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Synthesis of cationic allyl complexes from trinuclear carbonyl clusters of iron, ruthenium and osmium

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Abstract

Thermal and photochemical reactions of trinuclear carbonyls of Fe, Ru, Os with allyl alcohol in acidic medium as well as their reactions with $(CH_3)_3NO \cdot 2H_2O$ with subsequent protonation have been studied. Cationic mononuclear allyltetracarbonyl complexes of Fe, Ru, Os and a cationic Os cluster with π-allyl ligand, have been obtained.

We recently developed [1] a route to the allyl and diene complexes of transition metals which consists in the interaction of carbonyl complexes of transition metals with allyl alcohol or conjugated dienes in acidic medium with photochemical or thermal initiation. The behaviour of a large number of mono- and binuclear complexes was studied under the conditions indicated.

The purpose of this study was to investigate the possibility of the use of the cationic complexes of trinuclear carbonyl clusters of the iron sub-group for the synthesis of these complexes. As was learned from previous studies, iron dodecacarbonyl dissolves in acids with subsequent decomposition [2], and the analogous derivatives of ruthenium [3] and osmium [4] gave quite stable protonation products. Moreover, it was shown that UV irradiation of $M_3(CO)_{12}$ for all three metals and heating in the case of Fe and Ru in the presence of unsaturated compounds usually results in degradation of the cluster structure. At the same time $Os_3(CO)_{12}$ preserves the trigonal structure and yields complexes with Os–C σ-bonds [5]. The only known π-complex with ethylene was obtained by step-by-step treatment of $Os_3(CO)_{12}$ with trimethylamine oxide in the presence of CH_3CN with the subsequent substitution of the latter for ethylene [6].

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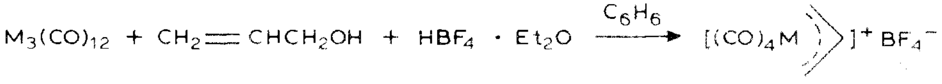
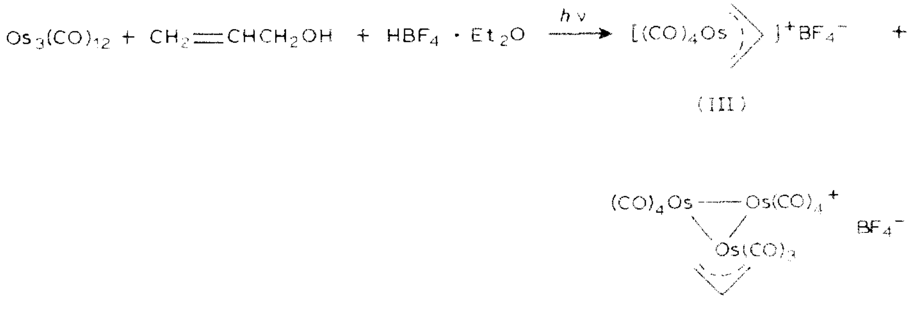


(I, M = Fe; II, M = Ru)

We have found that heating under reflux a benzene solution of iron or ruthenium dodecacarbonyl with allyl alcohol in the presence of $HBF_4 \cdot Et_2O$ resulted in the formation of traces of the mononuclear allyl complexe I or II, respectively.



(III)

(IV)

Osmium dodecacarbonyl does not react at all under these conditions. It should be noted that compound I has been studied previously [7] and here we propose a simple one-step preparation of this type of complex from $Fe(CO)_5$ or $Fe_2(CO)_9$ to give products in high yield [1f,h]. Compound II was obtained for the first time.

The use of UV irradiation increased the yields of I and II to 18 and 70%, respectively.

In the case of $Os_3(CO)_{12}$, the formation of the two compounds, namely, mono- III and trinuclear IV cationic allyl complexes was observed. The ratio in which they occur is dependent on the reaction conditions. If the reaction is carried out in ether at room temperature, the ratio of III to IV is 1/1 according to the PMR data, whereas UV irradiation in hot benzene results in a decrease in the amount of IV, to as little as 1/14 *. Compound III was obtained pure only after numerous reprecipitations from nitromethane/ether.

We consider complex IV to be the most interesting because up to now there are only a few known cationic clusters, and the cationic clusters with a π-allyl ligand are novel. Thus an attempt was made to isolate complex IV pure. Since separation of a mixture of III and IV is rather difficult, we decided to use $(CH_3)_3NO \cdot 2H_2O$ [8] for the replacement of allyl alcohol with CO ligand followed by protonation of the product to give IV. In fact, when a solution of $(CH_3)_3NO \cdot 2H_2O$ (2–2.5 molar excess) in allyl alcohol is added to a solution of $Os_3(CO)_{12}$ in methylene chloride the replacement of the olefin ligand with a CO group (IR and TLC control) takes place. After the $(CH_3)_3N$ and the excess of its oxide had been separated off by

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* The PMR spectrum of one more unidentified π-allyl complex, present in a concentration less than that of (IV), shows well-resolved signals of H_{anti} and H_{centr}, (1.87 dd (J_1 13.3, J_2 3.7 Hz), 5.17tt).

filtration of the reaction mixture through a layer of silica gel, and the solution treated with acid, the only product which was isolated was IV in 30% yield *.

$$\mathrm{Os_3(CO)_{12}} \xrightarrow[\mathrm{CH_2Cl_2}]{\mathrm{(CH_3)_3NO\cdot 2H_2O/CH_2{=}CHCH_2OH}}$$

$$\mathrm{Os_3(CO)_{11}}(\eta^2\text{-}\mathrm{CH_2{=}CHCH_2OH}) \xrightarrow{\mathrm{HBF_4\cdot Et_2O}} \mathrm{IV}$$

No attempt was made to obtain olefin complex V pure. However, its IR spectrum in the reaction mixture (ν(CO) 2116w, 2064s, 2046s, 2026vs, 2002s cm^{-1}) bears a strong resemblance to that for $Os_3(CO)_{11}(\eta\text{-}CH_2{=}CH_2)$ [6]. $Fe_3(CO)_{12}$, treated in the same way, resulted only in the formation of I in low yield. At the same time, it was found that decomposition of the trinuclear structure occurred after protonation. In the case of $Ru_3(CO)_{12}$, a mixture of cationic complexes is formed in low yield. One of these complexes appears to be II, from the IR data the other was seen to be analogous to IV.

The composition and structure of the complexes obtained were established by elemental analysis, IR and PMR spectroscopy.

Experimental

Synthesis and isolation of the complexes were performed under argon with the use of absolute solvents. UV irradiation was carried out with a PRK-7 lamp (1000 W). The IR spectra were recorded on a "SPECORD 75IR" spectrophotometer, the PMR spectra were recorded on a Bruker WP 200SY spectrometer (200.13 MHz).

Irradiation of $Fe_3(CO)_{12}$

A mixture of $Fe_3(CO)_{12}$ (0.25 g, 0.5 mmol), allyl alcohol (0.5 ml), $HBF_4\cdot Et_2O$ (0.2 ml) in 100 ml of ether was irradiated until the green colour disappeared (after about 11 h). Then the precipitate was filtered off, washed with ether, dissolved in a minimal amount of nitromethane, and filtered into 10 ml of ether. The precipitate that formed was separated off and dried. The yield of allyltetracarbonylirontetrafluoroborate was 0.08 g (18%). IR (CH_3NO_2): 2155m, 2105sh, 2094vs cm^{-1}.

Irradiation of $Ru_3(CO)_{12}$

A mixture of $Ru_3(CO)_{12}$ (0.13 g, 0.2 mmol), allyl alcohol (0.1 ml), $HBF_4\cdot Et_2O$ in 100 ml ether was irradiated for 16 h. The reaction mixture was then treated according to the method for $Fe_3(CO)_{12}$. The yield of allyltetracarbonylrutheniumtetrafluoroborate was 0.142 g (70%). Found: C, 25.26; H, 1.88. $C_7H_5BF_4O_4Ru$ calc: C, 24.66; H, 1.48%. IR: 2172w, 2117sh, 2106vs, 2092s, 2078m cm^{-1}. PMR (δ, ppm): 3.29 ddd (2H, J_1 12.6, $J_2 \sim J_3 \sim 1.5$ Hz, H_{anti}), 4.25 ddd (2H, J_1 7.3, $J_2 \sim J_3 \sim 1.5$ Hz, H_{syn}), 5.99 tt (1H, $H_{centr.}$).

Irradiation of $Os_3(CO)_{12}$

A mixture of $Os_3(CO)_{12}$ (0.45 g, 0.5 mmol), allyl alcohol (0.5 ml), $HBF_4\cdot Et_2O$ (0.2 ml) in 200 ml of benzene was irradiated for 20 h at 75 °C. The reaction mixture was cooled to room temperature and evaporated under vacuum, and then the procedure, as described for $Fe_3(CO)_{12}$, was followed. Yellow powder, 0.20 g.

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* Preliminary X-ray data for IV confirm its structure.

The analytical sample was obtained by numerous reprecipitations from nitromethane/ether. For III Found: C, 19.89; H, 1.29. $C_7H_5BF_4O_4Os$ calc: C, 19.55; H, 1.17%. IR: 2176m, 2094vs, 2075vs cm^{-1}. PMR (δ, ppm): 3.11 ddd (2H, J_1 12.4, J_2 2.5, J_3 1.6 Hz, H_{anti}), 4.16 ddd (2H, J_1 7.2, J_2 2.5, J_3 1.6 Hz, H_{syn}), 5.69 tt (1H, $H_{centr.}$).

Synthesis of $[Os_3(CO)_{11}(\eta\text{-}C_3H_5)]^+BF_4^-$ *(IV)*

A solution of $(CH_3)_3NO \cdot 2H_2O$ (0.06 g, 0.54 mmol) in allyl alcohol (1 ml) was slowly added dropwise to a solution of $Os_3(CO)_{12}$ (0.2 g, 0.22 mmol) in 150 ml of CH_2Cl_2 with vigorous stirring. The mixture was stirred for 1 h and evaporated to dryness in vacuo. The residue was dissolved in 15 ml of CH_2Cl_2, and diluted with 15 ml of ether, then cooled to −78 °C and filtered through a layer of silica gel (1 cm). The silica gel was washed with a mixture of CH_2Cl_2/Et_2O (1/1) (2 × 5 ml) and 0.2 ml of $HBF_4 \cdot Et_2O$ was added to the filtrate and the solution was evaporated to dryness. The residue was washed with ether (3 × 10 ml) and reprecipitated from nitromethane/ether. The yellow-orange precipitate was filtered off and dried. The yield of IV was 0.068 g (30%). Found: C, 16.68; H, 0.75. $C_{14}H_5BF_4O_{11}Os_3$. calc: C, 16.70; H, 0.50%. IR: 2147w, 2099s, 2092sh, 2061vs, 2040s, 2022vs cm^{-1}. PMR: 3.00 d (2H, J_1 12.1 Hz, H_{anti}), 4.65 ddd (2H, J_1 6.7, $J_2 \sim J_3 \sim$ 1.3 Hz, H_{syn}), 4.98 tt (1H, $H_{centr.}$).

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