LIGAND SUBSTITUTION AND NUCLEOPHILIC REACTIVITY OF TRICARBONYL(1–3:5,6-η-CYCLOOCTADIENYLIUM)RUTHENIUM CATION AND ITS DERIVATIVES

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Summary

Nucleophilic attack of triphenylphosphine on tricarbonyl(1–3:5,6-η-cycloocta-dienylium)ruthenium cation initially gives a phosphonium ion, which, during three weeks isomerizes to the dicarbonyl(4–6-η,1-σ-cyclooctenediyl)triphenylphosphineruthenium cation. (This species was also obtained by two other routes.) Nucleophilic attack on the latter of I^- gives dicarbonyl(4–6-η,1-σ-cyclooctadienylium)iodoruthenium, which with $AgPF_6$ gives the coordinatively unsaturated dicarbonyl(1–3:5,6-η-cyclooctadienylium)ruthenium cation as an intermediate. Reactions of this cation with triphenylphosphine and with hydride ion give rise, respectively, to dicarbonyl(1–3:5,6-η-cyclooctadienylium)triphenylphosphineruthenium hexafluorophosphate and the metallic hydride dicarbonyl(4–6-η,1-σ-cyclooctadienylium)hydrideruthenium.

Introduction

It is well known [1] that the cyclic dienes 1,3-cyclooctadiene (1,3-COD) and 1,5-cyclooctadiene (1,5-COD) can coordinate with iron(0) to give compounds of the type (diene)$Fe(CO)_3$. In contrast, only the diene having non-conjugated double bonds, 1,5-COD, coordinates to the $Ru(CO)_3$ unit, giving two isomeric monomers: tricarbonyl(η-cycloocta-1,5-diene)ruthenium (I) and tricarbonyl(4–6-η,1-σ-cyclooc-tenediyl)ruthenium (II). The action of the electrophilic reagent Ph_3CBF_4 on the neutral adduct (1,5-COD)$Ru(CO)_3$ produces, by hydride ion extraction, the salt (1–3:5,6-η-cyclooctadienylium)ruthenium tetrafluoroborate (III), which, on reduction with $NaBH_4$ yields exclusively the neutral adduct tricarbonyl(4–6-η,1-σ-cyclooctenediyl)ruthenium (II). This contrasts with the behaviour of the analogous cationic iron(0) compound, which on reduction yields a mixture of the two isomeric adducts, one in which the diene is coordinated via the non-conjugated double bonds chelating system and the other having a σ,η-allyl bond connecting the coordinating organic molecule to the metal. Thus it appears that the iron compounds has two sites

for the nucleophilic attack by the H^- ion, namely carbon atoms C(3) and C(5) of the ring, while in the case of ruthenium compound III nucleophilic attack is restricted to the C(5) atom of the coordinated organic molecule [1].

We have studied the reactions of the cationic compound tricarbonyl($1-3:5,6$-η-cyclooctadienylium)ruthenium tetrafluoroborate (III) with the nucleophiles PPh_3 and I^-, and the reactions of the iodo derivative, dicarbonyl($1-3:5,6$-η-cyclooctadienylium)iodoruthenium (VII), with the nucleophiles H^- and PPh_3 following pretreatment of compound VII with $AgPF_6$ which removes the iodine atom from the coordination sphere. We have examined the reactivities of these iodo derivatives and compared then with those of the corresponding iron complexes.

The reactions studied are reported in Scheme 1.

SCHEME 1
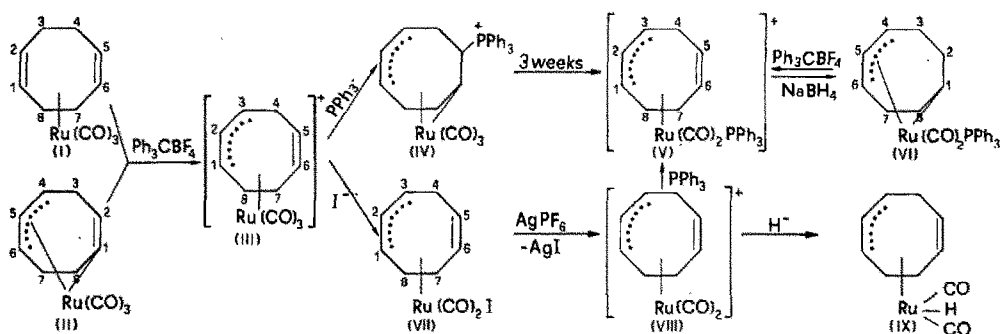
Results and discussion

Deeming et al. [1] have described the preparation of the dienylic salt III by treating the neutral adduct I with triphenylmethyl tetrafluoroborate, and this shows that the site of electrophilic attack is the C(3) carbon atom of the organic ring. In our experiments we have observed that the cationic compound III is invariably exclusively formed even when the starting compound is the neutral species II. This means that the isomeric mixture obtained by Deeming's method [1] can be treated directly with Ph_3CBF_4 without chromatographic separation of the isomers I and II. By this procedure we have been able to establish not only that the dienylic salts of iron(0) and ruthenium(0) differ in their behaviour towards H^- but that the two neutral isomeric adducts of the two metals also differ in this respect. Thus the two isomers of Ru, I and II, undergo electrophilic attack by Ph_3C^+ with hydride ion extraction, the sites attacked being the C(3) and C(5) carbon atoms of the metal-coordinated organic molecule.

Reaction of cation III and PPh_3 initially gives a compound for which we propose the phosphonium ion structure IV. In solution in dichloromethane this is transformed after three weeks into compound V. (The latter can also be obtained via a different route, as described later.) The assignment of this structure to compound IV is substantiated by IR spectral analysis, the carbonyl bands (in CH_2Cl_2) appear at ν 2075, 2000 cm^{-1}, and the corresponding bands of compound V appear at ν 2051, 2007 cm^{-1}.

The above results agree with those obtained for the reactions between PPh_3 and the cations (cyclohexadienyl)- and (cycloheptadienyl)-$Fe(CO)_3{}^+$ [2] and with those we described for the reactions of PPh_3 with (1–5-η-cyclooctadienylium)$Fe(CO)_3{}^+$ or (1–3 : 5,6-η-cyclooctadienylium)$Fe(CO)_3{}^+$ [3,4]. In every instance the compounds having a phosphonium ion structure have the carbonyl bands at a higher frequency than those having metal-coordinated phosphine; in the latter the substitution of a carbonyl by phosphine increases the electron density on the metal, raising the back-donation to the residual carbonyls, and thus lowering the carbonyl frequencies. Support for the assignment of structure V is given by the ^{1}H NMR spectrum in $CDCl_3$, which has multiplets at τ 2.0 (15), 4.2 (2), 5.7 (1), 7.2–7.5 (8) ppm.

Reduction of compound V with $NaBH_4$ yields compound VI, dicarbonyl(4–6-η,1-σ-cyclooctenediyl)triphenylphosphineruthenium cation. Its IR spectrum in C_6H_6 shows the carbonyl bands at ν 2007,1947 cm^{-1} and its mass spectrum shows a parent peak at m/e 528 and sequential loss of two carbonyls. Its ^{1}H NMR spectrum displays multiplets at τ 2.42 (15); 5.5 (2); 6.1 (1); 7.2–8.3 (9) ppm. This compound was previously obtained by direct attack of phosphine on the neutral adduct II formed by substitution of the carbonyl to the metal–carbon σ-bond [1].

In the reaction between III and NaI the metal undergoes nucleophilic attack and carbonyl is replaced by iodide ion with formation of VII, dicarbonyl(1–3 : 5,6-η-cyclooctadienylium)iodoruthenium. Its IR spectrum in dichloromethane has carbonyl bands at ν 2040 and 1990 cm^{-1}. Its mass spectrum shows a parent peak at m/e 392 and sequential loss of two carbonyls. Its ^{1}H NMR spectrum in $CDCl_3$ shows multiplets at τ 4.4 (1); 5.7 (4); 6.8 (2); 7.3–9.9 (4) ppm, as expected for coordination via the 1–3 : 5,6-η-bonding system.

The reaction between VII and $AgPF_6$ in dichloromethane and removal of the AgI gives a solution of the pentacoordinated dicarbonyl(1–3:5,6-η-cyclooctadienylium)-ruthenium cation (VIII), which has carbonyl bands 2050 and 2000 cm^{-1}.

Further reaction of VIII in CH_2Cl_2 with a stoichiometric quantity of PPh_3 gives V, the compound already obtained by direct attack of phosphine on cation III, as indicated in Scheme 1. On the other hand, reduction of compound VIII with $NaBH_4$ results in the isolation of a neutral species, denoted by IX in the scheme. Its IR spectrum in CH_2Cl_2 has carbonyl bands at 2070 and 2000 cm^{-1}. The mass spectrum shows a parent peak at m/e 266 and sequential loss of two carbonyls, which supports the proposed metal hydride structure.

Before we consider the nature of the way the metal affects the organic molecule in compounds of general formula (1–5-COD)$M(CO)_3$, M = Fe, Ru, and in their derivatives we should recall the discussions of the formal oxidation state of the metal presented in ref. 1, where the cyano derivative of the cationic complex III is regarded as an octahedral complex of ruthenium(II) with electronic configuration d^6. This follows the familiar pattern of Group VIII chemistry: in general, the tendency of d^8 complexes to form oxidized adducts of d^6 configuration increases upon descending a triad or passing from right to left within Group VIII. If it is assumed that the formal charge of ruthenium is $+2$, this accounts for the differences between the adducts of ruthenium and those of iron in the reactions investigated. In particular we have shown that the preferential site of nucleophilic attack by PPh_3 and I^- on cation III is the ruthenium atom, leading to the formation of stable compounds dicarbonyl–ligand (ligand = PPh_3, I^-) where the organic molecule is coordinated via the 1–3 : 5,6-η-bonding system. In contrast towards both nucleophiles the iron(0) com-

plex has two sites for nucleophilic attack, namely the metal and the organic nucleus in position 5 [4].

Another major difference appears when the reactions of the iodo derivatives of iron and ruthenium with $AgPF_6$ are compared. The reaction produces tricarbonyl $(1-3:5,6-\eta$-cyclooctadienylium)iron cation when the reagent is tricarbonyl$(1-3:5,6-\eta$-cyclooctadienylium)iodoiron, as inferred from IR and mass spectrometry data [4]. When the reagent is VII, the product is cation VIII, a coordinatively unsaturated species, which upon reaction with phosphine yields compound V. This species can also be obtained by (a) reaction of compound III with PPh_3 (through the intermediate IV), and (b) by abstraction of hydride ion by Ph_3CBF_4 from compound VI.

Finally, the reaction between cation VIII and $NaBH_4$ gives compound IX, which shows the characteristics of a metal hydride. This supports the proposed formal $+2$ charge for ruthenium (d^6) in these adducts, compared with the zero oxidation state for Fe (d^8) in the analogous compounds.

Experimental

Tricarbonyl(η-cycloocta-1,5-diene)ruthenium (I) and tricarbonyl$(4-6-\eta,1-\sigma$-cyclooctenediyl)ruthenium (II) were prepared by published procedures [1]. The IR spectra were recorded on Perkin–Elmer 397 infrared spectrophotometer; NMR spectra were recorded on Perkin–Elmer R12 B nuclear magnetic resonance spectrometer; mass spectra were obtained with a Finnigan-Mate 112S spectrometer. All starting materials and solvents were purified before use. All reactions were carried out under argon.

(a) Tricarbonyl(1–3 : 5,6-η-cyclooctadienylium)ruthenium tetrafluoroborate (III)

A CH_2Cl_2 solution of the mixture of isomers I and II (1 g, 3.4 mmol in 1 cm^3) obtained according to ref. 1, and purified by passage through a short silica gel column, was treated for 30 min with triphenylmethyltetrafluoroborate (1.12 g, 3.4 mmol in 7 cm^3). Following the procedure described in ref. 1, complex III was obtained as air stable white crystals (983 mg, 2.75 mmol, 75%). It was characterized by its IR and mass spectra.

(b) Reaction between complex III and PPh₃

Triphenylphosphine (100 mg, 0.381 mmol) was added in small portions to a dichloromethane solution of compound III (134 mg, 0.347 mmol in 4 cm^3) and the mixture was stirred for 3 h at room temperature, during which it cleared rapidly. Addition of diethyl ether produced a white precipitate of the unchanged started compound which was filtered off. The solvent was removed under vacuum to give 2-phosphonium ion of tricarbonyl$(4-6-\eta,1-\sigma$-cyclooctenyl)ruthenium tetrafluoroborate as a light yellow oil. The complex was characterized by its IR spectrum.

(c) Isomerization of compound IV to dicarbonyl(1–3 : 5,6-η-cyclooctadienylium)triphenylphosphineruthenium tetrafluoroborate (V)

A dichloromethane solution of compound IV (100 mg, in 25 cm^3) was kept for three weeks then treated with diethyl ether to yield a crystalline white precipitate, which was purified by dissolution in diethyl ether and shown to be V (85 mg) (Found: C, 54.96; H, 8.98. $C_{28}H_{26}O_2PBF_4Ru$ calcd.: C, 54.82; H, 9.24%). The complex was characterized by IR and NMR spectra.

(d) Dicarbonyl(4–6-η,1-σ-cyclooctenedyil)triphenylphosphineruthenium (VI)

A solution of V (180 mg) in water (10 cm³) was treated with a solution of the stoichiometric quantity of sodium tetrahydroborate in the minimum of water. Extraction with diethyl ether, drying over MgSO₄ and evaporation under vacuum, gave complex VI as white crystals. It was characterized by IR and mass spectra.

(e) Reaction of compound VI with Ph₃CBF₄ to give dicarbonyl(1–3 : 5,6-η-cycloocta-dienylium)triphenylphosphineruthenium tetrafluoroborate (V)

A mixture of dichloromethane solutions of compound VI (441 mg, 0.835 mmol in 5 cm³) and Ph₃CBF₄ (304 mg, 0.921 mmol in 5 cm³) was kept under argon for 30 min, during which the colour turned from yellow to brown. Addition of diethyl ether gave a yellowish white precipitate, which was purified by dissolution in CH₂Cl₂ and reprecipitation with diethyl ether. The compound was identical to that obtained by procedure (c).

(f) Dicarbonyl(1–3 : 5,6-η-cyclooctadienylium)iodoruthenium (VII)

Sodium iodide (111 mg, 0.74 mmol) was added to an acetone solution of complex III (251 mg, 0.65 mmol in 30 cm³) and the mixture was stirred for 80 min. After removal of the solvent under vacuum the residue was dissolved in benzene and chromatographed on alumina which had been deactivated by exposure to air for 6 h. Yellow crystals of complex VII were obtained by evaporation of the solvent (82.5 mg, 75%). m.p. 133–134°C (Found: C, 30.98; H, 2.99; I, 32.66. C₁₀H₁₁O₂RuI calcd.: C, 30.61; H, 2.88; I, 32.4%). The complex was characterized by IR, NMR and mass spectra.

(g) Dicarbonyl(1–3 : 5,6-η-cyclooctadienylium)ruthenium hexafluorophosphate (VIII)

Dicarbonyl(1–3 : 5,6-η-cyclooctadienylium)iodoruthenium (VII) (339 mg, 0.86 mmol) was dissolved in dichloromethane (30 cm³) and a stoichiometric quantity of AgPF₆ was added. The mixture was stirred for 10 min at room temperature and the AgI precipitate was filtered off. The yellow solution containing complex VIII was examined by IR spectroscopy.

(h) Reaction of complex VIII with triphenylphosphine to give: dicarbonyl (1–3 : 5,6-η-cyclooctadienylium)triphenylphosphineruthenium hexafluorophosphate (V)

The solution of complex VIII described in (g) was treated with PPh₃ (0.66 mmol) and the mixture was stirred for 2 h at room temperature. The precipitate was filtered off and diethyl ether was added to the solution to yield complex V as white crystals.

(i) Reaction of complex VIII with sodium tetrahydroborate to give: dicarbonyl-(1–3 : 5,6-η-cyclooctadienylium)hydrideruthenium (IX)

A solution of sodium tetrahydroborate (0.86 mmol) in a water/ether mixture (30 cm³ 1/1 V/V), was added dropwise to a dichloromethane solution of cation VIII obtained as described in (g). After stirring for 3 h at 0°C the solution was extracted with diethyl ether (3 × 20 cm³). The extracts were dried over MgSO₄ and the solvent was removed. The residue was chromatographed on silica gel with petroleum ether as solvent. Removal of the solvent gave a colourless oil, which was characterized as IX by IR and mass spectra.

Acknowledgment

References

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