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Carbon–Hydrogen Bond Activation in Novel Cyclopentadienyl Acetylenic Carbonyl Clusters of Iron, Ruthenium and Nickel

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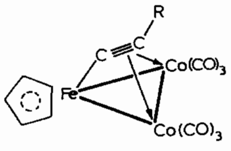
Condensation of $(\pi\text{-}C_5H_5)_2Ni_2(HC_2Me)$ with $Fe_3(CO)_{12}$ leads to two novel complexes, $Fe_2(CO)_7(\pi\text{-}C_5H_5)Ni(CEt)$ and $Fe_2(CO)_6(\pi\text{-}C_5H_5)Ni(C_2Me)$ based on a Fe_2Ni core; intramolecular and intermolecular hydrogen shifts account for the reduction of the triple bond in one case and for the dehydrogenation of the alkyne in the second. The tetranuclear cluster $Fe_2(CO)_6(\pi\text{-}C_5H_5)_2Ni_2(C_2Et_2)$ is the main product of the reaction of $[(\pi\text{-}C_5H_5)Ni(CO)]_2$ with $Fe_3(CO)_9C_2Et_2$. Cyclopentadiene reacts with $HRu_3(CO)_9C_2Bu^t$ affording $(\pi\text{-}C_5H_5)Ru_3(CO)_8(CCH_2Bu^t)$; also in this case the triple bond is hydrogenated and an apical carbon triply bridging the Ru_3 unit is formed. Structures are proposed on i.r., mass spectra and ^1H n.m.r. evidence.

Introduction

Reactions of metal acetylides containing a cyclopentadienylic ligand η bonded to the metal atom with binuclear metal carbonyls usually afford condensation products still containing the cyclopentadienyl and in which the acetylene is bonded as a $\mu_3\text{-}\eta^2$ C_2R group [1]. Thus, $(\pi\text{-}C_5H_5)(CO)_2Fe(C_2R)$ reacts with $Co_2(CO)_8$ or with $Fe_2(CO)_9$ to give respectively $(\pi\text{-}C_5H_5)FeCo_2(CO)_6(C_2R)$ (I) and $(\pi\text{-}C_5H_5)Fe_3(CO)_7(C_2R)$ (II) [2]; the latter complex is also obtained by reacting the dimeric $[\{Fe(CO)_2(\pi\text{-}C_5H_5)(C_2Ph)\}CuCl]_2$ with $Fe_2(CO)_9$ [3] and its structure has been determined by an X-ray analysis [4]. Mixed trinuclear clusters, cyclopentadienyl substituted and containing a $\mu_3\text{-}\eta$ acetylene were also obtained from the reaction of $(\pi\text{-}C_5H_5)_2Ni$ and $Fe(CO)_5$ in presence of diphenylacetylene, or from the reaction of iron carbonyls and $(\pi\text{-}C_5H_5)_2Ni_2(HC_2Ph)$ [5]; the same reactions yield $Fe_2(CO)_6(\pi\text{-}C_5H_5)_2Ni_2(C_2RR')$ tetranuclear derivatives (III).



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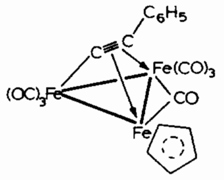

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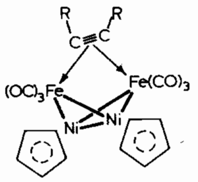

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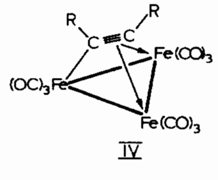

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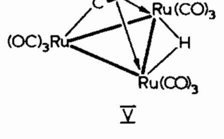

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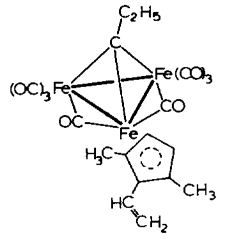


VI

Complexes in which C_2R or C_2R_2 groups are μ_3-η^2 bonded to the metallic core are also obtained by reacting the $M_3(CO)_{12}$ carbonyls (M = Fe, Ru) with alkynes, $Fe_3(CO)_9C_2R_2$ (IV) [6] and $HRu_3(CO)_9C_2R$ (V) [7]. When M = Fe, derivatives in which the cyclo-oligomerization of the alkynes leads to co-ordinated cyclopentadienylic groups are obtained, as $Fe_2(CO)_6(C_2H_2)_3$ (deep red isomer) [8] and $Fe_3(CO)_8(HC_2Me)_4$ (VI) [9]. In the latter compound, formed from $Fe_3(CO)_{12}$ and propyne, is noteworthy also an apical CCH_2CH_3 group bridging the three iron atoms similarly as in the $Co_3(CO)_9CR$ [10] and $H_3M_3(CO)_9CR$ (M = Ru, Os) [11] derivatives.

Thus, the activation of the carbon–hydrogen bond of the alkyne is promoted in some cases by the metallic unit. We have further investigated this feature together with the reactivity of co-ordinated acetylenic groups by reacting $HRu_3(CO)_9(C_2Bu^t)$ [7] with cyclopentadiene, $(\pi\text{-}C_5H_5)_2Ni_2(HC_2Me)$ with $Fe_3(CO)_{12}$, and $[(\pi\text{-}C_5H_5)Ni(CO)]_2$ with $Fe_3(CO)_9(C_2Et_2)$ [6].

Experimental

All reactions were carried out in an atmosphere of nitrogen. Solvents (n-heptane and benzene) were dried over molecular sieves. Dodecacarbonyltriiron was prepared according to the literature [12]. Separations of the reaction mixtures were performed by TLC, absorbent Kieselgel PF Merck, eluents mixtures of petroleum ether and diethylether; the compounds were crystallyzed by n-heptane at 0 °C.

Elemental analyses were performed by means of an F. & M. 187 Model C,H,N Analyzer and of a 303 Model Perkin Elmer Atomic Absorption Spectrophotometer. Infrared spectra were recorded on a double beam Beckman IR-12 with KBr optics and with carbon monoxide as calibrant. ^1H n.m.r. spectra (CCl_4 solution) were registered on a JEOL 60 HL instrument. The mass spectra were registered on a Varian CH-5 single-focusing instrument equipped with direct inlet system and electron impact ion source, operating at 70 and 10 eV; all the spectra were registered at the lowest possible temperatures.

Reactions of $Fe_3(CO)_{12}$ with $(\pi\text{-}C_5H_5)_2Ni_2(HC_2CH_3)$

The acetylenic cyclopentadienyl derivative of nickel was obtained by literature methods [13]. Equimolecular amounts of the iron carbonyl (1.0 g, 2 m*M ca.*) and of bis-cyclopentadienylpropynedinickel (550 mg, 2 m*M ca.*) were refluxed in benzene for 30 min. After cooling, the solution was filtered and the solvent removed under reduced pressure. The residue was extracted with CCl_4 and separated by TLC to give $Fe_2(CO)_6Ni(\pi\text{-}C_5H_5)(C_2Me)$(VII), grey–violet prismatic crystals, and $Fe_2(CO)_7(\pi\text{-}C_5H_5)Ni(CEt)$ (VIII), grey–violet needles.

Anal. Calcd for $C_{14}H_8Fe_2NiO_6$ (VII); C% 37.99, H% 1.82, Fe% 25.23, Ni% 13.26, O% 21.69. Found: C% 38.04, H% 1.88, Fe% 25.57, Ni% 13.80, O% 20.71. I.r. spectrum (n-heptane solution); 2060 s, 2020 vs, 1990 s, 1982 s(sh), 1968 m, cm^{-1}. ^1H n.m.r. (τ): 4.80 s (5H), 7.94 s (3H). Mass spectrum, m/e 442, M^+. Calcd for $C_{15}H_{10}Fe_2NiO_7$ (VIII): C% 38.12, H% 2.13, Fe% 23.63, Ni% 12.42, O% 23.70. Found: C% 38.15, H% 2.22, Fe% 23.44, Ni% 12.36, O% 23.83. I.r. spectrum (n-heptane solution): 2070 s, 2036 vs, 2012 s, 1986 m, 1974 m, 1754 m–w, cm^{-1}. ^1H n.m.r. (τ): 4.85 s (5H), 5.75 q (2H), 8.25 t (3H). Mass spectrum, m/e 472, M^+.

Reactions of $Fe_3(CO)_9C_2Et_2$ and $(\pi\text{-}C_5H_5)_2Ni_2(CO)_2$

The nickel derivative was obtained by literature methods [14] and the iron acetylenic carbonyl by refluxing in n-heptane $Fe_3(CO)_{12}$ and hex-3-yne [15] and was crystallized from n-heptane. Equimolecular amounts of $Fe_3(CO)_9C_2Et_2$ (500 mg, 1 m*M ca.*) and of $(\pi\text{-}C_5H_5)_2Ni_2(CO)_2$ (300 mg, 1 m*M ca.*) were refluxed in n-heptane for 40 min; a metallic mirror was deposited on the walls of the reaction vessel. The extraction of the residue gave as main product $Fe_2(CO)_6(C_2Et_2)(\pi\text{-}C_5H_5)_2Ni_2$ (IIIa).

Anal. Calcd for $C_{22}H_{20}Fe_2Ni_2O_6$: C% 43.35, H% 3.31, Fe% 18.32, Ni% 19.26, O% 15.75. Found: C% 43.38, H% 3.46, Fe% 18.51, Ni% 19.18, O% 15.47. I.r. spectrum (n-heptane solution): 2020 m (broad), 2000 vs, 1956 s (broad) cm^{-1}. Mass spectrum, m/e 608, M^+.

Reaction of $HRu_3(CO)_9C_2Bu^t$ with Cyclopentadiene

The acetylenic hydrido carbonyl of ruthenium was prepared as already reported [7]. The cyclopentadiene (Fluka) was distilled and used without further purification. $HRu_3(CO)_9C_2Bu^t$ (600 mg, 1 m*M ca.*) was refluxed with 1 ml of cyclopentadiene in n-heptane for 24 hours. The extraction of the residue gave, besides some unreacted $HRu_3(CO)_9C_2Bu^t$, six products in very small yields. One of them has been identified as $(\pi\text{-}C_5H_5)Ru_3(CO)_8(CCH_2CMe_3)$ (IX), yellow–orange solid.

Anal. Calcd for $C_{19}H_{16}O_8Ru_3$: C% 33.69, H% 2.38, O% 18.89, Ru% 45.04. Found: C% 33.75, H%

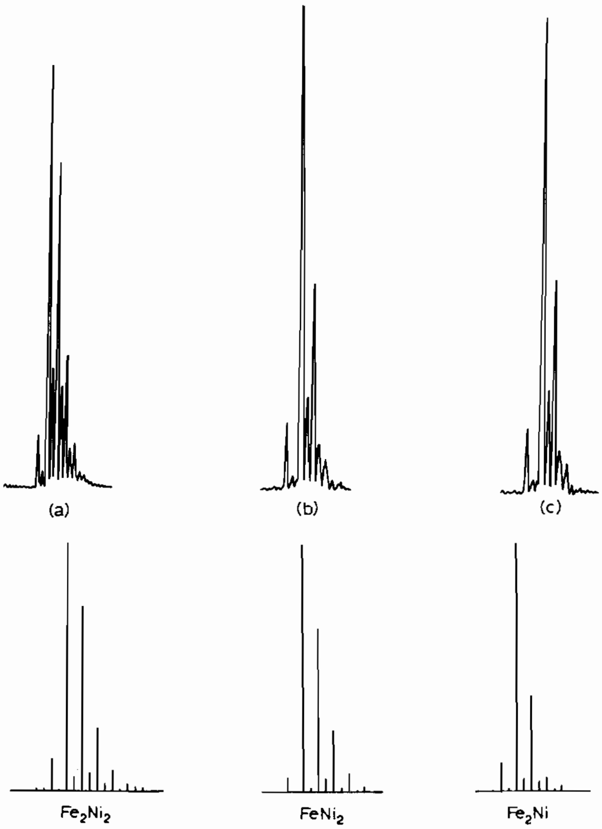


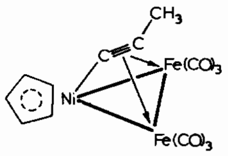
Figure 1. Observed isotopic patterns for $(\pi\text{-}C_5H_5)_2Ni_2Fe_2(CO)_6(C_2Et_2)$ (a), $Fe_2(CO)_7(\pi\text{-}C_5H_5)Ni(CEt)$ (b), and $Fe_2(CO)_6(\pi\text{-}C_5H_5)Ni(C_2Me)$ (c) (top); calculated isotopic patterns (bottom).

2.41, O% 18.78, Ru% 45.06. I.r. spectrum (n-heptane solution): 2070 s, 2054 vs, 2025 vs(sh), 2018 vs, 1966 s, 1868 m, 1848 m, cm^{-1}; ^{1}H n.m.r. (τ): 4.65 s (5H), 6.70 s (2H), 8.55 s (9H). Mass spectrum, m/e 678, M^+.

Results and Discussion

The above compounds were mainly characterized on the basis of their mass spectra. For the mixed iron–nickel derivatives, different attributions were possible, as iron and nickel have close m/e values. Thus, the isotopic patterns for Fe_2Ni, $FeNi_2$ and Fe_2Ni_2 were calculated; the observed and calculated patterns are reported in Figure 1. It appears that the trinuclear derivatives are Fe_2Ni clusters and that the tetranuclear one is Fe_2Ni_2. Thus evidence is achieved that, in the formation of the trinuclear derivatives cleavage of both the Fe–Fe and Ni–Ni bonds of the starting products occurs.

The mass spectrum of $Fe_2(CO)_6(\pi\text{-}C_5H_5)Ni(C_2Me)$ (VII) shows the parent ion, stepwise loss of the CO groups, then easy loss of one iron atom, as already observed in other μ_3-η^2-alkyne containing iron carbonyls, like $Fe_3(CO)_9C_2Et_2$ [16]; the fairly abundant $(\pi\text{-}C_5H_5)NiFe(C_2Me)^+$ ion contains a FeNi ensemble isoelectronic with the Co_2 ensemble in $Co_2(CO)_6(C_2R_2)$ [17]. The i.r. spectrum shows for the carbonyls absorptions only in the region of the terminal CO's. The signals in the ^{1}H n.m.r. spectrum are in the region normally found for cyclopentadienyl group η bonded to a metal and for a methyl bonded to an η^2 bridging alkyne. On this evidence we propose for VII a structure with the alkyne η^2 bridging two $Fe(CO)_3$ units and σ bonded to the $(\pi\text{-}C_5H_5)Ni$ moiety. This structure, which satisfies the E.A.N. rule, is closely related to those determined for $(\pi\text{-}C_5H_5)Fe_3(CO)_7(C_2Ph)$ (II) [4] and $HRu_3(CO)_9C_2Bu^t$ (V) [18].



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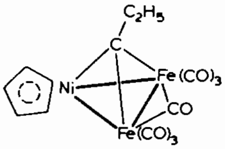

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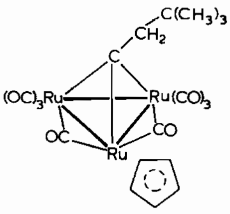

IX

The mass spectrum of $Fe_2(CO)_7(\pi\text{-}C_5H_5)Ni(CEt)$ (VIII) shows the parent ion, loss of seven CO groups, one of which more tightly bound, as shown by the intensity of the $(\pi\text{-}C_5H_5)NiFe_2(CO)(C_3H_5)^+$ ion. This is in agreement with the observation in the i.r. spectrum of a band in the region of bridging CO. Further the compound loses a Fe atom to give mixed bimetallic ions. Besides the resonance of the cyclopentadienyl group, those typical of an ethyl group are observed in the ^{1}H n.m.r. spectrum, indicating that reduction of the triple bond occurs. The resonances of the methylene group (τ 5.75) and, to a lesser extent, of the methyl group (τ 8.25) are at lower field than normally observed for these moieties. It has been shown by ^1H and ^{13}C n.m.r. that the resonances of the carbon triply bridging the Co atoms in the $Co_3(CO)_9CR$ complexes are highly deshielded and that this effect is transmitted to the substituents R [19]. According to the above results and to the E.A.N. rule structure VIII is suggested with an apical carbon triply bridging a Fe_2-Ni core. This feature relates VIII with VI [9]. Thus $Fe_3(CO)_{12}$ is capable of the activation of the acetylenic bond either by reaction with free alkyne or by reaction with a μ_3-η^2 alkyne.

Condensation of nickel derivatives containing cyclopentadienyl ligand and HC_2R alkyne with the iron carbonyl affords either μ_3-η^2 containing alkyne derivatives, or apical C–R containing clusters, both still containing the cyclopentadienylic ligand. In the formation of VII and VIII the acetylenic hydrogen of the $(\pi\text{-}C_5H_5)_2Ni_2(HC_2Me)$ complex is activated, since in both cases the carbon atom bearing hydrogen of the HC_2Me entity forms at least one σ bond with a metal atom. Net intermolecular hydrogen transfer is suggested in the course of the reaction, since in VII a methyl is present, whereas in VIII an ethyl group is formed. Intramolecular hydrogen shift from H–C≡ to ≡C–Me is also required to explain the formation of the methylene group in VIII.

Spectroscopic evidence shows that the main product of the reaction of $Fe_3(CO)_9C_2Et_2$ with $[(\pi\text{-}C_5H_5)Ni(CO)]_2$, $(\pi\text{-}C_5H_5)_2Ni_2Fe_2(CO)_6(C_2Et_2)$ (IIIa) is homologue of the complexes III [5]. The alkyne is μ_3-η^2 bridging two $Fe(CO)_3$ units which are bridging a $(\pi\text{-}C_5H_5)_2Ni_2$ moiety. The formation of IIIa adds chemical evidence to the fragmentation observed in the mass spectrum of $Fe_3(CO)_9C_2Et_2$ [16], *i.e.* to the high intensity of the $Fe_2(CO)_6(C_2Et_2)^+$ ions. Noteworthy is the fragmentation in the mass spectrum of IIIa; the parent ion is observed, then loss of one iron atom before the relaese of the CO groups, as shown by isotopic pattern calculations (in the spectrum registered at 10 eV, the two fragmentation patterns become competitive, although the first prevails). Doubly charged ions, corresponding to the fragmentation with the loss of one iron atom, are also detected. This behaviour suggests that in the mass spectrometer, the tetranuclear derivatives are converted into a trinuclear species, in which the acetylene is likely to be triply bridging the cluster.

The mass spectrum of $(\pi\text{-}C_5H_5)Ru_3(CO)_8(CCH_2CMe_3)$ (IX) shows the parent ion, followed by stepwise loss of eight CO groups, the latter two peaks being more intense, as normally found for bridging CO's. The chemical shifts, the multiplicity and the integrated intensities of the ^1H n.m.r. spectrum suggest the presence in the molecule of a cyclopentadienyl group η bonded, of a methylene group and of a CMe_3 moiety. On these bases, structure IX is suggested with an apical triply bridging carbon atom, six terminal CO's and two CO's bridging $(\pi\text{-}C_5H_5)Ru$ with each $Ru(CO)_3$ moiety. The formation of the methylene group is accounted for assuming hydrogen transfer either from C_5H_6 and from the hydride to the acetylenic carbon of V bonded to Bu^t.

Acknowledgements

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