A New Synthetic Method for the Preparation of Cyclo-olefin Ruthenium Complexes

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Hydrated ruthenium trichloride reacts with cyclohexa-1,3-diene and cyclo-octa-1,5-diene, in the presence of metallic zinc, to give the ruthenium(0) compounds 1—6-η-benzene(1—4-η-cyclohexa-1,3-diene)ruthenium, (1), and (1—2 : 5—6-η-cyclo-octa-1,5-dinee)(1—6-η-cyclo-octa-1,3,5-triene)ruthenium, (2), respectively. The analogous reaction with cyclo-octa-1,3-diene, cyclohepta-1,3-diene, and cyclopentadiene leads to the isolation of the corresponding dienyl complexes bis(1—5-η-cyclo-octadienyl)ruthenium, (3), bis(1—5-η-cycloheptadienyl)-ruthenium, (4), and ruthenocene, (5). Complex (3) is best prepared by heating (2) in hydrocarbon solvents at *ca.* 100 °C.

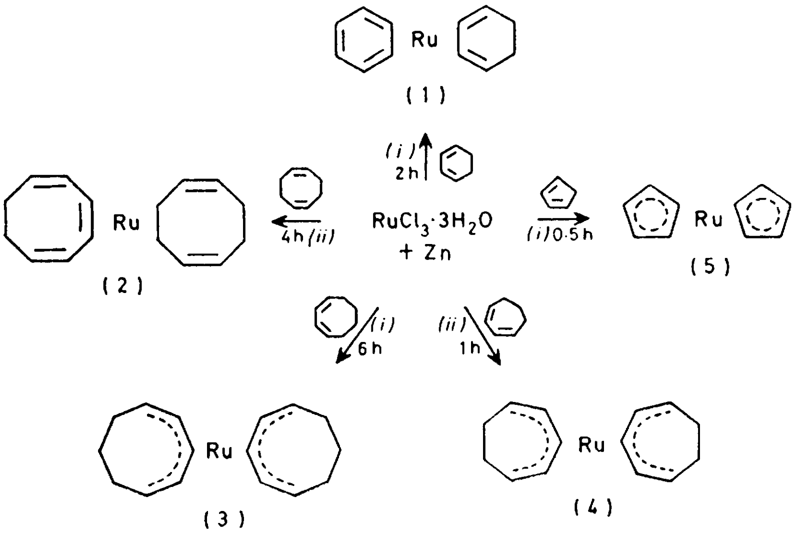
CYCLO-OLEFIN complexes of metals in the iron triad have received a good deal of attention in recent years as potential catalysts,[1] as models for oxidative-addition reactions,[2] as a means of studying electrophilic and/or nucleophilic attack on co-ordinated organic molecules,[3] and, most recently, as examples of highly fluxional compounds.[4] In general, however, the availability of convenient synthetic routes to such species, particularly to those not containing carbon monoxide, has proved to be a particular problem.

We report that the direct reaction of cyclo-olefins with $RuCl_3{\cdot}3H_2O$, in the presence of metallic zinc, seems to be an extremely versatile and useful reaction for the preparation of cyclo-olefin ruthenium complexes, many of which are inaccessible or obtained with great difficulty by classical methods.[5] A summary of this work has been given.[6]

RESULTS AND DISCUSSION

Hydrated ruthenium trichloride reacts with a variety of cyclodiolefins, in the presence of metallic zinc, to give cyclo-olefin–ruthenium(0) or cyclodienyl–ruthenium(II) compounds. Some examples are given in Scheme 1.

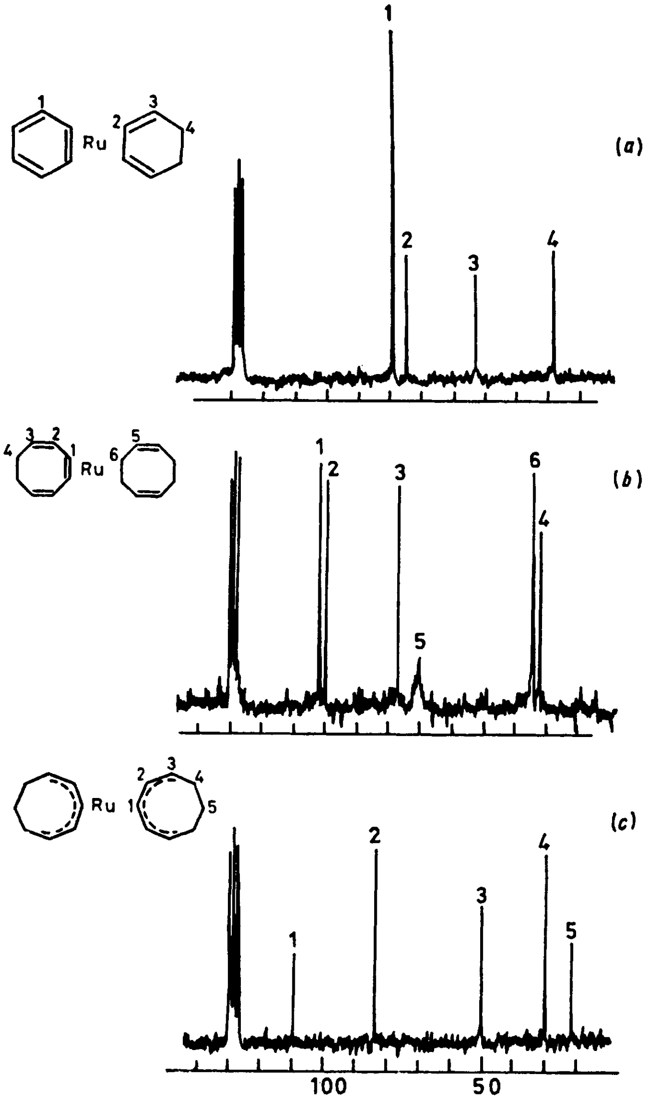
By treatment at room temperature of cyclohexa-1,3-diene with hydrated ruthenium trichloride and zinc, in tetrahydrofuran (thf) or ethanol as solvent, (1—6-η-benzene)(1—4-η-cyclohexa-1,3-diene)ruthenium, (1), has been obtained with yields of *ca.* 80%. The corresponding reaction with cyclohexa-1,4-diene, again yielded (1), with isomerization of cyclohexa-1,4-diene to the conjugated form (*ca.* 40%). The compound has been characterized by elemental analysis, spectroscopic properties, and comparison of the i.r. and ^1H n.m.r. spectra with those of an authentic sample.[5b]



SCHEME 1 (*i*) EtOH or thf, 20 °C; (*ii*) EtOH or thf, reflux

The ^{13}C n.m.r. spectrum is presented in part (*a*) of the Figure. Signals are observed at 79.5 (C^1), 75.2 (C^2), 53.3 (C^3), and 28.1 (C^4) p.p.m. Those due to the arene carbons directly bonded to the metal are shifted upfield with respect to the free ligand; similar phenomena have previously been noted for many arene ligands,[7,8] although cases are reported in which a shift to lower field is observed.[9] The upfield shift is 49 p.p.m. relative to benzene, close to the value reported for the full-sandwich compound bis(1—6-η-benzene)chromium (53.9 p.p.m.).[8] The cause of these high-field co-ordination shifts is still not fully understood and is currently the subject of much discussion.[10]

The (1—2:5—6-η-cyclo-octa-1,5-diene)(1—6-η-cyclo-octa-1,3,5-triene)ruthenium complex, (2), has been obtained in consistent yields (*ca.* 50%) in the analogous reaction of cyclo-octa-1,5-diene with hydrated ruthenium trichloride and zinc. In contrast to the method previously reported [5c] this new route enabled us to prepare large amounts of (2) and to greatly extend studies of its chemistry.



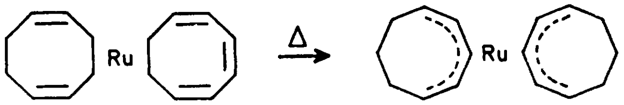
^{13}C Proton-decoupled n.m.r. spectra of: (*a*) [Ru(η^6-C_6H_6)(η^4-C_8H_8)], (1); (*b*) [Ru(η^6-C_8H_{10})(η^4-C_8H_{12})], (2); (*c*) [Ru(η^5-C_8H_{11})$_2$], (3)

During the reaction, isomerization of the cyclo-octa-1,5-diene to 1,4- (50%) and 1,3-diene (30%) occurred. Cyclo-octene (7%) was also detected in the mother-liquor. Additional experiments showed that complex (2) catalyzed a similar isomerization of the cyclo-octa-1,5-diene to 1,4- and 1,3-diene, at temperatures of *ca.* 80 °C and that the catalyst itself was converted to the bis(1—5-η-cyclo-octadienyl)ruthenium complex, (3).

The ^{13}C n.m.r. spectrum of (2) [Figure (*b*)] had signals at 101.4 (C^1), 99.3 (C^2), 76.7 (C^3), 70.1 (C^5), and at 33.0 (C^4) and 31.6 (C^6) p.p.m. in the region characteristic of ring methylene carbons. The resonances noted were in agreement with the ^{13}C n.m.r. data reported for similar cyclo-octa-1,5-diene and cyclo-octa-1,3,5-triene metal complexes.[11]

Complex (2) can be prepared in a similar way to that above by treating [{$RuCl_2$(η^4-cyclo-octa-1,5-diene)}$_n$] with cyclo-octa-1,5-diene, in the presence of ethanol and zinc, with a yield of *ca.* 20%.

Unlike cyclo-octa-1,5-diene, cyclo-octa-1,3-diene reacts with hydrated ruthenium trichloride and zinc to give the previously unknown dienyl complex bis(1—5-η-cyclo-octadienyl)ruthenium, (3). Complex (3) can also be obtained, in better yields, by heating complex (2) in hydrocarbon solvents at 100 °C for *ca.* 10 h (see below).



The ^{13}C n.m.r. spectrum is shown in part (*c*) of the Figure. The three different dienyl carbon-atom environments were indicated by resonances at 109, 83.9, and 49.6 p.p.m., assigned to the single central carbon, C^1, two intermediates, C^2, and two terminal carbons, C^3. The carbons C^4 and C^5 give rise to signals at 29.6 and 21.2 p.p.m., in the region characteristic of ring methylene carbons. The assignments are in agreement with those reported in the literature for cyclodienyl transition-metal complexes.[12]

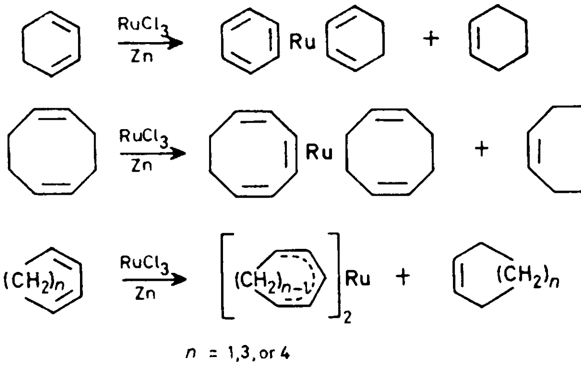
The ^1H n.m.r. spectrum in C_6D_6 showed the following absorptions: τ 4.42 (triplet), corresponding to the protons H^1; 6.16 (doublet of doublets), assigned to the protons H^2; 6.45 (multiplet), corresponding to the protons H^3; and 7.45—8.95 (overlapping multiplets), assignable to the protons H^4 and H^5.

Complex (3) has also been obtained, as a by-product, in the preparation of complex (2), using a longer reaction time, and has been separated by chromatography on alumina. It seems reasonable to assume that isomerization of (2) to (3), as reported previously, probably occurs under these experimental conditions.

Cyclohepta-1,3-diene reacts in a similar manner to cyclo-octa-1,3-diene in the presence of ruthenium trichloride and zinc, under reflux, giving the corresponding dienyl complex bis(1—5-η-cycloheptadienyl)ruthenium, (4), in yields of *ca.* 50%. Unchanged cyclohepta-1,3-diene (80%) and cycloheptene (20%) were detected in the mother-liquor. The spectroscopic properties of (4) were identical to those of an authentic sample.[5d]

Using cyclopentadiene as the cyclodiolefin, bis(1—5-η-cyclopentadienyl)ruthenium (ruthenocene) (5), was obtained. The complex has been identified by comparing the i.r. and n.m.r. spectra with those of an authentic sample.[13] Relative to the methods previously employed, this new route allowed the formation of ruthenocene under very mild conditions (room temperature, 0.5 h), with yields of *ca.* 80%, a most convenient synthesis of such a complex.

The mechanism by which the cyclo-olefin complexes (1)—(5) are formed in the reaction of ruthenium trichloride with cyclodiolefin and zinc is probably complicated. The formation of complexes containing trienyl or dienyl ligands bonded to the metal and the presence of a monoene in the mother-liquor of the reaction seems consistent with a disproportionation reaction of the starting diene, as shown in Scheme 2.



SCHEME 2

The absence of acetaldehyde or its diethyl acetal as by-product, using ethanol as solvent, suggests that there is no solvent participation in the reaction and that the cyclodiene disproportionation and/or isomerization takes place by hydride abstraction directly from the ligand.[14]

In the preparation of complexes (2) and (4), under reflux it has been observed that the amount of monoene in the reaction mixture is substantially larger than that expected from diene disproportionation. This suggests that hydrogenation occurs as a side reaction. In the presence of water, hydrolysis of zinc dichloride to give hydrochloric acid and subsequent reaction with metallic zinc in excess could occur, yielding hydrogen, as observed in the analogous reactions of nickel chloride and cobalt chloride with diolefins and zinc.[15]

EXPERIMENTAL

All the reactions described here were carried out under a dry oxygen-free nitrogen atmosphere, using conventional Schlenk-tube techniques.

Hydrated $RuCl_3$ (Fluka), zinc dust (C. Erba), and alumina (Merck, Brockman activity II—III) were used without further treatments.

Solvents were purified by conventional methods, distilled, and stored under nitrogen. Cyclodiolefins (Fluka) were distilled prior to use. Cyclopentadiene and cyclohepta-1,3-diene were prepared as described in the literature.[16,17]

Hydrogen-1 n.m.r. spectra were obtained with a Varian T-60 spectrometer. Carbon-13 n.m.r. spectra were recorded on a Bruker WH 90 spectrometer at 22.63 MHz, a 20° pulse was applied in broad-band decoupled mode, accumulation was made on 16 K memory, chemical shift δ is referred to $SiMe_4$.

Infrared spectra (KBr discs) were performed on a Perkin-Elmer 225 and the mass spectra on a Varian MAT CH7 spectrometer. G.l.c. analyses were carried out with a Perkin-Elmer F30, using a 2-m column packed with 8% Carbowax 20 M and 2% K[OH] on Chromosorb W (80—100 mesh). Melting or decomposition points (uncorrected) were measured with a Kofler hot-stage apparatus. Microanalyses were performed by the Laboratorio di Microanalisi, Istituto di Chimica Organica, Facoltà di Farmacia, Università di Pisa.

Preparations.— *(1—6-η-Benzene)(1—4-η-cyclohexa-*1,3-*diene)ruthenium*, (1). Cyclohexa-1,3-diene (4.2 g, 52 mmol) and zinc dust (2.5 g) were added to a solution of $RuCl_3\cdot3H_2O$ (320 mg, 1.24 mmol) in ethanol (5 cm^3). The mixture was stirred for 3 h at room temperature, the resulting yellow-brown solution was filtered, and the solvent completely evaporated under reduced pressure. To the solid residue n-pentane (70 cm^3) was added and the yellow solution obtained was filtered through a column of alumina (20 cm). Reduction of the volume of the solvent, *in vacuo*, to *ca.* 5 cm^3 and cooling to -78 °C gave, in *ca.* 6 h, light yellow crystals of (1) (250 mg, 80%), m.p. 118—119 °C (Found: C, 56.1; H, 5.5; *M*, 260. $C_{12}H_{14}Ru$ requires C, 55.5; H, 5.4%; *M*, 260).

The ^1H n.m.r. spectrum ($[^2H_6]$acetone) showed resonances at τ 4.60 (s, 6 H), 5.25 (dd, 2 H), 6.98 (m, 2 H), and 8.61 (m, 4 H).

The reaction with cyclohexa-1,4-diene, performed in the same way, yielded 0.095 g (30%) of (1).

*(1—2: 5—6-η-Cyclo-octa-*1,5-*diene)(1—6-η-cyclo-octa-*1,3,5-*triene)ruthenium*, (2). Cyclo-octa-1,5-diene (8.8 g, 81 mmol) and zinc dust (3.5 g) were added to a solution of $RuCl_3\cdot3H_2O$ (0.34 g, 1.3 mmol) in ethanol (10 cm^3). The mixture was heated under reflux with magnetic stirring for 3 h and then filtered. The resulting yellow-brown solution was evaporated *in vacuo* until the residue was completely dry. Extraction with n-pentane (70 cm^3) gave a yellow-brown solution which was filtered through a column of alumina (20 cm). The volume of the solvent was reduced to *ca.* 5 cm^3 and the yellow solution was cooled to -78 °C to give, in 6 h, yellow crystals of (2) (0.20 g, 50%), m.p. 92—94 °C (Found: C, 59.55; H, 7.10; *M*, 316. $C_{16}H_{22}Ru$ requires C, 60.9; H, 7.00%; *M*, 316).

The ^1H n.m.r. spectrum ($[^2H_6]$benzene) showed resonances at τ 4.78 (dd, 2 H), 5.22 (m, 2 H), 6.21 (m, 2 H), 7.08 (m, 4 H), 7.78 (m, 8 H), 8.36 (m, 2 H), and 9.10 (m, 2 H).

Bis(1—5-η-cyclo-octadienyl)ruthenium, (3). (*a*) *From* $RuCl_3\cdot3H_2O$. To a solution of hydrated $RuCl_3$ (0.35 g, 1.33 mmol) in ethanol (10 cm^3), cyclo-octa-1,3-diene (8.7 g, 80 mmol) and zinc dust (3.5 g) were added. The mixture was stirred at room temperature for 6 h and then filtered. The resulting yellow-brown solution was evaporated *in vacuo* to dryness, extracted with n-pentane, and filtered through alumina, as above. The volume of the solvent was reduced to *ca.* 5 cm^3 and the solution was cooled to -78 °C to give yellow crystals of (3) (0.042 g, 10%), m.p. 89—90 °C (Found: C, 60.7; H, 7.15; *M*, 316. $C_{16}H_{22}Ru$ requires C, 60.9; H, 7.00%; *M*, 316).

The ^1H n.m.r. spectrum ($[^2H_6]$benzene) showed resonances at 4.42 (t, 2 H), 6.15 (dd, 4 H), 6.45 (m, 4 H), and 7.49—8.95 (m, 12 H).

(*b*) *From* (1—2 : 5—6-η-cyclo-octa-1,5-diene)(1—6-η-*cyclo-octa*-1,3,5-*triene*)*ruthenium*. A solution of (1—2 : 5—6-η-*cyclo-octa*-1,5-*diene*)(1—6-η-cyclo-octa-1,3,5-triene)ruthenium (0.15 g, 0.48 mmol) in toluene (10 cm^3) was heated under reflux with magnetic stirring, for 10 h. The solvent was evaporated *in vacuo* and the yellow residue was dissolved in n-pentane (10 cm^3). From this solution, kept at -78 °C for 6 h, bis(1—5-η-cyclo-octadienyl)ruthenium was obtained with almost quantitative yield.

Bis(1—5-η-*cycloheptadienyl*)*ruthenium*, (4). Cyclohepta-1,3-diene (8.7 g, 92.5 mmol) and zinc dust (4 g) were added to a solution of hydrated RuCl$_3$ (0.60 g, 2.3 mmol) in ethanol (10 cm^3). The mixture was heated for 45 min under reflux and then filtered. The resulting yellow-brown solution was evaporated *in vacuo* to dryness, extracted with n-pentane, and filtered through alumina, as above. The yellow solution obtained, concentrated to 5 cm^3, was cooled to -78 °C to give, in 6 h, yellow crystals of bis(1—5-η-cycloheptadienyl)-ruthenium, (4) (0.33 g, 50%), m.p. 43—44 °C (Found: C, 57.95; H, 6.25; *M*, 288. C$_{14}$H$_{18}$Ru requires C, 58.55; H, 6.25%; *M*, 288). The ^{1}H n.m.r. spectra ([^{2}H$_6$]benzene) showed resonances at τ 4.97 (t, 2 H), 5.60 (dd, 4 H), 6.10 (m, 4 H), and 7.53—8.63 (bm, 8 H).

Bis(1—5-η-*cyclopentadienyl*)*ruthenium*, (5). Freshly distilled cyclopentadiene (5 cm^3) and zinc dust (2.5 g) were added to a solution of hydrated RuCl$_3$ (0.25 g, 0.95 mmol) in ethanol (5 cm^3). The mixture was stirred for 1 h at room temperature and then filtered. The resulting yellow-brown solution was handled as above. Light yellow crystals of bis(1—5-η-cyclopentadienyl)ruthenium, (5) (ruthenocene) (0.165 g, 75%), were obtained, m.p. 199—200 °C (Found: C, 52.95; H, 4.60; *M*, 232. C$_{10}$H$_{10}$Ru requires C, 52.0; H, 4.35%; *M*, 232). The ^{1}H n.m.r. spectra ([^{2}H$_6$]benzene) showed a resonance at τ 5.4 (s).

[9/1707 *Received, 24th October*, 1979]

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