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REACTIVITY OF DI- AND TRI-NUCLEAR ANIONIC IRON COMPLEXES DERIVED FROM DIPHENYLACETYLENE TOWARD ELECTROPHILES

RAMON YANEZ, JOSEP ROS,

Departament de Quimica Inorganica, Facultat de Ciencies, Universitat Autonoma de Barcelone, Cerdanyola, Barcelona (Spain)

RENÉ MATHIEU and JOAN SUADES

Laboratoire de Chimie de Coordination du CNRS, Unité no. 8241 liée par convention à l'Université Paul Sabatier, 205 route de Narbonne, 31400 Toulouse (France)

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Summary

The anionic complexes $[Fe_3(CO)_{10}(\mu_2\text{-}C(C_6H_5)C(C_6H_5)H]^-$ (III), $[HFe_3(CO)_9(\mu_3\text{-}C(C_6H_5)C(C_6H_5)]^-$ (IV) and $[Fe_2(CO)_6(\mu_2\text{-}CO)(\mu_2\text{-}C(C_6H_5)C(C_6H_5)H)]^-$ (V) reacts with CF_3COOH or the trityl cation to give the known complex $Fe_2(CO)_6(C_6H_5)CC(C_6H_5)$ (I). Complex IV reacts with triethyloxonium tetrafluoroborate at room temperature to give $Fe_3(CO)_9(\mu_3\text{-}C(C_6H_5)C(C_6H_5))$ (II). Complexes I and II were also obtained in fair yield by treatment of V and IV, respectively, with $AgClO_4$. The behaviour of $[HFe_3(CO)_9(\mu_3\text{-}C(CH_3)C(CH_3))]^-$ (VI) toward the same electrophiles was also examined for comparison and the results suggest that the $[HFe_3(CO)_9RCCR]^-$ anions may be good precursors for the synthesis of $Fe_3(CO)_9(RCCR)$ complexes.

Introduction

Alkynes react with iron carbonyls to give a great variety of compounds [1]. These reactions are complex, and depend on the nature of the alkynes and of the reaction conditions [2–5], and there is no general way of obtaining only monoalkyne iron carbonyl complexes. Among di- and tri-nuclear iron carbonyl complexes with diphenylacetylene, "$Fe_2(CO)_6(C_6H_5)CC(C_6H_5)$" [6] and $Fe_3(CO)_9(\mu_3\text{-}C(C_6H_5)C(C_6H_5))$ (II) [7] represent different modes of bonding between the alkynes and the iron centres. The former contains a ferraindene system and the latter an unusual $\mu_3\text{-}\eta^2$ ($\perp$) mode of bonding. Both I and II can be synthesized from $Fe(CO)_5$, $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$, showing the extraordinary capability of diphenylacetylene to acquire $Fe(CO)_3$ fragments.

It has been recently shown that anionic clusters such as $[Fe_3(CO)_{10}(\mu_2\text{-}$

$C(C_6H_5)C(C_6H_5)H]$ (III), $[HFe_3(CO)_9(\mu_3\text{-}C(C_6H_5)C(C_6H_5)]^-$ (IV) and $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}C(C_6H_5)C(C_6H_5)H]$ (V) are readily obtained by treatment of $[HFe_3(CO)_{11}]^-$ with diphenylacetylene [8]. In view of the anionic nature of these complexes it seemed of interest to examine their reactivities toward electrophiles, and so we have studied the reactions of III, IV and V with the electrophilic reagents H^+, $C_2H_5^+$, $C(C_6H_5)_3^+$ and Ag^+. The behaviour of $[HFe_3(CO)_9(\mu_3\text{-}C(CH_3)C(CH_3)]^-$ (VI) toward proton acids and $C_7H_7^+$ has also been checked for comparison.

Results and discussion

In the case of the dinuclear anionic complex V, we have recently shown that the triethyloxonium tetrafluoroborate gives the neutral complex $Fe_2(CO)_6(\mu_2\text{-}COC_2H_5)(\mu_2\text{-}C(C_6H_5)C(C_6H_5)H)$ (VII) [9] (an expected reaction when bridging carbon monoxide is present in an anionic complex [10]). Complex V also reacts under mild conditions with CF_3CO_2H or trityl cation although in a different way, both electrophiles giving the same product in reasonable yield; this product has been identified by IR and mass spectrocopy as $Fe_2(CO)_6((C_6H_5)CC(C_6H_5))$ (I). As the two electrophiles are very different, two different mechanisms are involved in the attack on the anionic complex V.

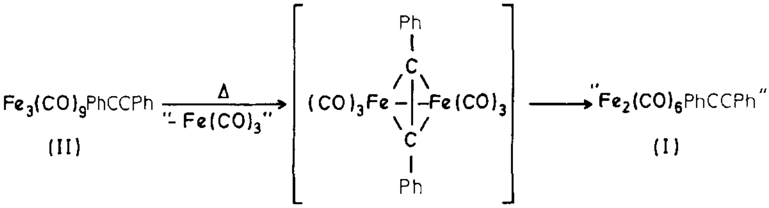
By comparison with polynuclear iron complexes containing bridging carbonyl [10] we may assume that the proton of the acid first attacks the bridging CO in V, leading to an unstable intermediate complex "$Fe_2(CO)_6(\mu_2\text{-}COH)(\mu\text{-}C(C_6H_5)C(C_6H_5)H)$" with a similar structure to that of VI, and this then loses CO and H_2 to give the known complex I. Similar behaviour has been observed for the reaction of $[HFe_3(CO)_{11}]^-$ with acids at low temperature, in which the protonated complex $HFe_3(CO)_{10}(\mu_2\text{-}COH)$ first formed decomposes above −30°C [11].

The trityl ion probably attacks the 1,2-diphenylethenyl ligand to abstract the vinyl hydrogen of the anionic complex V. The ferraindene complex I is then formed by elimination of one molecule of CO and triphenylmethane.

Quite unexpectedly, the neutral complex VIII also reacts readily with CF_3COOH to give the same complex I. This reactivity is probably due to the residual nucleophilic character of oxygen in the ethoxycarbyne bridge, giving rise to a similar situation as for V.

Another way of obtaining I starts from the trinuclear hydride complex IV; reaction of IV with triethyloxonium tetrafluoroborate or $C(C_6H_5)_3^+$ gave the neutral complex I, but under mild conditions only the trinuclear complex II was obtained. These findings suggest that II may be formed by removal of one hydride ligand by the electrophilic reagents. Thus the formation of I must be the second step, involving decomposition of the trinuclear unit.

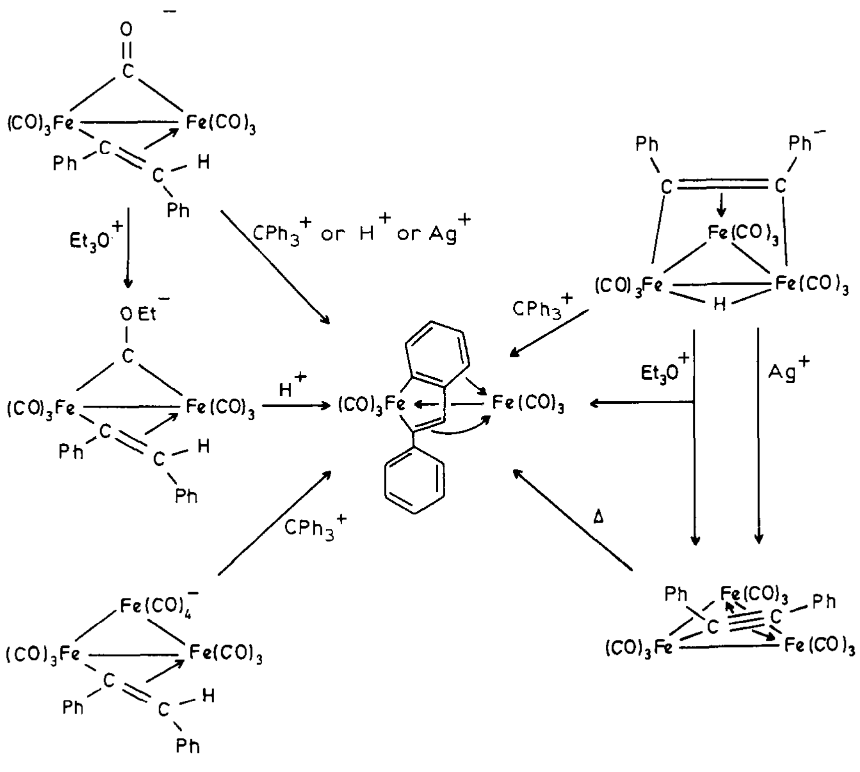
The decomposition of II to I was confirmed. Thus when II was refluxed in benzene, the neutral dinuclear complex I was slowly formed by break up of the triiron unit. A possible mechanism for the transformation of II into I is presented in Scheme 1. A similar type of intermediate was proposed for the reaction involved in the synthesis of $Fe_2Ru(CO)_9(RCCR)$ complexes [12]. Unexpectedly, we observed the same transformation when II was stirred with $C(C_6H_5)_3^+$ in dichloromethane at room temperature, but when CF_3COOH or $C_2H_5^+$ is used at room temperature no appreciable reaction occurs.



SCHEME 1

For comparison with the behaviour of IV, which seems to be due to the high stability of I, we examined the reactivity of VI which has a similar structure as IV but with 2-butyne as the alkyne. Protonation of VI gives the dihydride $H_2Fe(CO)_9(CH_3CCCH_3)$ (VIII) as the main product along with the analogue of II, $Fe_3(CO)_9(CH_3CCCH_3)$ (IX). The latter is obtained in fair yield when tropylium tetrafluoroborate is used instead of the trityl iron. Moreover IX is stable and recovered unchanged after 18 h in boiling hexane. This seems to confirm that the behaviour observed for IV is due to the specific reactivity of diphenylacetylene in this case.

A better way to convert the anionic complexes IV and V into the neutral complexes I and II involves chemical oxidation by the silver cation: when IV and V



SCHEME 2

are treated with $AgClO_4$, the conversions of IV to I and V to II take place readily in good yield.

Finally, the reaction of the $[Fe_3(CO)_{10}(\mu_2\text{-}C(C_6H_5)C(C_6H_5)H]^-$ (III) with $C(C_6H_5)_3^+$ at room temperature was examined; the ferraindene complex I was isolated as the only product.

The observations are summarized in Scheme 2.

Conclusion

This study has shown that "$Fe_2(CO)_6(C_6H_5)CC(C_6H_5)$" (I) and $Fe_3(CO)_9(C_6H_5)CC(C_6H_5)$ (II) are readily formed from anionic diphenylacetylene di- or tri-iron complexes by reaction with electrophiles. Complex I is obtained in all the reactions, but when the conditions are mild some complex II is isolated. All the results suggest that I is more stable than II, and that II is converted into I. If an oxidizing agent such as Ag^+ is used the trinuclear cluster unit is preserved. These reactions open a new route to synthesis of the alkyne-iron complexes I and II, which by currently used methods are obtained mixed with other iron complexes. The reactions also seem to provide a good procedure for synthesis of other $Fe_3(CO)_9(\mu_3\text{-}RCCR)$ complexes.

Experimental

All reactions were performed under nitrogen. The ^1H NMR spectra were recorded on a Bruker WM80 spectrometer. Infrared spectra were recorded on a Beckman IR20A or on a Perkin–Elmer 225 spectrometer in cyclohexane solutions using NaCl cells. Mass spectra were measured on a Varian MAT 311A spectrometer. The complexes $[HFe_3(CO)_{11}][P(C_6H_5)_4]$, $[Fe_3(CO)_{10}(C(C_6H_5)C(C_6H_5)H][P(C_6H_5)_4]$, $[Fe_2(CO)_7(C(C_6H_5)C(C_6H_5)H)][P(C_6H_5)_4]$, $Fe_2(CO)_6(COC_2H_5)(C(C_6H_5)C(C_6H_5)H)$, and $[HFe_3(CO)_9(CH_3CCCH_3)][P(C_6H_5)_4]$ were prepared by published procedures [8,9,13].

Reaction of $[Fe_2(CO)_7(C(C_6H_5)C(C_6H_5)H)][P(C_6H_5)_4]$ *(V) with* CF_3COOH

A stoichiometric amount of CF_3COOH was added to a solution of V in dichloromethane. After 1 h sitrring the solution was evaporated to dryness and the residue was extracted with pentane. After evaporation of the extract the crude product was chromatographed over silicagel. Elution with hexane and crystallization from pentane gave I in 20% yield.

IR $\nu(CO)$: 2069m, 2034s, 2002m, 1996m, 1930w cm^{-1}. Mass spectrum $m/z = 458$.

Reaction of $[Fe_2(CO)_7(C(C_6H_5)C(C_6H_5)H)][P(C_6H_5)_4]$ *(V) with* $[C(C_6H_5)_3]BF_4$

A solution of a 1 : 1 mixture of V and $[C(C_6H_5)_3]BF_4$ in the minimum amount of dichloromethane was stirred for 2 h at room temperature. The solvent was then evaporated to dryness and the residue was extracted with pentane. Crystallization from a minimum amount of pentane gave I in 55% yield.

Reaction of $Fe_2(CO)_6(COC_2H_5)(C(C_6H_5)C(C_6H_5)H)$ *(VII) with* CF_3COOH

An excess of CF_3COOH was added to a solution of VII in dichloromethane at room temperature. The solution was stirred for 1 h and then evaporated to dryness.

The residue was crystallized from a minimum amount of pentane to give I in 65% yield.

Reaction of $[HFe_3(CO)_9(C(C_6H_5)C(C_6H_5))][P(C_6H_5)_4]$ *(IV) with* $[(C_2H_5)_3O]BF_4$ *at room temperature*

A solution of a 1/1 mixture of VI and $[(C_2H_5)_3O]BF_4$ in a minimum amount of dichloromethane was stirred for 12 h at room temperature then evaporated to dryness. The residue was extracted with pentane. After evaporation of the extract under reduced pressure, the residue was chromatographed over silicagel. Elution with hexane gave I (15% yield) and II (5% yield).

IR ν(CO) for II: 2082m; 2042s; 2026s, 2010m, 1995w. $m/z = 598$.

Reaction of $[HFe_3(CO)_9(C(C_6H_5)C(C_6H_5))][P(C_6H_5)_4]$ *(IV) with* $[(C_2H_5)_3O]BF_4$ *in refluxing acetone*

A solution of a 1 : 1 mixture of IV and $[(C_2H_5)_3O]BF_4$ in acetone was refluxed for 2 h then evaporated to dryness. The residue extracted with pentane. Crystallization from this solvent gave I in 32% yield.

Reaction of $[HFe_3(CO)_9(C(C_6H_5)C(C_6H_5))][P(C_6H_5)_4]$ *(IV) with* $[(C_6H_5)_3C]BF_4$

A 1 : 1 mixture of IV and $[(C_6H_5)_3C]BF_4$ was dissolved in a minimum amount of dichloromethane at room temperature. The solution was stirred for 1 h then evaporated to dryness and the residue extracted with pentane. Crystallization from pentane gave I in 30% yield.

Reaction of $[HFe_3(CO)_9(C(C_6H_5)C(C_6H_5))][P(C_6H_5)_4]$ *(IV) with* $AgClO_4$

A solution of $AgClO_4$ (0.23 g, 1.3 mmol) in benzene was added with stirring to a solution of IV (1.2 g, 1.3 mmol) in dichloromethane/benzene (5/1). After 15 min stirring the solvent was evaporated to dryness and the crude product was extracted with hexane. Crystallization from this solvent gave II in 25% yield.

Reaction of $[Fe_3(CO)_{10}(C(C_6H_5)C(C_6H_5)H)][P(C_6H_5)_4]$ *(III) with* $[(C_6H_5)_3C]BF_4$

A stoichiometric mixture of III and $[(C_6H_5)_3C]BF_4$ was dissolved in the minimum amount of dichloromethane at room temperature. After 6 h stirring the solution was evaporated to dryness. The residue was extracted with pentane, and crystallization from this solvent gave I in 25% yield.

Reaction of $[HFe_3(CO)_9CH_3CCH_3][P(C_6H_5)_4]$ *(VI) with* CF_3COOH

A threefold excess of CF_3COOH was added to a solution of VI in dichloromethane. The solution was stirred for 1 h, then evaporated to dryness. The residue was extracted with pentane. Chromatography on Florisil gave two products, VIII, and IX, in 40 and 20% yield, respectively.

$H_2Fe_3(CO)_9(CH_3CCCH_3)$ *(VIII).* IR ν(CO): 2091m, 2055s, 2037vs, 2023s, 2000s, 1997sh cm^{-1}. ^1H NMR (C_6D_6 solution): 2.20 (CH_3), -22.47 (H) ppm. Mass spectrum: $m/z = 476$.

$Fe_3(CO)_9(CH_3CCCH_3)$ *(IX).* IR ν(CO): 2083m, 2031s, 2007s, 1997m, 1992m, 1973w cm^{-1}. Mass spectrum: $m/z = 474$.

Reaction of $[HFe_3(CO)_9CH_2CCH_3][P(C_6H_5)_4]$ *(VI) with* $C_7H_7BF_4$

A mixture of VI with a slight excess of $C_7H_7BF_4$ was stirred for 1 h in CH_2Cl_2 solution. The resulting solution was evaporated to dryness and then extracted with pentane. Chromatography on Florisil gave trace amounts of VIII and IX, which were isolated by crystallization from pentane (45% yield).

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