Journal of Organometallic Chemistry, 247 (1983) 223–225
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

SYNTHESIS AND SOME REACTIONS OF $HFe_3(CO)_9(SR)$ CLUSTERS CONTAINING PRIMARY ALKYL GROUPS

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(Received December 8th, 1982)

Summary

$Fe_3(CO)_{12}$ and sodium thiolates react in THF to form the trinuclear anions $Fe_3(CO)_9(SR)^-$. The corresponding hydrides $HFe_3(CO)_9(SR)$ can be obtained by acidification and this enables the preparation of complexes containing primary alkyl groups. When R = Ph only the anion is stable at room temperature. When heated in polar solvents all the complexes readily loose the R group to give $HFe_3(CO)_9S^-$ or $Fe_3(CO)_9S^{2-}$ and hydrocarbons or carbonylated organic products.

Introduction

The trinuclear thiolato complexes $HFe_3(CO)_9(SR)$ were first described by Haines and de Beer [1], and their structure was confirmed later by Bau et al. using X-ray and Mössbauer spectroscopy [2]. Recently Huttner et al. have shown [3], that such complexes are deprotonated by bases like amines to give the corresponding anions $Fe_3(CO)_9(SR)^-$. Up till now, however, only complexes with secondary or tertiary alkyl groups had been described, since the method of preparation used (reaction of RSH and $Fe_3(CO)_{12}$ in boiling benzene) was not successful with primary or aromatic thiols. In this paper we report the preparation of $HFe_3(CO)_9(SR)$ complexes containing primary alkyl groups and discuss some of their reactions.

Results and discussion

The successful direct preparation of the sulfur-containing anionic clusters $Fe_2Co(CO)_9S^-$ and $HFe_3(CO)_9S^-$ from the corresponding metal carbonyls and Na_2S or EtSNa under CO pressure and 150°C with good yields [4] suggested that an analogous synthesis of the $Fe_3(CO)_9(SR)^-$ cluster anions should be possible if milder reaction conditions were used (to avoid the cleavage of the R group, cf. ref. 4). A suitable method was indeed found, involving allowing to react equimolar amounts of $Fe_3(CO)_{12}$ and RSNa in dry THF under reflux.

The infrared spectra of the red brown solutions obtained in this way depended on

0022-328X/83/$03.00

the structure of the thiolate. In the case of R = alkyl (primary, secondary or tertiary) and phenyl the four bands characteristic for the $Fe_3(CO)_9(SR)^-$ anions dominated (2033m, 1971vs, 1946s, 1919m cm^{-1} in methanol). If R was CN, CH_2Ph, $CH_2CH(NH_2)COO^-$, or C(S)OEt the $HFe_3(CO)_9S^-$ anion [5] was formed, whereas the reaction with the sodium salt of mercaptobenzthiazol furnished an unidentified carbonylferrate anion which was not investigated further.

After acidification of the products containing $Fe_3(CO)_9(SR)^-$ the $HFe_3(CO)_9(SR)$ complexes could be isolated in all cases when R was an alkyl group, but the phenyl derivative was found to be rather unstable and rapidly decomposed during this procedure to give $H_2Fe_3(CO)_9S$, $H_2Fe_3(CO)_9S_2$ and $Fe_2(CO)_6(SPh_2)$. Table 1 lists the spectroscopic data for the new $HFe_3(CO)_9(SR)$ complexes prepared in this way.

This new method can be used also for the preparation of $HFe_3(CO)_9(SR)$ complexes involving secondary or tertiary alkyl groups, as exemplified by the synthesis of the R = s-butyl and t-butyl derivatives in 58 and 18% yield, respectively. These complexes have been previously described [1].

The formation of the $HFe_3(CO)_9S^-$ anion from RS^- and $Fe_3(CO)_{12}$ in the cases mentioned earlier suggested that the carbon–sulfur bond in the $Fe_3(CO)_9(SR)^-$ anions may be rather weak. This was shown to be the case, because upon refluxing of the ethanol solutions of $HFe_3(CO)_9(SR)$ complexes, the $Fe_3(CO)_9(SR)^-$ anions (formed by spontaneous dissociation in this polar solvent) were gradually transformed into the $HFe_3(CO)_9S^-$ anion. Among the complexes examined, that with R = Et proved to be the most labile (complete transformation within 25 min) and that with R = s-Bu the most stable (about 20% transformation in 200 min).

The organic decomposition products were identified by GC-MS; in the case of the n-Bu derivative, for example, butane, butene-1, BuCOOEt, BuSH, BuSSBu and BuCOSBu were found. The formation of these compounds suggests a radical pathway for the rupture of the C–S bond, and furthermore indicates that some decomposition of the Fe_3S cluster core also takes place. Similar reaction products

TABLE 1

SPECTROSCOPIC DATA FOR $HFe_3(CO)_9(SR)$ COMPLEXES

R	ν(CO) (cm^{-1}) in hexane	^1H NMR, δ (ppm) in C_6D_6	MS, *m/e* (relative intensity) [a]
Et	2084.5m, 2047s, 2025.5vs, 2012s, 2002m, 1995w, 1969sh, 1966.5m,	Fe_3H −23.95,s $>SCH_2$ 2.29,q CH_3 0.625,t	M^+ 482 (48) Fe_3S^+ 200 (100)
n-Bu	2084m, 2046.5s, 2025vs, 2011.5s, 2001m, 1994.5w, 1969sh, 1965.5m	Fe_3H −23.87,s $>SCH_2$ 2.55,t	M^+ 510 (44) M^+-5CO 370 (100) Fe_3S^+ 200 (80)
n-C_8H_{17}	2084m, 2046.5s, 2025vs, 2011.5s, 2001m, 1994w 1968.5sh, 1965m	Fe_3H −23.83,s $>SCH_2$ 2.64,t	M^+ 566 (32) M^+-5CO 426 (100) Fe_3S^+ 200 (70)

[a] All $HFe_3(CO)_n(SR)$ fragments (n = 0–8) appear.

were found when iron carbonyls and thiols were treated in hydrocarbon solvents at more elevated temperatures (160–170°C) [6].

In accordance with the above observations the $HFe_3(CO)_9(SR)$ complexes may be transformed directly into crystalline $(Et_4N)_2[Fe_3S(CO)_9]$ [5] in good yield (60–80%) by refluxing with Et_4NOH in ethanol. The latter ionic complex is also the product if a thiol, $Fe_3(CO)_{12}$ and Et_4NOH are refluxed in ethanol.

In light of all the accumulated information on the stability of $HFe_3(CO)_9(SR)$ complexes and their anions, the generalization seems to be justified that the strength of the carbon–sulfur bond decreases with the increasing electron-withdrawing character of R. The rupture of this bond may be regarded as a relatively simple model for the key step of the frequently encountered desulfurizations of organic molecules in the presence of transition metals.

Experimental

Synthesis of $HFe_3(CO)_9(SR)$ (R = Et, n-Bu and n-C_8H_{17})

A solution of 605 mg (1.2 mmol) of $Fe_3(CO)_{12}$ and 1 mmol of RSNa in 50 ml dry THF under Ar was refluxed for 30 min. The solvent was evaporated in vacuo, and the viscous residue was extracted with hexane (to remove $[Fe(CO)_3(SR)]_2$ complexes formed as by-products). The residue was dissolved in 50 ml methanol and the solution was acidified in the presence of 50 ml hexane with 80 ml 40% H_3PO_4. The hexane solution was separated, washed with water and dried over Na_2SO_4, and the complexes allowed to crystallize out at −78°C. Analytical data and yields:
R = Et, 56%. (Found: Fe, 34.5; C, 27.28; H, 1.46; S, 6.52. $C_{11}H_6O_9SFe_3$ calcd.: Fe, 34.77; C, 27.42; H, 1.26; S, 6.64%.)
R = n-Bu, 46%. (Found: Fe, 32.3; C, 30.15; H, 2.13; S, 5.70. $C_{13}H_{10}O_9SFe_3$ calcd.: Fe, 32.86; C, 30.62; H, 1.98; S, 6.27%)
R = n-C_8H_{17}, 60%. Viscous oil.

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