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$[Fe_3(\mu_3\text{-}CR)(CO)_{10}]^-$ CLUSTER ANIONS AS BUILDING BLOCKS FOR THE SYNTHESIS OF MIXED-METAL CLUSTERS

II *. SYNTHESIS OF $HFe_3Rh(\mu_4\text{-}\eta^2\text{-}C{=}CHR)(CO)_{11}$ CLUSTERS ($R = H$ OR C_6H_5) AND STUDY OF THEIR CATALYTIC ACTIVITY ($R = C_6H_5$) UNDER HYDROFORMYLATION AND HYDROGENATION CONDITIONS

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Summary

The mixed-metal vinylidene clusters $HFe_3Rh(CO)_{11}(C{=}CHR)$ ($R = H$, C_6H_5) have been synthesized via the reaction of $[HFe_3(CO)_3C{=}CHR][P(C_6H_5)_4]$ with $[RhCl(CO)_2]_2$ in the presence of a thallium salt. The reaction initially gives the $[Fe_3Rh(CO)_{11}CCHR][P(C_6H_5)_4]$ cluster which leads to the final products by protonation. Spectroscopic data indicate a $\mu_4\text{-}\eta^2$ mode of bonding for the vinylidene ligand. A structure with a Fe_3Rh core in a butterfly configuration and in which the rhodium atom occupy a wing-tip site is proposed. The catalytic activity of $HFe_3Rh(CO)_{11}(C{=}CH(C_6H_5))$ (80% yield) has been checked in hydroformylation and hydrogenation. In hydroformylation the cluster shows the same activity as $Rh_4(CO)_{12}$, whereas in hydrogenation the mixed-metal system shows specific activity; isomerization of 1-heptene to *cis* and *trans* 2-heptene takes place with no more than 14% heptane formation. The cluster is broken down during the catalysis, and some $H_3Fe_3(CO)_9(\mu_3\text{-}CCH_2(C_6H_5))$ is formed. The latter cluster is not an active catalyst, and under the same conditions use of $Rh_4(CO)_{12}$ results mainly in hydrogenation of 1-heptene. These observations suggest that the active species is a mixed iron-rhodium system.

Introduction

We have recently shown that the cluster anion $[Fe_3(\mu_3\text{-}CCH_3)(CO)_{10}]^-$ is readily available from the reaction of acetylene with the $[HFe_3(CO)_{11}]^-$ cluster anion [2]. This anionic cluster seemed a good candidate for building new mixed-metal cluster systems, e.g. by reaction with transition metal halide complexes. We expected that the capping ethylidyne ligand would preserve the initial trinuclear iron unit, avoid-

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ing or limiting metal redistribution during the synthesis (a frequently encountered problem in synthesis of mixed-metal clusters [3]).

One reason for the synthesis of mixed-metal clusters is to find out whether they are precursors of catalytic active species, in which the presence of two different metals brings new activity compared to homonuclear species. Some recent examples show this effect, but usually the cluster is broken down under catalytic conditions [4].

In this paper, we report the synthesis of new mixed iron-rhodium clusters with a Fe_3Rh core and a study of their catalytic activity in hydroformylation and hydrogenation.

Results and discussion

In the first approach we treated $[RhCl(CO)_2]_2$ with $[Fe_3(\mu_3\text{-}CCH_3)(CO)_{10}][P(C_6H_5)_4]$ in the presence of a thallium salt, $TlBF_4$. Surprisingly, the reaction did not yield a neutral complex but an anionic compound, which could not be isolated. Protonation of this compound gave a low yield of the neutral complex **1**. The infrared spectrum of this complex in the ν(CO) stretching region shows only characteristic bands of terminal CO groups. The proton NMR spectrum shows two signals, in 2/1 ratio, at 4.92 and −25.3 ppm; this suggests the presence of a hydride ligand and of a CH_2 group. The mass spectrum of **1** shows a parent ion ($m/z = 606$) and successive loss of 11 CO groups; this is consistent with the formulation $HFe_3Rh(CO)_{11}C{=}CH_2$ for **1**. The reaction appears to be more complex than expected, and during the addition of rhodium to the iron cluster anion hydrogen abstraction from the ethylidyne ligand occurs, giving a vinylidene ligand.

Since we planned to check the catalytic activity of the mixed Fe_3Rh cluster formed, it was necessary to improve the yield. We thus began directly with the $[HFe_3(\mu_3\text{-}C{=}CH_2)(CO)_9][P(C_6H_5)_4]$ cluster [2]; again the reaction gave an anion which on subsequent protonation gave **1**, in a similar yield to that from the first approach.

We next slightly changed the nature of the substrate cluster, and started with $[HFe_3(\mu_3\text{-}C{=}CHC_6H_5)(CO)_9][P(C_6H_5)_4]$. The reaction proceeded as with $[RhCl(CO)_2]_2$, initially giving mainly an anionic species **2** and upon protonation this gave the neutral cluster **3** in good yield. The infrared spectrum in the ν(CO) stretching region of **3** is very similar to that of (**1**), suggesting a similar structure. The proton NMR spectrum shows complex multiplets centred at 7.95, 7.62 and 7.30 ppm and a singlet at −25.52 ppm in 6/1 ratio. This and the mass spectrum, which shows

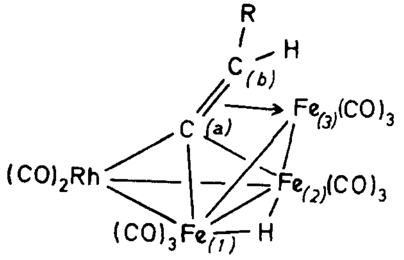

Fig. 1. Proposed structure for complex **1** (R = H) and complex **3** (R = C_6H_5).

a parent ion m/z at 682 and successive loss of 11 CO groups, are consistent with the formulation $HFe_3Rh(CO)_{11}C{=}CH(C_6H_5)$, confirming the similarity with **1**. In the ^{13}C NMR spectrum of **3**, in addition to phenyl resonances, we observed signals at 311.8 (d, J 34 Hz), 208.2 (dd, J 17, J(HCO) 5 Hz), 183.1 (d, J 73 Hz) and 97.5 ppm (d, J(CH) 161 Hz). The 208.2 ppm resonance is attributed to CO groups bonded to Fe atoms which are coupled with Rh atoms and with the hydride ligand, and the 183.1 ppm doublet to the carbonyls bonded to Rh. The vinylidene ligand is characterized by the 97.5 ppm resonances attributed to the $CH(C_6H_5)$ carbon, and the 311.8 ppm resonance arising from the carbon bonded to the metal centres. The latter value is rather low compared to that of the starting cluster anion (270 ppm) [2], and seems out of the normal range of vinylidene ligands μ_3-η^2 bonded to metal centres [5]. It is more consistent with a μ_4-η^2 bonding, as can be seen, for example, by comparison with the shift for the carbon bonded to iron in $Co_3Fe(\mu_4\text{-}C{=}CH_2)(\mu\text{-}CO)(CO)_7(\eta\text{-}C_5H_5)$ (304 ppm) [6]. Furthermore, the high value of the coupling to the rhodium atom indicates that this carbon is bonded to rhodium (J(RhC) 67.7 Hz in $(\eta\text{-}C_5H_5)Rh(C{=}CHC_6H_5)(P(i\text{-}Pr)_3)$ [7], J(RhC) 28 Hz in $[(\eta\text{-}C_5H_5)Rh(CO)]_2(\mu\text{-}CH_2)$ [8]).

Thus, the ^{13}C NMR data strongly support a μ_4-η^2 bonding for the vinylidene ligand in **3**, which implies a butterfly arrangement for the Fe_3Rh metal core and would require a 62-electron cluster. But if our formulation is correct we have a 60-electron cluster. To solve this problem, we have tried to grow single crystals of **1** or **3**, but so far, without success.

Taking account of all the spectroscopic data, the most reasonable structure which can be proposed is that based on the closely related 62-electron cluster, $HNiRu_3(\mu_4\text{-}\eta^2\text{-}C{=}CH\text{-}t\text{-}Bu)(CO)_9$, [9], and presented in Fig. 1. It consists of a butterfly arrangement of the Fe_3Rh metal core, each iron atom being surrounded by three carbonyl and the rhodium atom by two carbonyl ligands. A similar situation for a rhodium centre has been proposed for the $[Fe_2Rh(CO)_{10}]^-$ cluster anion [10]. The vinylidene ligand is σ-bonded via C(a) to Rh, Fe(1) and Fe(2) and η^2-coordinated to Fe(3) via C(a)C(b). As there is no apparent coupling of the hydride ligand to the rhodium nucleus, it is suggested that is bridges the Fe(1)–Fe(2) metal bond, a situation identical to that in the $HNiRu_3$ cluster already mentioned [9].

The anionic species **2** was isolated before protonation, and proton NMR shows that it is associated with the $[P(C_6H_5)_4]^+$ cation (resonance at 8.05 and 7.95 ppm). The ^1H spectrum also shows a broad resonance centred at 7.20 and a sharp resonance at 6.67 ppm. The relative intensities of these resonances are 20/5/1, in agreement with the presence of $P(C_6H_5)_4{}^+$ and of the $C{=}CH(C_6H_5)$ vinylidene ligand in the cluster. The chemical analysis agrees well with the $[Fe_3Rh(CO)_{11}\text{-}(C{=}CH(C_6H_5))][P(C_6H_5)_4]$ formulation, confirming that **2** is the anion of **3**. The infrared spectra in the ν(CO) stretching region provide evidence of exclusively terminal carbonyl groups, shifted to lower frequencies compared to **3**. Thus we propose related structures for **2** and **3**, with the hydride ligand of **3** replaced by a negative charge in **2**.

Taking into account the nature of **2**, the equation for the reaction can be written as:

$$1/2\,[RhCl(CO)_2]_2 + [HFe_3(C{=}CHR)(CO)_9][P(C_6H_5)_4] + TlBF_4 \rightarrow [Fe_3Rh(C{=}CHR)(CO)_9][P(C_6H_5)_4] + TlCl + HBF_4$$

This implies the formation of tetrafluoroboric acid, suggesting that **2** is not basic enough to be protonated by a stoichiometric amount of acid, and only trace amounts of **3** are detected before addition of an excess of acid.

The catalytic activity of **3** was examined for two reactions: (i) the hydroformylation of 1-pentene and (ii) the hydrogenation of 1-heptene, in order to see whether the known activity of rhodium compounds [11,12] in these reactions is maintained or modified.

Hydroformylation experiments

The catalytic activity of **3** was checked under mild conditions: ($CO + H_2$, 1/1, 20 atm, 60°C) with a molar ratio 1-pentene/**3** equal to 250. The conversion of 1-pentene into a mixture of methyl-2-pentanal and 1-hexanal proceeds smoothly and 70% conversion of 1-pentene is achieved within 6 h. The ratio of branched to terminal aldehydes is roughly 1/2. At the end of the reaction IR analysis of the solution shows that **3** is no longer present, and that $Rh_4(CO)_{12}$ has been formed.

In the light of this result we examined the catalytic activity of $Rh_4(CO)_{12}$ under the same conditions and with the same concentration of Rh metal in solution. We obtained almost identical results, and we conclude that there is no specific activity due to the presence of iron under these conditions.

Hydrogenation experiments

With 1-heptene under 10 atm of hydrogen, isomerization of 85% 1-heptene into *cis* and *trans* 2-heptene (*cis*/*trans* ratio ca. 0.3) occurs during 6 h, with formation of 14% heptane. Isomerization of 2-heptene into 3-heptene subsequently takes place at a lower rate. After 26 h, the ratio 3-heptene/2-heptene is 6/10.

By the end of the catalysis, only a small amount of the starting cluster remains and new infrared bands are present in the ν(CO) stretching region. The new species was isolated and identified as $H_3Fe_3(\mu_3\text{-}CCH_2C_6H_5)(CO)_9$ (**4**), by comparison of its spectroscopic properties with an authentic sample prepared by hydrogenation of $HFe_3(\mu_3\text{-}CCH_2C_6H_5)(CO)_{10}$ (See Experimental).

It thus appears that under catalysis conditions fragmentation of **3** occurs with hydrogenation of the vinylidene ligand to give a carbyne ligand and with loss of rhodium. The fate of the rhodium is not known, but some decomposition is observed in the catalytic reaction.

Under nitrogen only a low catalytic activity is observed, and decomposition of cluster **3** occurs rapidly. To try to establish the nature of actual catalytic precursor, we first checked whether **4** was an active catalyst under similar conditions and found that no reaction occurred. To see whether the rhodium metal formed provided the active species we examined the catalytic reactivity of $Rh_4(CO)_{12}$ under the same conditions: some isomerization occurred, but 86% of the 1-heptene was rapidly hydrogenated into heptane, and some decomposition to metal rhodium is observed. This indicates that the catalytic active species generated by **3** under catalytic conditions is specific to this cluster and is not due solely to the presence of rhodium.

To see whether the active species was heterogeneous, the following experiments were performed.

(i) After a catalytic run, more 1-heptene was added to the solution which was then pressurized under 10 atm of hydrogen. There was some catalytic activity, and slow transformation into 2-heptene was observed (60% conversion within 1 day).

(ii) After a catalytic run, the solution was removed from the autoclave and filtered through Celite. This solution showed a similar activity to that described in experiment (i).

(iii) The deposit on the walls of the glass vessel after a catalytic run was washed with dichloromethane under nitrogen. A solution of 1-heptene in benzene was added and pressurized under 10 atm of hydrogen. Rapid hydrogenation into heptane took place with the formation of a small quantity of *cis* and *trans* 2-heptene.

(iv) A similar experiment to (iii) was carried out, but $H_3Fe_3(\mu_3\text{-}CCH_2(C_6H_5))(CO)_9$ was added to the benzene solution of 1-heptene. The activity was very similar to that in experiment (iii).

These results favour a homogeneous nature for the catalysts in isomerization of 1-heptene. Furthermore, the different activity of the mixed cluster **3** compared to that of the homometallic species suggests that the presence of iron "poisoned" the rhodium activity, favouring isomerization over hydrogenation.

Experimental

All reactions were carried out under nitrogen. ^1H NMR spectra were recorded on a Bruker WH90 spectrometer and IR spectra on a Perkin–Elmer 225 spectrometer in hexadecane solution in the $\nu(CO)$ stretching region. Mass spectra were recorded on a Varian MAT 311-A using 70 eV electron impact. Elemental analyses were performed in our laboratory.

Preparation of $HFe_3Rh(CO)_{11}(CCH_2)$ (1)

To 1 g of $[HFe_3(\mu_3\text{-}CCH_2)(CO)_9][P(C_6H_5)_4]$ [2] dissolved in acetone was added 0.247 g of $[RhCl(CO)_2]_2$ and 0.370 g of $TlBF_4$. The solution was stirred for 0.5 h then filtered and evaporated to dryness under vacuo. The residue was dissolved in a small amount of dichloromethane and 1 cm^3 of trifluoroacetic acid was added. The solution was stirred for 10 min then evaporated to dryness. Extraction of the residue with pentane followed by concentration of the solution afforded 0.2 g of **1** as green crystals (26% yield). IR $\nu(CO)$: 2089w, 2051s, 2044s, 2026m, 2015m, 1994m, 1985w cm^{-1}. ^1H NMR (CD_2Cl_2): 4.92 (CH_2), −25.3 ppm (H). Mass spectrum $m/z = 606$. Found: C, 25.15; H, 0.63. $C_{13}H_3Fe_3O_{11}Rh$ calcd.: C, 25.74; H, 0.49%.

Preparation of $HFe_3Rh(CO)_{11}(CCH(C_6H_5))$ (3)

This was prepared by a similar procedure to that used for **1**, but starting with 1.8 g of $[HFe_3(\mu_3\text{-}CCH(C_6H_5))(CO)_9][P(C_6H_5)_4]$ [2], 0.405 g of $[RhCl(CO)_2]_2$ and 0.607 g of $TlBF_4$. After protonation, $HFe_3Rh(CO)_{11}CCH(C_6H_5)$ (1.2 g; 84%) was isolated as green crystals. IR $\nu(CO)$: 2088w, 2050s, 2042s, 2027m, 2014m, 1994w, 1984w. ^1H NMR (CD_2Cl_2): 7.95, 7.62, 7.30 ppm (C_6H_5 + CH); −25.52 (FeH). ^{13}C NMR (CD_2Cl_2): 311.8 (d, J 34 Hz), 202.2 (dd, J_1 19, J_2 5 Hz), 183.7 (d, J 73 Hz), 142.4 (C_6H_5), 128.6 (d, J 161 Hz) (C_6H_5), 97.5 ppm (d, J 161 Hz). Mass spectrum $m/z = 682$. Found: C, 33.42; H, 1.07. $C_{19}H_7Fe_3O_{11}Rh$ calcd.: C, 33.43; H, 1.03%.

Preparation of $[Fe_3Rh(CO)_{11}(CCH(C_6H_5))]^-$ (2)

The procedure described for **3** was followed but omitting the protonation. After the filtration and evaporation, the residue was dissolved in a small amount of methanol to give 0.6 g of $[Fe_3Rh(CO)_{11}(CCH(C_6H_5))][P(C_6H_5)_4]$ (50.6% yield). IR

ν(CO) (CH_2Cl_2 solution): 2050w, 2015s, 1980s, 1917m, 1900m. ^1H NMR ($(CD_3)_2CO$): 8.05, 7.95 ($P(C_6H_5)_4$), 7.20 (C_6H_5), 6.67 ppm (CH). Found: C, 51.00; H, 2.70. $C_{43}H_{26}Fe_3O_{11}PRh$ calcd.: C, 50.58; H, 2.55%.

Preparation of $H_3Fe_3(\mu_3\text{-}CCH_2(C_6H_5))(CO)_9$ (4)

A solution of 0.1 g of $HFe_3(\mu_3\text{-}CCH_2(C_6H_5))(CO)_{10}$ [2] in hexane was heated for 16 h at 60°C under 20 atm of hydrogen in a stainless steel autoclave. The solution was then filtered, concentrated, and cooled to −20°C, to give 0.05 g of **4** (52%) m.p. 100°C (dec.) as orange crystals. IR ν(CO): 2094vw, 2059s, 2020sh, 2016s, 2008m, 2000m. ^1H NMR (CD_2Cl_2): 7.55 (complex multiplet (C_6H_5)), 5.75 (qt, J 1.5 Hz) (CH_2), 23.62 ppm (t, J 1.5 Hz) (3 H). Mass spectra $m/z = 526$. Found: C, 38.65; H, 1.93. $C_{17}H_{10}Fe_3O_9$ calcd.: C, 38.78; H, 1.90%.

Catalytic experiments

All experiments were carried out in a 100 ml stainless steel autoclave fitted with a glass liner. Chromatographic analyses of the catalysis reactions were performed on an Instersmat IGC 120F apparatus using a 2 m Carbowax column operating at 100°C for aldehyde analyses and 25°C for olefin analyses. The mixture of *cis* and *trans* 2-heptene was separated on a 4 m SE 30 column at 25°C.

Hydroformylation reactions

A solution of 50 mg of **3** or 13.5 mg of $Rh_4(CO)_{12}$ in 15 cm^3 of benzene and 26 cm^3 of 1-pentene was pressurized with a mixture of 10 atm of hydrogen and 10 atm of carbon monoxide, and kept at 60°C. Samples were periodically withdrawn from the solution and analyzed.

Hydrogenation reactions

The solutions were prepared as described for the hydrogenations except that 2 cm^3 of 1-heptene were used. The solutions were pressurized under 10 atm of hydrogen and stirred at room temperature. In the experiment involving isolation of the complex subsequent to catalysis, 0.1 g of **3** and 4 cm^3 of 1-heptene were used. At the end of the reaction, the solution was filtered and evaporated to dryness under vacuo, and the residue was redissolved in a small amount of pentane. Some crystals of **4** were isolated, and were identified by infrared spectra in the carbonyl stretching region and by mass spectroscopy. The infrared spectrum of the mother liquor gave no evidence for the presence of carbonyl complexes other than **4**.

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