Journal of Organometallic Chemistry, 299 (1986) 363–367
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

REACTION OF $[Fe_4(\mu_3\text{-}CCH_3)(CO)_{12}]^-$ WITH ALKYNES: ETHYLIDYNE–ALKYNE COUPLING ON A TETRANUCLEAR IRON CLUSTER ANION

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(Received July 24th, 1985)

Summary

The $[Fe_4(\mu_4\text{-}\eta^3\text{-}C(CH_3)C(R)C(R')(\mu\text{-}CO)_2(CO)_9]^-$ cluster anions have been obtained by the reaction of the $Fe_4(\mu_3\text{-}CCH_3)(CO)_{12}^-$ anion with RC≡CR alkynes in boiling 3-pentanone. In the cases in which $R = R' = C_6H_5$ or CH_3, and R = H, $R' = C_6H_5$ or t-Bu, only one isomer has been detected. In the case in which $R = CH_3$ and $R' = C_6H_5$, two isomers with the $C(CH_3)C(C_6H_5)C(CH_3)$ and $C(CH_3)C(CH_3)C(C_6H_5)$ fragments have been identified.

Introduction

During a study of the reactivity of the cluster anion $[HFe_4(CO)_{13}]^-$ toward alkynes, we observed that the products of the reaction are very alkyne-dependent [1]. In the case of acetylene, we showed that the first product formed is $[Fe_4(\mu_3\text{-}CCH_3)(CO)_{12}]^-$ (I), which then reacts at higher temperature with a second molecule of acetylene to give $[Fe_4(\mu_4\text{-}\eta^3\text{-}C(CH_3)CHCH)(\mu\text{-}CO)_2(CO)_9]^-$ (II). This suggests that carbon–carbon coupling of alkynes with the ethylidyne ligand is a quite easy reaction when starting with the cluster I. The problem of carbon–carbon bond formation between alkylidyne ligands and unsaturated hydrocarbons on polynuclear metal complexes is a field of increasing interest; in particular, coupling with alkynes has attracted much attention [2–10], but most of the work was done with di- or tri-nuclear complexes. For this reason, we have studied the reactions of the tetranuclear complex I (which can be easily synthesized by the action of acetylene on $[HFe_4(CO)_{13}]^-$) with the symmetrical and unsymmetrical alkynes RC≡CR' with R = H, $R' = C_6H_5$ or $C(CH_3)_3$; $R = C_6H_5$, $R' = CH_3$; and $R = R' = C_6H_5$ or CH_3.

Experimental

All reactions were performed under nitrogen. Infrared spectra were recorded in dichloromethane solution with a Perkin–Elmer 225 spectrometer. ^1H NMR spectra

TABLE 1

PHYSICAL AND ANALYTICAL DATA FOR THE $[Fe_4(\mu_4\text{-}\eta^3\text{-}C(CH_3)C(R_1)C(R_2)(\mu\text{-}CO)_2(CO)_9]$ COMPLEXES

Complex	Reaction time (h)	Yield (%)	M.p. (°C)	Analysis (Found (calcd.) (%))	
				C [a]	H
$[Fe_4(\mu_4\text{-}\eta^3\text{-}C(CH_3)CHC(C(CH_3)_3))(\mu\text{-}CO)_2(CO)_9][P(C_6H_5)_4]$ (III)	6	30	122	52.95 (52.69)	3.39 (3.39)
$[Fe_4(\mu_4\text{-}\eta^3\text{-}C(CH_3)CHC(C_6H_5)(\mu\text{-}CO)_2(CO)_9][N(P(C_6H_5)_3)_2]$ (IV)	4	45	81	56.53 (57.09)	3.29 (3.28)
$[Fe_4(\mu_4\text{-}\eta^3\text{-}C(CH_3)C(CH_3)C(CH_3))(\mu\text{-}CO)_2(CO)_9][P(C_6H_5)_4]$ (V)	12	20	146	50.86 (51.73)	2.99 (3.07)
$[Fe_4(\mu_4\text{-}\eta^3\text{-}C(CH_3)C(CH_3)C(C_6H_5))(\mu\text{-}CO)_2(CO)_9][P(C_6H_5)_4]$ (VI)	6	25	145	53.28 (54.48)	3.10 (3.08)
$[Fe_4(\mu_4\text{-}\eta^3\text{-}C(CH_3)C(C_6H_5)C(C_6H_5))(\mu\text{-}CO)_2(CO)_9][P(C_6H_5)_4]$ (VII)	7	30	148	56.38 (56.92)	3.09 (3.09)

[a] Some of the samples gave systematic low carbon analysis perhaps due to formation of carbides.

were obtained with a Bruker WH90 instrument and ^{13}C NMR spectra on a Bruker WM250 machine. Microanalyses were carried out in our laboratory. The $[Fe_4(\mu_3\text{-}CCH_3)(CO)_{12}]^-$ anion associated either with the $[P(C_6H_5)_4]^-$ or $[(P(C_6H_5)_3)_2N]^+$ cations was prepared by a published procedure [1].

General method of synthesis of the $[Fe_4(\mu_4\text{-}\eta^3\text{-}C(CH_3)C(R_1)C(R_2)(\mu\text{-}CO)_2(CO)_9]^-$ *anions*

A slight excess of the alkyne was added to a solution of $[Fe_4(\mu_3\text{-}CCH_3)(CO)_{12}][P(C_6H_5)_4]$ or $[Fe_4(\mu_3\text{-}CCH_3)(CO)_{12}]$ $[(P(C_6H_5)_3)_2N]$ (1 g) dissolved in 3-pentanone and the mixture was heated under reflux. At the end of the reaction, the solvent was evaporated to dryness under vacuo and the residue dissolved in 10 cm^3 of methanol. Cooling to −20°C gave crystals of the black complexes. Reaction time, yield, analysis and physical properties are listed in Table 1.

Results and discussion

Complex I reacts quite readily with the various alkynes in boiling 3-pentanone to give reasonable yields of the $[Fe_4C(CH)_3C(R)C(R')(CO)_{11}]^-$ (III–VII) anions, associated in most cases with the $[P(C_6H_5)_4]^+$ cation. For complex IV only, the $[N(P(C_6H_5)_3)_2]^+$ cation was retained because it makes the isolation easier.

Infrared spectra of the isolated products (Table 2) in the ν(CO) stretching region are very similar, and closely resemble those of II, the X-ray structure of which has been determined [1]. It consists of an allylic fragment $C(CH_3)CHCH$ $\mu_4\text{-}\eta^3$ bonded to a butterfly core formed by the four iron atoms (Fig. 1). The only noticeable differences in the infrared spectra of these compounds involve the expected shift toward lower wave number with the increasing electron-donor properties of the R^1 and R^2 groups of the alkynes.

TABLE 2

ν(CO) STRETCHING FREQUENCIES (cm^{-1}) AND ^{1}H NMR DATA (δ (ppm)) FOR THE $[Fe_4(\mu_4\text{-}\eta^3\text{-}C(CH_3)C(R)C(R'))(\mu\text{-}CO)_2(CO_9)]^-$ COMPLEXES

Complex	IR (in CH_2Cl_2)	^{1}H NMR data (in $(CCD_3)_2CO$)		
		$\delta(CH_3)$	δ(R)	δ(R′)
III	2031m, 1971vs, 1924m, 1800sh, 1789w	2.41	7.41	1.81
IV	2036m, 1974vs, 1924m, 1800sh, 1789w	2.38	7.21	–
V	2031m, 1969vs, 1924m, 1803sh, 1785w	3.03	2.98	3.03
VI	2034m, 1974vs, 1922m, 1799sh, 1784w	2.55	2.30	–
		2.89	–	2.89
VII	2036m, 1977vs, 1927m, 1800sh, 1784w	1.97		

This close similarity of the infrared spectra allows the complexes III–VII to be assigned the same structure as II (Fig. 1), with a $C(CH_3)C(R)C(R')$ dimetallo-allylic fragment. The precise nature of this fragment for the isolated complexes was deduced from the ^{1}H and ^{13}C NMR data. More specifically, the nature of the group in position 2 was determined by comparison with the data for II. The ^{1}H and ^{13}C NMR data are listed in Tables 2 and 3, respectively. In the case of the products isolated with symmetrical alkynes V ($R = CH_3$) and VII ($R = C_6H_5$) this attribution is straightforward.

The ^{1}H NMR spectrum of V shows two resonances in a 2/1 intensity ratio. This first resonance is broad, and is attributed to the CH_3 and $R' = CH_3$ groups. In the ^{13}C NMR spectrum, one singlet is also observed for these two groups, at 38.5 ppm, with another methyl resonance at 25.3 ppm for the $R = CH_3$ group. The other signals noted, except for the phenyl resonances of the cation and the carbonyl resonances, are attributed to the carbon atom in position 2 (98.7 ppm) and to the carbon atoms in positions 1 and 3 (221.6 and 218.4 ppm). One broad signal only is observed for the carbonyl resonances: it is centred at 214.2 ppm and is consistent with the fluxional nature of these complexes in solution [1].

For VII, the ^{13}C resonance of the carbon in position 2 was not observed, and is possibly obscured by the phenyl resonances of the cation, but apart from this the NMR data are in good agreement with the formulation.

Two situations were encountered for the products obtained with the unsymmetrical alkynes: in one only one isomer was detected (complexes III and IV) and in the other two isomers were identified (complex VI).

Thus in the case of complexes III and IV, only one resonance was observed for

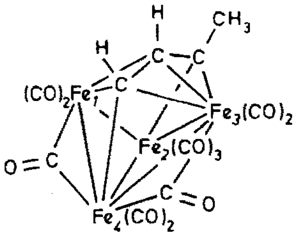

Fig. 1. Structure of complex II.

TABLE 3

^{13}C NMR DATA (δ (ppm)) FOR THE $[Fe_4(\mu_4\text{-}\eta^3\text{-}C^1(CH_3)C^2(R)C^3(R'))(\mu\text{-}CO)_2(CO)_9]^-$ COMPLEXES (in CD_2Cl_2)

Complex	CO [a]	C^1	C^2	C^3	R	R'	CH_3
III	217.9	218.5	96.4 (*J* 168.5 Hz)	-	-	37.4	39.1
IV	216.4	218.5	99.9 (*J* 178.2 Hz)	157.2	-	-	36.9
V	214.2	221.6 or 218.4	98.7	221.6 or 218.4	25.3	38.5	38.5
VIa	208	218.4	-	157.9	26.07		38.3
VIb		216		216 or 218.4			or 35.6
VII	214	215.7	-	152.8	-	-	36.0

[a] Broad resonance.

the CH group in the ^{1}H and ^{13}C NMR spectra. Furthermore, the chemical shifts of the ^{13}C resonance of this group (96.4 ppm for III and 99.9 ppm for IV) compare well with those observed for the CH group in position 2 for II (92.6 ppm) and so the allylic fragment is $C(CH_3)CHCR'$ in both cases. The present of one single isomer is confirmed by the observation of a single resonance for the $C(CH_3)$ groups in both cases.

For complex VI, three signals are observed for the methyl groups in the proton NMR spectrum, in the intensity ratio 0.6/1/1, with a broad resonance at 2.89 ppm as the first signal. This indicates that VI is a mixture of two isomers, involving the allylic fragments $C(CH_3)C(CH_3)C(C_6H_5)$ (VIa) and $C(CH_3)C(C_6H_5)C(CH_3)$ (VIb). By comparison with the data obtained for V, the broad resonance at 2.89 ppm is attributed to the methyl groups of isomer VIb in positions 1 and 3. The ^{13}C NMR data for VI (Table 3) are in agreement with this hypothesis, but the resonance of the carbon atom of isomer VIa in position 2 was not observed.

To summarize, complex I reacts quite readily with alkynes $RC{\equiv}CR'$ to give the complexes $[Fe_4(\mu_4\text{-}\eta^3\text{-}C(CH_3)C(R)C(R')(\mu\text{-}CO)_2(CO)_9]^-$, in which the metalla-allylic fragment results from the coupling of the ethylidyne ligand of I with the alkyne. For the monosubstituted alkynes only one isomer was detected, with R = H; this contrasts with the results obtained during the reaction of the clusters $H_3Ru_3(\mu_3\text{-}CX)(CO)_9$ with monosubstituted alkynes for which both isomers were detected in most cases [3]. However, in the case of $CH_3C{\equiv}CC_6H_5$ we detected the two possible isomers. This suggests that steric interactions are important in determining the regiochemistry of the reaction: when the two substituents R and R' have very different steric properties, only one isomer is observed, with the less encumbered group occupying position 2 of the allylic fragment. This effect seems more pronounced for these tetranuclear clusters than that observed with the di- [8] or tri-nuclear [3] complexes.

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