# Reactivity of Co-ordinated Ligands. Part XXVI.[1] Some Substitution Reactions of Tricarbonyl($\eta$-cyclo-octa-1,5-diene)ruthenium †

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Tricarbonyl($\eta$-cyclo-octa-1,5-diene)ruthenium is a useful precursor in the preparation of a wide range of [(olefin)$Ru(CO)_3$] complexes. Thus reaction with olefin (olefin = cyclohexa-1,3-diene, cyclo-octatetraene, cyclo-octa-1,3,6-triene, cyclohepta-2,4,6-trien-1-one, cyclohepta-1,3-diene, or cycloheptatriene) in benzene under reflux gives moderate to good yields of the appropriate [(olefin)$Ru(CO)_3$] complex.

A PROBLEM often encountered in the preparation of organometallic complexes is the availability of convenient starting materials. This has proved to be a particular problem in the synthesis of organometallic derivatives of the $Ru(CO)_3$ unit. Thus, although the reaction of olefins with dodecacarbonyltriruthenium can produce monomeric species containing an $Ru(CO)_3$ unit, in general such reactions proceed with the formation of polymeric materials based on $Ru_3$ and $Ru_4$ units. However, in the course of our studies of the reactivity of cyclic dienes bonded to $M(CO)_3$ moieties we prepared the complex tricarbonyl($\eta$-cyclo-octa-1,5-diene)ruthenium, (I).[1] We now report some displacement reactions of (I) which offer a convenient route to a number of monomeric tricarbonylruthenium complexes of cyclohexa-1,3-diene, cyclo-octatetraene, bicyclo[4.2.0]octa-2,4-diene, bicyclo[3.2.1]octa-2,6-diene, cyclohepta-2,4,6-trien-1-one, cyclohepta-1,3-diene, and cycloheptatriene. Certain of these derivatives have not been reported previously. A brief summary of this work has been given.[2]

## RESULTS AND DISCUSSION

The [(diene)$Ru(CO)_3$] complexes which have been prepared by displacement of cyclo-octa-1,5-diene (cod) from (I) are presented in the Scheme. Some of these are new; others, *e.g.* complexes (II) [3] and (III),[4-7] have been prepared by alternative methods, but the displacement method described here offers the advantages of high yields and since reaction times are short (*ca.* 0.5 h) decomposition to polymeric materials is minimised leading to ease of purification.

*Tricarbonyl($\eta$-cyclohexa-1,3-diene)ruthenium,* (II).—Cyclohexa-1,3-diene (chd) readily displaced cod from complex (I) in benzene under reflux to yield tricarbonyl($\eta$-cyclohexa-1,3-diene)ruthenium, (II), as the only organometallic product. The spectroscopic properties of (II) are identical to those reported previously.[8] In the corresponding displacement reaction with cyclohexa-1,4-diene no tricarbonyl($\eta$-cyclohexa-1,4-diene)ruthenium was detected and the reaction again yielded (II). Surprisingly, although the co-ordinated diene has been isomerised, separation of the reaction mixture by g.l.c. revealed that only *ca.* 0.5% of the 100-fold excess of the cyclohexa-1,4-diene employed was isomerised to the conjugated form. Longer reaction times (*ca.* 0.5 h) did not lead to increased amounts of (II) indicating that this complex resists substitution by cyclohexa-1,4-diene. The isomerisation of the initially formed tricarbonyl($\eta$-cyclohexa-1,4-diene)ruthenium presumably takes place by the now generally accepted hydride-transfer mechanism. Unlike our observations with the carbonyl($\eta$-cycloheptadiene)($\eta$-cyclohexadiene)iron species,[9] no spectroscopic evidence for the intermediate 1,4-diene derivative was obtained.

*Tricarbonyl($\eta$-cyclo-octatetraene)ruthenium,* (III).—This complex has been reported previously by several groups of workers.[4,6,7] The reaction of cyclo-octatetraene (cot) with complex (I) led to the formation of [(cot)$Ru(CO)_3$], (III). In contrast to the methods previously employed, complex (III) was formed in *ca.* 100% yield and [(cot)$Ru_2(CO)_5$], [(cot)$Ru_2(CO)_6$], and [$(cot)_2Ru_3(CO)_4$] which are the major products of the other methods [4,6,7] were not detected. Over longer reaction times a complex of empirical formula $C_{16}H_{16}Ru(CO)_3$ is produced. On the basis of its i.r., mass, and $^1H$ n.m.r. spectra this complex is assigned the tricarbonyl(12—13:14—15-$\eta$-tetracyclo[$8.6.0.0^{2,9}.0^{11,16}$]hexadeca-4,6,12,14-tetraene)ruthenium, structure (IV) (Scheme). Thus the i.r. spectrum exhibited bands at 2 060, 1 994, and 1 984 $cm^{-1}$ consistent with the presence of a $Ru(CO)_3$ unit within the molecule. This is supported by the mass spectrum which contained peaks corresponding to the molecular ion [$(H_{16}C_{16})Ru(CO)_3$]$^+$ and peaks resulting from successive loss of three CO groups, [$(C_{16}H_{16})Ru(CO)_n$]$^+$ ($n = 0$—2). Other peaks in the spectrum correspond to [$(H_{10}C_{10})Ru(CO)$]$^+$ and [$(H_{10}C_{10})Ru$]$^+$. The $^1H$ n.m.r. spectrum in $C_6D_6$ showed the following

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† No reprints available.

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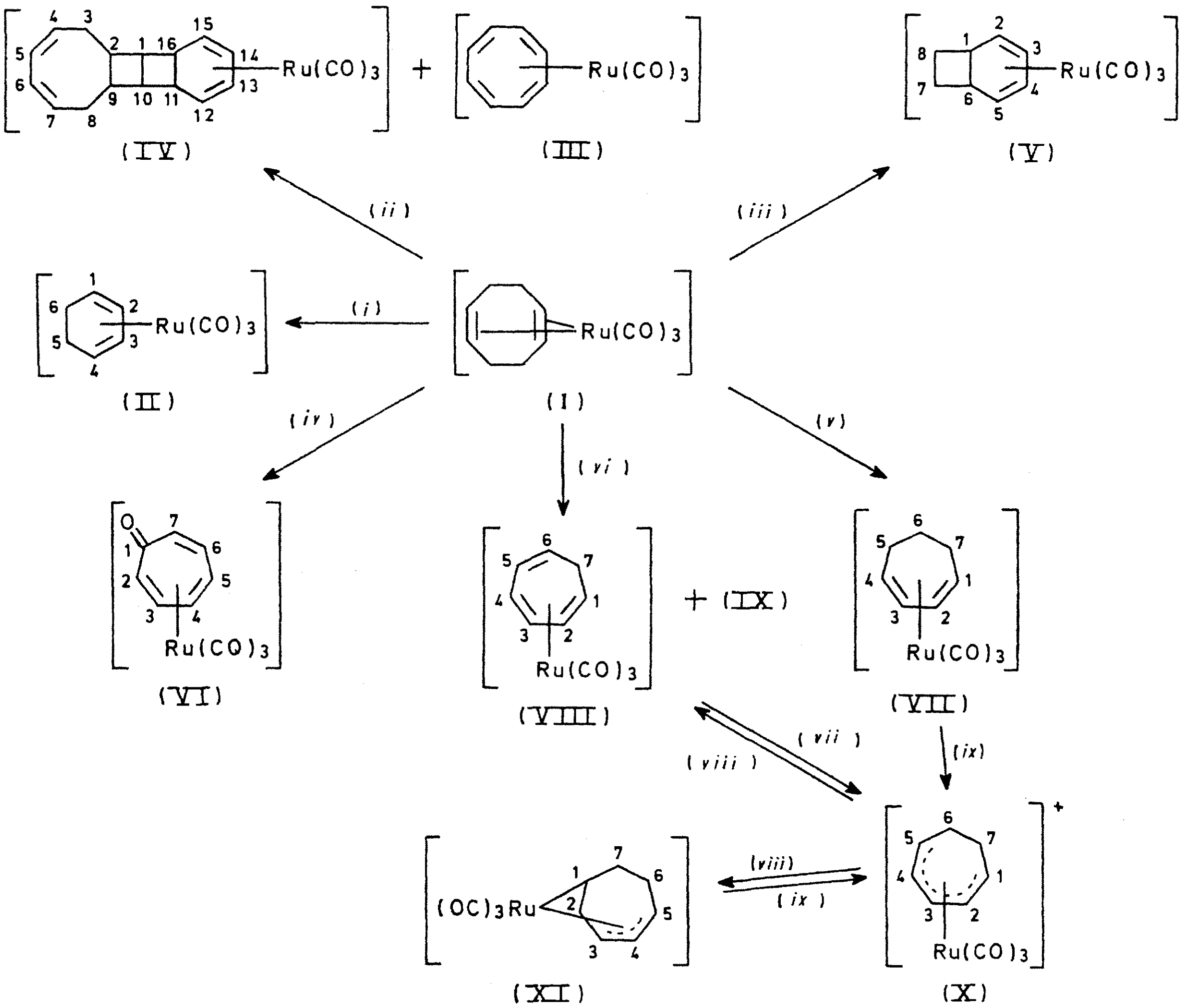
absorptions: $\tau$ 4.2—4.8 (m), corresponding to the six olefinic protons $H^3$ to $H^8$ (see Scheme); 4.95 (doublet of doublets), assigned to the ' inner ' olefinic protons $H^{13}$ and $H^{14}$; 7.27 and 7.40 (overlapping multiplets), assignable to protons $H^2$, $H^9$, $H^{11}$, and $H^{16}$; and finally a multiplet at 8.54 corresponding to protons $H^{10}$ and $H^{17}$. On irradiation of $H^{12}$ and $H^{15}$ the doublet of doublets at $\tau$ 4.95 collapsed to a singlet and on irradiation of $H^{13}$ and $H^{14}$ the multiplet at $\tau$ 6.89 also collapsed to a singlet. These data closely resemble those observed with the iron analogue which has been fully established by single-crystal *X*-ray analysis.[10–12]



SCHEME (*i*), 1,3- or 1,4-chd; (*ii*), cot; (*iii*), 1,3,5-$C_8H_{10}$; (*iv*), chto; (*v*), 1,3-$C_7H_{10}$; (*vi*), $C_7H_8$; (*vii*), $HPF_6$; (*viii*), $Na[BH_4]$; (*ix*), $[Ph_3C][BF_4]$.

(*η-Bicyclo*[4.2.0]*octa*-2,4-*diene*)*tricarbonylruthenium*, (V).—Of the three isomers cyclo-octa-1,3,6-triene, cyclo-octa-1,3,5-triene, and bicyclo[4.2.0]octa-2,4-diene the first is the least and the third the most thermodynamically stable. Thermal or photochemical reactions of iron pentacarbonyl with cyclo-octa-1,3,5-triene give only the (η-bicyclo[4.2.0]octa-2,4-diene)tricarbonyliron complex.[13–16] In the reaction of the same triene with dodecacarbonyltri-iron the less stable isomer tricarbonyl-(η-cyclo-octa-1,3,5-triene)iron is produced.[13,14,16]

In the reaction of (I) with cyclo-octa-1,3,5-triene over a range of experimental conditions the sole organometallic product was (η-bicyclo[4.2.0]octa-2,4-diene)-(tricarbonyl)ruthenium, (V). This complex, which is obtained as a colourless oil, has been reported previously[17a] as a product of the reaction of either $Ru_3(CO)_{12}$ or $[Ru(SiMe_3)_2(CO)_4]$ with the $C_8H_{10}$ mixture.

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The $^1$H n.m.r. spectrum in $C_6D_6$ consisted of the following absorptions (Scheme): $\tau$ 4.96 (doublets of doublets), assigned to the 'inner' diene protons $H^3$ and $H^4$; 6.87, which corresponds to the 'outer' diene protons $H^2$ and $H^5$; 7.71, assignable to the bridge protons $H^1$ and $H^6$; and finally 8.35 and 9.05, which correspond to the methylene protons 2 $H^7$ and 2 $H^8$. These assignments were based on double-irradiation experiments. Thus the doublet of doublets at $\tau$ 4.96 became a singlet on irradiation of $H^2$ and $H^5$, and the absorption corresponding to the protons $H^2$ and $H^5$ changed to a doublet or a simplified multiplet on irradiation of $H^3$ and $H^4$ and $H^1$ and $H^6$ respectively. Finally the multiplet $H^1$ and $H^6$ changed on irradiation at $H^2$ and $H^5$. These data compare closely to those reported for ($\eta$-bicyclo[4.2.0]-octa-2,4-diene)tricarbonyliron [17b] and its ruthenium analogue.[17a]

*Tricarbonyl*($\eta$-*cyclohepta*-2,4,6-*trien*-1-*one*)*ruthenium*, (VI).—This complex was obtained as an orange oil by a similar route and is moderately stable under nitrogen. Again, as expected, the spectroscopic data for the complex are very similar to those of the corresponding iron complex.[18] In the i.r. spectrum three sharp metal–carbonyl bands were observed at 2 081, 2 022, and 2 005 cm$^{-1}$ and a ketonic C–O stretching vibration appeared at 1 637 cm$^{-1}$; this is very similar to the value in cyclohepta-2,4,6-trien-1-one (chto) (1 638 cm$^{-1}$) and indicates that the $Ru(CO)_3$ unit has little effect on the ketonic group. The $^1$H n.m.r. spectrum of (VI) in $C_6D_6$ was as predicted with absorptions at: $\tau$ 3.99 (doublet of doublets) ($H^6$); 4.74 (m) ($H^3 + H^4$); 5.04 (doublet of multiplets) ($H^7$); 6.77 (doublet of triplets) ($H^2$); and 8.01 (m) ($H^5$). These assignments were confirmed by double-irradiation experiments. Thus on irradiation of $H^2$ the multiplet at $\tau$ 4.74 was simplified and the $H^7$ absorption changed to a sharp singlet; on irradiation of $H^5$ the absorptions of $H^6$, $H^5$ and $H^4$, and $H^7$ changed respectively to a doublet, a simplified multiplet, and a doublet of doublets, and on irradiation of $H^3$ and $H^4$ the $\tau$ 6.77 absorption become a doublet ($J$ 2 Hz) and that at $\tau$ 8.01 (m) ($H^5$) also changed to a doublet ($J$ 8 Hz).

*Tricarbonyl*($\eta$-*cyclohepta*-1,3-*diene*)*ruthenium*, (VII).—Prepared in the same way as the complexes reported above, this complex is very similar to its iron analogue.[19,20] Characterisation rests largely on the $^1$H n.m.r. and i.r. spectroscopic data. Thus in the $^1$H n.m.r. spectrum resonances were observed at: $\tau$ 5.14 (doublet of doublets), corresponding to the 'inner' diene protons $H^2$ and $H^5$; 7.22 (m), corresponding to the 'outer' protons $H^1$ and $H^4$; and 8.36 (m) and 8.82 (m), corresponding to the two sets of methylene protons 2 $H^5$ + 2 $H^7$ and 2 $H^6$. This assignment was based on double-irradiation experiments. Irradiation of $H^2$ and $H^3$ led to simplification of the multiplet $H^1 + H^4$ to a triplet ($J$ 4 Hz); on irradiation of $H^1 + H^4$ the doublet of doublets at $\tau$ 5.14 ($H^2 + H^3$) became a sharp singlet and the multiplet at $\tau$ 8.36 simplified, no change being observed in the multiplet at $\tau$ 8.82. In the i.r. spectrum the three carbonyl bands anticipated for the $Ru(CO)_3$ unit were observed at 2 059, 1 988, and 1 984 cm$^{-1}$.

*Tricarbonyl*($\eta$-*cycloheptatriene*)*ruthenium*, (VIII).—The reaction of (I) with cycloheptatriene was more complicated than the other reactions described above. In this case two products, tricarbonyl($\eta$-cycloheptatriene)-ruthenium, (VIII), and an unknown complex, (IX), were obtained. All attempts to obtain pure samples of (IX) failed since it is extremely unstable and decomposed on t.l.c. separation. The i.r. spectrum of the mixture of products showed the presence of five carbonyl bands. Three of these (2 063, 1 998, and 1 987 cm$^{-1}$) were clearly associated with complex (VIII) and the other two (2 012 and 1 954 cm$^{-1}$) were assigned to (IX). The structure of (VIII) was readily established from spectroscopic evidence. The i.r. spectra in the carbonyl region (see above) exhibited the expected three bands and the mass spectrum, which is similar to $[(H_7C_7)Fe(CO)_3]$,[21] exhibited peaks corresponding to the ions $[(H_7C_7)Ru(CO)_n]^+$ ($n$ = 0—2). In addition some peaks were observed at higher mass numbers. Although the peaks were not identified it is assumed that they arise from thermal decomposition of (VIII) in the ion source. The n.m.r. spectrum of (VIII) showed the following features: $\tau$ 4.30 (m) ($H^5$), 5.18 (m) ($H^2 + H^3 + H^6$); 7.04—7.38 (complex multiplet) ($H^1 + H^4$); and 8.13 (m) (2 $H^7$). This spectrum is very similar to that observed for $[(H_8C_7)Fe(CO)_3]$ [19] and was assigned accordingly. Characterisation of the salt (X) obtained on protonation of (VIII) with $HPF_6$ provided further confirmation of the formulation of this complex (see below).

*Some Reactions of Complex* (VIII).—Addition of $HPF_6$ to a solution of (VIII) in $Et_2O$ produced white crystals of tricarbonyl(1—5-$\eta$-cycloheptadienylium)ruthenium hexafluorophosphate, (X). The i.r. spectrum of this salt in $CH_2Cl_2$ exhibited a sharp band at 2 128 cm$^{-1}$ and a broad band at 2 071 cm$^{-1}$ with a shoulder at 2 083 cm$^{-1}$ corresponding to the CO absorptions of a $Ru(CO)_3$ unit in a cationic complex. Its $^1$H n.m.r. spectrum in liquid $SO_2$ consisted of the following absorptions: $\tau$ 3.14 (triplet of triplets) ($H^3$); 3.87 (doublets of doublets) ($H^2 + H^4$); 4.91 (m) ($H^1 + H^5$); and 7.42 (m) and 7.89 (m) (2 $H^6$ + 2 $H^7$). This spectrum, apart from small differences in the chemical shifts, is identical to that of the iron analogue $[(H_9C_7)Fe(CO)_3][PF_6]$.[20,22]

The same cation was obtained as its tetrafluoroborate salt when (VII) was treated with $[Ph_3C][BF_4]$ in $CH_2Cl_2$. Reduction of (X) with $Na[BH_4]$ in water led to the formation of a mixture of (VII) and its isomer tricarbonyl-(1-$\sigma$,3—5-$\eta$-cycloheptenediyl)ruthenium, (XI), in the ratio 1 : 3 as determined by $^1$H n.m.r. spectroscopy. No method of separation of these isomers was found and

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they were characterised as the components of the mixture. No evidence was found for the 1,4-isomer corresponding to nucleophilic attack at C$^3$ of the dienyl system as has been observed with the system $[(H_9C_7)Fe(CO)(C_6H_8)]^+$. Isomer (XI) was identified on the basis of its $^1$H n.m.r. spectrum which was obtained by subtraction of resonances due to (VII) and exhibited the following features: $\tau$ 5.51 (m) (H$^5$); 5.94—6.21 (m) (H$^3$ + H$^4$); 7.45—7.59 (m) (2H$^2$); 7.99—8.45 (m) (2 H$^6$ + 2 H$^7$); and 8.87 (m) (H$^1$). Again this assignment was fully supported by double-irradiation experiments.

The production of both the $\sigma,\eta$-allyl complex (75%) and the 1,3-diene complex in the reaction of (X) with $Na[BH_4]$ is another example of a commonly emerging feature of nucleophilic addition to cationic dienyl complexes of Fe, Ru, and Os. Apart from $[(H_9C_7)Fe(CO)(C_6H_8)]^+$, the mechanism of attack is unknown, but as with this Fe system attack may initially occur at the C$^3$ atom followed by rearrangement to yield the 1- and 2-substituted derivatives. Attack by $[Ph_3C][BF_4]$ on the $\sigma,\eta$-allyl derivative is specific yielding only complex (X).

*Conclusions.*— Tricarbonyl($\eta$-cyclo-octa-1,5-diene)ruthenium has been shown to be an extremely versatile and useful reagent for the preparation of $Ru(CO)_3$ derivatives, many of which are inaccessible or obtained in low yields by the commonly adopted route of direct reaction of diene with $Ru_3(CO)_{12}$.

## EXPERIMENTAL

Tricarbonyl($\eta$-cyclo-octa-1,5-diene)ruthenium, (I), was prepared by the method described previously.[1] Cyclo-octa-1,3,5-triene was prepared by the reduction of cyclo-octatetraene with zinc in ethanol. Column chromatographies were monitored by i.r. spectroscopy as the eluate was allowed to pass through an i.r. cell. All reactions and purifications were carried out under purified nitrogen. Analytical data are presented in the Table.

*Ligand-displacement Reactions.*—Complex (I) was treated with the appropriate diene in benzene under reflux. The solvent and remaining unco-ordinated diene were removed by distillation *in vacuo* and the complexes purified by chromatography followed by sublimation.

*Protonation of Tricarbonyl($\eta$-cyclohepta-*1,3,5-*triene)ruthenium,* (VIII).—Hexafluorophosphoric acid was added dropwise to a solution of complex (VIII) (34 mg, 0.123 mmol) in diethyl ether (5 cm$^3$) until no further precipitate was formed. The precipitate was then separated by filtration with diethyl ether and crystallised from liquid sulphur dioxide to yield *tricarbonyl*(1—5-*$\eta$-cycloheptadienylium)ruthenium hexafluorophosphate,* (X) (36 mg, 0.085 mmol, 69%), as air-stable white crystals (Found: C, 28.3; H, 2.3. Calc. for $C_{10}H_9F_6O_3PRu$: C, 28.4; H, 2.1%).

Analytical data (%) for complexes

| | Analyses | | | | |
|---|---|---|---|---|---|
| | Found | | Calc. | | |
| Complex | C | H | C | H | Yield |
| (IV) | 58.0 | 4.1 | 58.0 | 4.1 | 54 |
| (V) | 45.2 | 3.4 | 45.4 | 3.5 | 42 |
| (VI) | 41.1 | 2.4 | 41.1 | 2.1 | 26 |
| (VII) | 42.9 | 3.7 | 43.0 | 3.6 | 75 |

*Reaction of Tricarbonyl($\eta$-cyclohepta-*1,3-*diene)ruthenium,* (VII), with $[Ph_3C][BF_4]$.—Solutions of complex (VII) (60 mg, 0.215 mmol in 1 cm$^3$) in $CH_2Cl_2$ and $[Ph_3C][BF_4]$ (83 mg, 0.25 mmol in 2 cm$^3$) in the same solvent were mixed and shaken for 30 min. Addition of $Et_2O$ precipitated white crystals. After hydrolysis of any remaining $[Ph_3C][BF_4]$ by exposure to air the product was separated by filtration and recrystallised from liquid sulphur dioxide. The product, the $[BF_4]^-$ salt of (X) (74 mg, 0.203 mmol, 95%), was obtained as air-stable white crystals The similar reaction of a mixture of (VII) and tricarbonyl-(1-$\sigma$,3—5-$\eta$-cycloheptenediyl)ruthenium, (XI), gave the same salt in 96% yield.

*Reduction of Complex* (X) *with* $Na[BH_4]$.—An aqueous solution of the $[PF_6]^-$ salt (159 mg, 0.436 mmol) and excess of $Na[BH_4]$ (500 mg, 13.3 mmol) were mixed and stirred for 10 min. The products were extracted into diethyl ether, the so-formed solution dried over $Mg[SO_4]$, and the ether then removed *in vacuo.* The oil obtained by this method was dissolved in pentane and passed down a silica column when separation into two components occurred. After elution in pentane, the solvent was removed and the product distilled at −20 °C *in vacuo* to yield a mixture of the two isomers (XI) (75%) and (VII) (25%) as a colourless oil (76 mg, 0.272 mmol, 63%).

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