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PREPARATION AND REACTIONS OF CYCLOOCTATETRAENE-RUTHENIUM CARBONYL COMPLEXES

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SUMMARY

Reaction between $Ru_3(CO)_{12}$ and cyclooctatetraene gives the complexes $C_8H_8Ru(CO)_3$ and $C_8H_8Ru_2(CO)_6$. The latter complex loses carbon monoxide on heating to form $C_8H_8Ru_2(CO)_5$. The structures of these complexes are discussed in the light of their IR and NMR spectra, and are shown to be similar to the corresponding iron complexes. A low temperature study of the proton NMR spectrum of $C_8H_8Ru(CO)_3$ has enabled further information to be obtained concerning the nature of the "ring-whizzing" phenomenon.

Cyclooctatetraene is displaced from $C_8H_8Ru(CO)_3$ by I_2 or $P(OCH_2)_3CEt$ giving $[Ru(CO)_3I_2]_2$ and *trans*-$[P(OCH_2)_3CEt]_2Ru(CO)_3$, respectively. Mercury(II) chloride, bromide, or thiocyanate also react with $C_8H_8Ru(CO)_3$ to afford the binuclear complexes $[Ru(CO)_3(HgX)X]_2$ (X=Cl, Br, or SCN), which undergo bridge-splitting reactions with pyridine without breaking the Ru–Hg bond, to give the complexes $Ru(CO)_3py(HgX)X$.

INTRODUCTION

Much interest has been evoked by the interesting complexes obtainable from reactions between cyclooctatetraene and iron pentacarbonyl[1-3] or di-iron enneacarbonyl[4]. The crystal structures of the complexes $C_8H_8Fe(CO)_3$[5], *trans*-$C_8H_8[Fe(CO)_3]_2$[5], and $C_8H_8Fe_2(CO)_5$[6] have been reported. In solution, many of these complexes undergo rapid valence tautomerism, resulting in simple proton nuclear magnetic resonance (NMR) spectra; recently, the application of low temperature NMR techniques in investigations of $C_8H_8Fe(CO)_3$ has resulted in several different interpretations[7-10] of the fine structure which develops in the proton NMR spectrum below −100°. An infrared study of this molecule suggested that the solid state geometry is retained in solution[11].

Even at the lowest temperatures, however, the proton NMR spectrum of $C_8H_8Fe(CO)_3$ remains incompletely resolved. We have prepared the ruthenium complex, with others, in the hope of obtaining more data on these systems. Some preliminary results have already appeared[12].

RESULTS AND DISCUSSION

Cyclooctatetraene reacts slowly with triruthenium dodecacarbonyl[13] in refluxing cyclohexane, presumably due to the stability of the Ru_3 cluster. However, by irradiating benzene solutions of the reactants we have isolated the complexes $C_8H_8Ru(CO)_3$ (I) and $C_8H_8Ru_2(CO)_5$ (II) from the reaction mixture. In refluxing xylene, (I) and (II) are formed together with a third complex, $C_8H_8Ru_2(CO)_6$ (III). Optimum yields (~60%) of (II) were obtained by periodic examination of the infrared spectrum of the reaction mixture. The identity of the complexes was established by elemental analysis and molecular weight measurements (Table 1), and from the similarity of their infrared and proton NMR spectra to those of the corresponding iron complexes.

TABLE 1

SOME RUTHENIUM CARBONYL COMPLEXES

	Compound	M.p.	Analysis: found (calcd.) (%)						Mol. wt.
		(°C)	C	H	O	Ru	Hg	N	Found^{a} (calcd.)
(I)	$C_8H_8Ru(CO)_3$	75–76	46.0	2.9					289^{b}
			(45.7)	(2.8)					(289)
(II)	$C_8H_8Ru_2(CO)_5$	224–225	35.2	1.7	17.5	45.5			430
			(35.0)	(1.8)	(18.0)	(45.3)			(446)
(III)	$C_8H_8Ru_2(CO)_6$	101–104	34.9	1.7	20.3	43.3			
			(35.4)	(1.7)	(20.2)	(42.7)			
(IV)	$[P(OCH_2)_3CEt]_2Ru(CO)_3$^{c}	176–178	39.1	4.7		22.1			450
			(39.0)	(4.8)		(21.9)			(461)
	$(Ph_3P)_2Ru(CO)_3$		66.1	4.5					
			(66.0)	(4.3)					
	$[Ru(CO)_3I_2]_2$	325	8.6	0.0		23.2			880^{b}
			(8.2)	(0.0)		(23.0)			(880)
(V)	$[Ru(CO)_3(HgCl)Cl]_2$^{d}	>250^{e}	7.3	0.0		22.5	44.2		
			(7.9)	(0.0)		(22.2)	(43.8)		
(VI)	$[Ru(CO)_3(HgBr)Br]_2$^{f}	>250^{e}	7.2	0.0		18.2	37.2		
			(6.6)	(0.0)		(18.5)	(36.7)		
(VII)	$[Ru(CO)_3(HgSCN)SCN]_2$^{g}	>250^{e}	12.4	0.0				5.8	
			(12.0)	(0.0)				(5.6)	
(VIII)	$Ru(CO)_3py(HgCl)Cl$	89–91	18.1	1.0		18.6		2.7	545
			(17.9)	(0.9)		(18.9)		(2.6)	(536)
(IX)	$Ru(CO)_3py(HgBr)Br$	108–109	15.0	1.0				2.3	610
			(15.4)	(0.8)				(2.2)	(625)

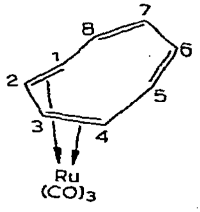
[a] Determined in $CHCl_3$ (Mechrolab vapour pressure osmometer). [b] Mass spectrometry. [c] Found: P, 13.2; calcd.: P, 13.4%. [d] Found: Cl, 13.1; calcd.: Cl, 12.8%. [e] Decomposition. [f] Found: Br, 29.6; calcd.: Br, 29.4%. [g] Found: S, 12.2; calcd.: S, 12.7%.

In dichlorofluoromethane, the proton NMR spectrum of cyclooctatetraeneruthenium tricarbonyl (I) showed a single sharp peak at room temperature, at 4.79 τ, which may be compared to that shown by the iron complex at 4.76 τ^1. On cooling the solution the line broadens, and complete collapse of the signal occurs at −95°. The iron complex shows this effect at ~ −100°[7-9]. At −97°, two peaks appear on either side of the original signal at 4.19 and 5.31 τ (relative intensity, 1 : 1), which increase in intensity on further cooling to −109°. Below this temperature, the spectrum changes to three peaks centered at 4.03, 5.12, and 5.88 τ (intensity, 2 : 1 : 1). At the lowest temperature we were able to reach (−130°), the lowest field peak splits into two resonances centred at 3.88 and 4.17 τ; all lines were resolved into triplets at this temperature. Further lowering of the temperature resulted in crystallisation of (I) in the NMR tube.

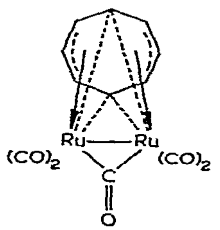
The interpretations of the low temperature proton NMR spectrum of the related iron complex, which consists of two broad unsymmetrical peaks at 3.83 and 5.41 τ, differ. Kaesz *et al.*[7] favour a situation analogous to that found in the crystal, in which the motion of the ring relative to the metal has slowed down sufficiently to allow observation of the resonances due to the 1,3-diene bonded form; the high field resonance was assigned to the coordinated 1,3-diene protons. Infrared data support this interpretation[11]. Cotton and his coworkers[8] have proposed a model in which C_8H_8 is bonded as a 1,5-diene to a $Fe(CO)_3$ moiety. Pettit *et al.*[9] suggested an alternative assignment, based on chemical shift interpretations, and proposed a tautomerism involving shift of the $Fe(CO)_3$ group between the two 1,3-diene systems. Recently[10], evidence has been presented which refutes both the proposals of Cotton and of Pettit, and further supports the original suggestion of a 1,3-diene–metal system.

It seems reasonable to compare the iron and ruthenium complexes, on the basis of the similarity of their infrared spectra (see Experimental) in both the carbonyl and fingerprint regions, of the chemical shift values, and of their behaviour on cooling.

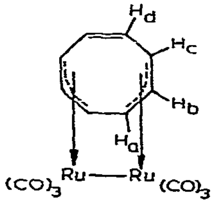
The resolution of the proton NMR spectrum of (I) into four bands at the lowest temperatures attained indicates a structure in which there must be at least four non-equivalent hydrogen atoms. The 1,3-diene bonded structure meets this requirement, and we suggest that the form present in the solution at −130° corresponds to that found in the crystal. The resonances at lowest field (3.88 and 4.17 τ) are assigned to the free diene protons, *i.e.*, $H_{5,8}$ and $H_{6,7}$, respectively. The other two resonances (5.12 and 5.88 τ) are assigned to $H_{2,3}$ and $H_{1,4}$, respectively. The terminal protons of 1,3-diene–metal systems generally occur at higher field than the inner protons[14], but the unusual nature of these cyclic diene complexes probably makes extrapolations of chemical shift values from known acyclic 1,3-diene–metal systems of little use. The average value of the four observed resonances (4.76 τ) agrees well with the observed value of 4.79 τ at room temperature.



(I)



(II)



(III)

On warming, the merging of the two low field resonances must correspond to some motion of the uncomplexed diene protons which is rapid on the NMR timescale, but which leaves the diene–metal system essentially unchanged. Such a process could involve a "wagging" of the free diene system. The signal for the free protons occurs at 4.03 τ (calculated average, 4.03 τ). A further increase in temperature results in only two signals being distinguished, at 5.26 and 4.32 τ. It is evident that these positions do not represent the averaging of $H_{1,4}$ and $H_{2,3}$, and of $H_{5,8}$ and $H_{6,7}$ (calculated values, 5.50 and 4.03 τ, respectively), nor of a situation where the metal group oscillates between the two diene systems {calculated values: $H_{1,4,5,8}$, $\{5.88\,[H_{1,4}]+3.88\,[H_{5,8}]\}\cdot\frac{1}{2}=4.88$; $H_{2,3,6,7}$, $\{5.12\,[H_{2,3}]+4.17\,[H_{6,7}]\}\cdot\frac{1}{2}=4.65\,\tau$}.

However, if a 1,2-shift of the metal group relative to the ring is occurring, the expected positions would result from the averaging of all these values, *i.e.*, $(5.50+4.88)\cdot\frac{1}{2}=5.19$, and $(4.03+4.65)\cdot\frac{1}{2}=4.34\ \tau$, which are in reasonable agreement with the observed values. The final stage is a gradual increase in rate of rotation so that all protons become equivalent, and give one resonance absorption at 4.79 τ (calcd. value, $(5.19+4.34)\cdot\frac{1}{2}=4.77\ \tau$).

Our results indicate that the instantaneous configuration of cyclooctatetraeneruthenium tricarbonyl in solution, and by implication, that of the analogous iron complex, is similar to that found in the solid state, namely, with the hydrocarbon bonded as a 1,3-diene to the metal tricarbonyl group. In solution, there is a motion of the ring relative to the metal, which proceeds by a 1,2-shift mechanism, and the rate of which is dependent on the temperature*. The more facile slowing down of this valence tautomerism in the ruthenium complex compared to the iron compound, may be naively explained in terms of better overlap of the appropriate metal orbitals with the diene π-system in the case of the ruthenium complex.

The IR spectrum of cyclooctatetraenediruthenium hexacarbonyl (III), a yellow crystalline solid, shows complex terminal carbonyl bands, and a band at 770 cm^{-1} which is consistent with the presence of an uncomplexed *cis* double bond. The proton NMR spectrum of (III) shows three bands centred at 4.20 (H_a, quartet), 5.75 (H_c and H_d, multiplet), and 7.32 τ (H_b, multiplet), of relative intensity 1 : 2 : 1. Double irradiation of the band at 4.20 τ collapsed the high field multiplet to a sharp doublet, whereas irradiation of the high field band caused the low field signal to collapse to a singlet. These observations clearly show that (III) is isostructural in solution with the iron complex which contains a bis(π-allyl) system, as illustrated[4]. In contrast with the iron system, (III) does not isomerise in solution, nor does it lose carbon monoxide at room temperature.

When (III) is heated to 110°, decarbonylation occurs, with the formation of cyclooctatetraenediruthenium pentacarbonyl (II), a relatively insoluble orange crystalline solid. The IR spectrum of (II) shows terminal carbonyl bands at 2038, 2011 and 1972 cm^{-1}, and a bridging carbonyl band at 1822 cm^{-1}, and the proton NMR spectrum (in CS_2) shows only a single peak at 5.2 τ. These properties are similar to those exhibited by the iron complex[4] [ν(bridge CO) 1803 cm^{-1}; sharp singlet at 5.33 τ], and we suggest that our complex has a similar structure**.

It has been shown previously[1] that triphenylphosphine displaces cycloocta-

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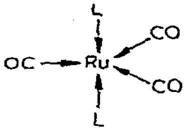
* *Note added in proof.* A report of a similar investigation appeared while this paper was being prepared, in which substantially the same results and conclusions were reached (W. K. Bratton, F. A. Cotton, A. Davison, A. Musco and J. W. Faller, *Proc. Natl. Acad. Sci. U.S.*, 58 (1967) 1324).

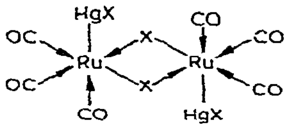
** A recent note records the isolation of several cyclooctatetraene–ruthenium complexes, including (I), (II) and (III) (F. A. Cotton, A. Davison and A. Musco, *J. Amer. Chem. Soc.*, 89 (1967) 6796).

tetraene from $C_8H_8Fe(CO)_3$. Analogous reactions occur with $C_8H_8Ru(CO)_3$. Triphenylphosphine affords the known complex *trans*-$(Ph_3P)_2Ru(CO)_3$[15], and the sterically compact ligand 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane also displaces the tetraene from (I) to give $[P(OCH_2)_3CEt]_2Ru(CO)_3$ (IV). The IR spectrum of (IV) shows a single carbonyl peak at 1941 cm^{-1}, confirming that the phosphite ligands occupy apical positions in a trigonal bipyramidal structure.

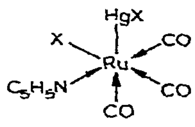
Neither bromine[1] nor iodine reacts with cyclooctatetraeneiron tricarbonyl. However, treatment of (I) with iodine at room temperature results in an immediate reaction to give the binuclear complex $[Ru(CO)_3I_2]_2$, identified by elemental analyses, and its IR and mass spectra.



(IV) L = $P(OCH_2)_3CEt$



(V), X = Cl
(VI), X = Br
(VII), X = SCN



(VIII), X = Cl
(IX), X = Br

The electrophilic reagents $HgCl_2$, $HgBr_2$ and $Hg(SCN)_2$ also react rapidly with (I) with loss of cyclooctatetraene, and the formation of the insoluble halogen-bridged binuclear complexes $[Ru(CO)_3(HgX)X]_2$ [(V), X=Cl; (VI), X=Br; (VII), X=SCN]. The IR spectra of (VI), (VII), and (VIII) (measured in KBr discs) show three terminal carbonyl bands, suggesting that the carbonyl groups are mutually *cis*. The complexes (V) and (VI) undergo bridge-splitting reactions on warming with an excess of pyridine, to give the soluble crystalline mononuclear complexes $[Ru(CO)_3py(HgX)X]$ [(VIII), X=Cl; (IX), X=Br]. The infrared spectra of (VIII) and (IX) both show three terminal carbonyl bands again suggesting that the carbonyl groups are mutually *cis*, and that the complexes have the structures shown. These complexes contain a Ru–Hg bond, and it is of interest that the reaction with pyridine leaves this metal–metal bond intact.

Cyclooctatetraeneiron tricarbonyl does not undergo analogous reactions with mercuric halides. The reactions detailed here are examples of d^8 to d^6 oxidative addition reactions, and the higher reactivity of ruthenium compared to iron in the complexes *trans*-$(Ph_3P)_2M(CO)_3$ (M=Fe or Ru) has been noted previously.

These reactions differ from those studied by Collman[15,16] in that, formally, a bidentate ligand is displaced by the addend, and it is of interest that cyclooctatetraene is displaced in preference to carbon monoxide. However, it is unlikely that these reactions involve prior displacement of the hydrocarbon from (I); more likely is the formation of an intermediate that is either seven-coordinate, retaining the diene system intact, or more reasonably, six-coordinate, in which the hydrocarbon is bonded to the metal by only one double bond. The reactions are envisaged as involving nucleophilic attack of the ClHg–Cl bond, for example, by the ruthenium complex, with simultaneous breaking of one of the metal–olefin π-bonds, to form a complex analogous to those formed in similar reactions, *e.g.*, with Vaska's complex[17]. This is followed by formation of a halogen-bridged binuclear species with simultaneous loss of cyclooctatetraene.

The lack of reactivity of the iron complex may be due to the difficulty of formation of a seven-coordinate intermediate because of its smaller size, or to the lower nucleophilicity of the iron complex, resulting from a tighter binding of the valence electrons. However, a full understanding of this interesting difference in reactivity of related complexes, and of the phosphine-substituted systems, must await the results of mechanistic studies now in progress.

EXPERIMENTAL

IR spectra were recorded with a Perkin–Elmer 257 grating spectrophotometer. The low-temperature proton NMR measurements were made with a Perkin–Elmer R10 spectrometer adapted to accommodate a variable temperature probe. A Varian HA100 spectrometer was used for the proton decoupling studies. Mass spectra were obtained with an AEI MS9 double-focussing spectrometer, operating at 70 eV ionising energy.

All reactions were carried out in an atmosphere of nitrogen. Melting points were taken in sealed evacuated capillaries.

Cyclooctatetraeneruthenium tricarbonyl (I)

A suspension of $Ru_3(CO)_{12}$ (0.75 g, 1.17 mmoles) in cyclooctatetraene (3.0 g, 28.8 mmoles) and cyclohexane (25 ml) contained in a sealed Pyrex tube, was irradiated with UV light (250 watt high pressure lamp) for 72 h with continuous shaking. Some unreacted $Ru_3(CO)_{12}$ was removed by filtration, and the solvent was removed *in vacuo*. Recrystallisation of the residue from hexane at $-78°$ gave cyclooctatetraeneruthenium tricarbonyl (I) (0.27 g, 60%) as an orange-red crystalline solid, which could be further purified by sublimation *in vacuo*.

IR spectrum: ν(CO), 2070 s, 2009 s, 1996 s cm^{-1} (cyclohexane); other bands at 3040 s, 3022 (sh), 1561 m, 1489 m, 1460 m, 1419 s, 1313 m, 1298 m, 1250 m, 1178 w, 1122 m, 982 m, 922 m, 898 s, 862 s, 847 m, 804 m, 777 m, 744 m, 707 s, 698 s cm^{-1} (CCl_4 and CS_2).

Cyclooctatetraenediruthenium pentacarbonyl (II)

A solution of $Ru_3(CO)_{12}$ (1.0 g, 1.56 mmoles) and cyclooctatetraene (8.0 g, 77 mmoles) in xylene (20 ml) was heated under reflux for 4 h, the progress of the reaction being followed by IR spectroscopy. The reaction mixture was allowed to cool to room temperature, and unreacted $Ru_3(CO)_{12}$ which separated was removed by filtration. Evaporation of solvent *in vacuo* led to the crystallisation of an orange material, which was recrystallised from hexane/methylene chloride to give orange cyclooctatetraenediruthenium pentacarbonyl (II) (0.42 g, 60%). On heating the complex decomposed at ~160° in air, but in an evacuated sealed tube, it melts sharply at 224–225°.

IR spectrum: ν(CO), 2038 s, 2011 s, 1972 s, 1822 m cm^{-1} (cyclohexane).

Cyclooctatetraenediruthenium hexacarbonyl (III)

The xylene mother liquors from the above reaction were chromatographed on a column of Florisil, and elution with hexane gave a yellow band. Evaporation and recrystallisation of the residue from hexane gave pale yellow cyclooctatetraenediruthenium hexacarbonyl (III) (0.22 g, 30%).

IR spectrum: ν(CO), 2080 s, 2048 s, 2012 s, 2008 (sh), 1989 m cm^{-1} (cyclohexane).

Reaction of (I) with 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane

4-Ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane (0.06 g, 0.37 mmole) and (I) (0.05 g, 0.17 mmole) were refluxed together in cyclohexane for 1.5 h, during which time complete reaction occurred, as determined by IR spectroscopy. On cooling, the product crystallised as a pale yellow solid, which on recrystallisation from hexane/methylene chloride gave bis(4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane)-ruthenium tricarbonyl (IV) (0.08 g, 98%).

IR spectrum: ν(CO), 1941 cm^{-1} (cyclohexane).

A similar reaction using triphenylphosphine gave an essentially quantitative yield of $(Ph_3P)_2Ru(CO)_3$, identified by analysis (Table 1) and its infrared spectrum [ν(CO), 1895; lit.[15] 1895 cm^{-1}].

Reaction of (I) with iodine

A solution of iodine (0.04 g, 0.34 mmole) in hexane (2 ml) was added to (I) (0.05 g, 0.17 mmole) in the same solvent (2 ml). The pale yellow solid which immediately formed was filtered off and recrystallised from hexane/methylene chloride to give $[Ru(CO)_3I_2]_2$ (0.06 g, 92%).

IR spectrum: ν(CO), 2125 s, 2067 s cm^{-1} (cyclohexane). Lit.[18] values, 2128 s, 2069 s, 2012 w (br) cm^{-1} (CCl_4).

Reaction of mercury(II) bromide with (I)

A solution of (I) (0.06 g, 0.21 mmole) in methyl ethyl ketone/benzene (30:70 v/v) (1 ml) was added to mercury(II) bromide (0.06 g, 0.17 mmole) in the same solvent (3 ml), when an immediate reaction occurred to give a yellow precipitate. This was filtered off, washed with methyl ethyl ketone, and dried to give complex (VI) (0.11 g, 98%) as an insoluble material.

The same procedure was followed in the reactions of (I) with mercury(II) chloride and thiocyanate, to obtain complexes (V) and (VII) in essentially quantitative yield.

IR spectra: ν(CO) (V), 2113 m, 2050 s, 2008 s; (VI), 2110 m, 2055 s, 2010 s; (VII), 2111 m, 2057 s, 2013s cm^{-1} (KBr disc).

Reaction of (V) or (VI) with pyridine

Pyridine (2 ml) was added dropwise to a stirred suspension of (V) or (VI) (0.1 mmole) in methylene chloride, when a clear solution was obtained. Removal of solvent *in vacuo* and recrystallisation of the white crystalline residue from hexane/methylene chloride gave quantitative yields of the complexes (VIII) or (IX).

IR spectra: ν(CO) (VIII), 2123 m, 2048 s, 2013 m; (IX), 2120 m, 2051 s, 2014 m cm^{-1} (cyclohexane).

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