1**, L = PPh_3), $\tilde{\nu}$(CO) = 2 001 and 1 944 cm^{-1}] suggested the formation of a dimeric bi(cyclo-octatetraenyl) derivative. Studies of the protonation of such a derivative, of which there are no known analogues, would shed light on the mechanism of the isomerisation reactions described above. Unfortunately, the low yields obtained for **(6)** prevented any further characterisation. Similarly, the reactions of **(2)** with $NaBH_4$, and with $[Co(\eta-C_5H_5)_2]$ as a one-electron reductant, gave only small quantities of neutral carbonyl-containing products.

Experimental

The preparation, purification, and the reactions of the complexes described were carried out under an atmosphere of dry nitrogen. Unless otherwise stated, products were purified by dissolution in CH_2Cl_2, filtration, addition of n-hexane, and partial evaporation of the solvent mixture *in vacuo* to induce precipitation. Unless otherwise stated, the complexes are air-stable, dissolving in polar solvents such as acetone and CH_2Cl_2 to give solutions which slowly decompose in air.

The complex $[Fe(\eta-C_5H_5)_2][PF_6]$ was prepared by the published method.[8] 1,8-Bis(dimethylamino)naphthalene ('proton sponge') and $HBF_4{\cdot}Et_2O$ were purchased from the Aldrich Chemical Co. Ltd.

Infrared spectra were recorded on a Perkin-Elmer PE 257 spectrophotometer or a Nicolet MX-1 FT instrument and, where necessary, were calibrated against the absorption band of polystyrene at 1 601 cm^{-1}. Proton n.m.r. spectra were recorded on JEOL PS 100 or FX 200 instruments, and ^{13}C n.m.r. spectra on JEOL FX 200 or FX 90Q spectrometers; both were calibrated against $SiMe_4$ as an internal reference.

Electrochemical studies were performed as previously described.[9] Microanalyses were by the staff of the Microanalytical Service of the School of Chemistry, University of Bristol.

Tricarbonyl(η^4-*cyclo-octatetraene*)*ruthenium*, $[Ru(CO)_3(\eta^4\text{-cot})]$.—A mixture of $[Ru_3(CO)_{12}]$ (7.0 g, 11.0 mmol) and cyclo-octa-1,5-diene (45 cm^3, *ca.* 400 mmol) was heated under reflux in benzene (300 cm^3) until the i.r. spectrum showed the absence of the dodecacarbonyl (*ca.* 6 h). After reducing the volume of the solution *in vacuo* to *ca.* 20 cm^3, n-hexane (50 cm^3) was added, the mixture was filtered through Celite, and the filtrate was again reduced in volume (*ca.* 20 cm^3) to give a dark brown liquid. Chromatography on an n-hexane–alumina column (20 × 4 cm), eluting with n-hexane, gave a yellow solution of $[Ru(CO)_3(\eta^4\text{-cod})]$. After reducing the volume of the eluate to *ca.* 20 cm^3, benzene (250 cm^3) and cot (8 cm^3, 77 mmol) were added and the mixture was heated under reflux for 1 h. The orange solution was then evaporated to low volume (*ca.* 15 cm^3) and chromatographed on an n-hexane–alumina column (40 × 4 cm). Elution with n-hexane, and careful monitoring of the eluate by i.r. spectroscopy, gave an orange solution which was evaporated to *ca.* 100 cm^3 and cooled to -78 °C to give orange crystals of $[Ru(CO)_3(\eta^4\text{-cot})]$, yield 3.58 g {38%, based on $[Ru_3(CO)_{12}]$}.

Dicarbonyl(η^4-*cyclo-octatetraene*)(*triphenylphosphine*)-*ruthenium*, $[Ru(CO)_2(PPh_3)(\eta^4\text{-cot})]$.—A solution of $[Ru(CO)_3(\eta^4\text{-cot})]$ (0.46 g, 1.60 mmol) and PPh_3 (0.45 g, 1.71 mmol) in n-heptane (200 cm^3) was heated under reflux for 6 h. After filtration to remove $[Ru(CO)_3(PPh_3)_2]$ (0.12 g, 10% yield), the mixture was evaporated to dryness and the residue extracted with toluene (8 cm^3). Chromatography on an n-hexane–alumina column (20 × 3 cm), eluting with 30% diethyl ether–n-hexane, gave an orange solution which was evaporated to dryness to give $[Ru(CO)_2(PPh_3)(\eta^4\text{-cot})]$ as an orange solid, yield 0.58 g (60%).

The complex is moderately soluble in n-hexane to give an orange solution which slowly decomposes in air.

($\eta^2,\eta^3:\eta'^2,\eta'^3$-*Bicyclo-octatrienyl*)*tetracarbonylbis*(*triphenylphosphine*)*diruthenium Bis*(*hexafluorophosphate*), $[Ru_2(CO)_4(PPh_3)_2(\eta^2,\eta^3:\eta'^2,\eta'^3\text{-}C_{16}H_{16})][PF_6]_2$.—To a stirred solution of $[Ru(CO)_2(PPh_3)(\eta^4\text{-cot})]$ (0.57 g, 1.10 mmol) in CH_2Cl_2 (55 cm^3) was added $[Fe(\eta-C_5H_5)_2][PF_6]$ (0.36 g, 1.10 mmol). After 45 min the pale yellow solution was filtered and reduced in volume (to *ca.* 15 cm^3) *in vacuo*. Addition of n-hexane (200 cm^3) gave the product as a white solid, yield 0.66 g (92%). It may be purified from CH_2Cl_2–diethyl ether if necessary.

Dicarbonyl(η^2,η^3-*cyclo-octatrienyl*)(*triphenylphosphine*)-*ruthenium Tetrafluoroborate*, $[Ru(CO)_2(PPh_3)(\eta^2,\eta^3\text{-}C_8H_9)][BF_4]$.—An excess (*ca.* 0.3 cm^3) of $HBF_4{\cdot}Et_2O$ in diethyl ether was added to a stirred solution of $[Ru(CO)_2(PPh_3)(\eta^4\text{-cot})]$ (76 mg, 0.145 mmol) in the same solvent (25 cm^3). The pale yellow precipitate was removed by filtration, washed well with diethyl ether, and dried in air, yield 72 mg (81%).

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