Preliminary communication

Cage expansion of alkyne clusters. An example of ligand assistance by alkyne substituents

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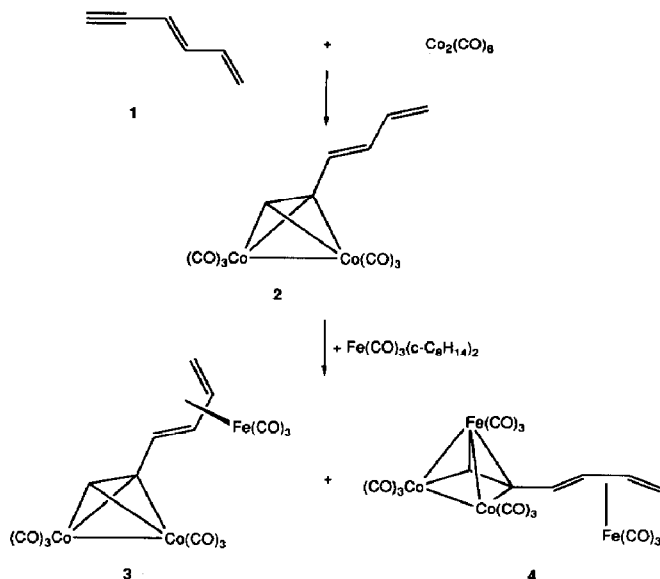rue Blaise Pascal, 67070 Strasbourg Cedex (France)*

Abstract

Starting from dicobalt hexacarbonyl complexes of ene-ynes or hetero-ene-ynes, $FeCo_2C_2$-clusters can be prepared in high yield by metal fragment condensation with (biscyclooctene)(tricarbonyl)iron. The reaction takes place at temperatures below $0\,°C$ and allows the introduction of terminal alkynes into the cluster framework. It has been shown that the ease of these reactions is due to the free double bond in α-position of the coordinated triple bond, thus providing direct evidence for a ligand-assisted cage expansion reaction, unprecedented in this field of chemistry. The crystal structure of a $FeCo_2C_2$-cluster bearing a chiral $Fe(CO)_3$-diene substituent has been determined.

During a study of the synthesis and properties of heterometallic complexes of conjugated diene-ynes [1] we have found a reaction which allows the construction of iron dicobalt alkyne cluster frameworks under very mild conditions and in high yields. Evidence is presented that C=X double bonds (X = C, O) conjugated with $Co_2(CO)_6$-coordinated alkynes exercise ligand assistance in the cage expansion reaction with an incoming iron tricarbonyl fragment. These results may serve as a basis for more systematic synthetic procedures directed towards $FeCo_2C_2$ and related cluster molecules. Since the discovery of the first $FeCo_2C_2$-cluster by Milone and Tiripicchio [2] some progress has been achieved in the synthesis of these

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Co$_2$(CO)$_8$

1

(CO)$_3$Co——Co(CO)$_3$

2

+ Fe(CO)$_3$(c-C$_8$H$_{14}$)$_2$

Fe(CO)$_3$

(CO)$_3$Co——Co(CO)$_3$

3

+

(CO)$_3$Co

Fe(CO)$_3$

Co(CO)$_3$

Fe(CO)$_3$

4

molecules, but in the main the reactions were restricted to simple and less reactive alkynes, and no terminal alkyne other than ethyne could be used [3].

The dicobalt hexacarbonyl complex (**2**) of 1,3-hexadiene-5-yne (**1**) was found to react with the Grevels reagent (biscyclooctene)(tricarbonyl)iron [4], above $-40°C$ to give the simple iron diene complex **3** as the major product, and the tetranuclear compound **4** as by-product in yields of up to 5% [10*]. The cluster compound **4** was identified from its ^{1}H-NMR-spectrum in which the acetylenic proton signal appears at 8.85 ppm and all other signals are rather similar to those for complex **3** [1]. The observed shift of about 9 ppm agrees well with the data published by Vahrenkamp et al. for the corresponding ethyne cluster [3].

Since we could not obtain suitable crystals for further characterisation of **4** we decided to introduce a polar ketone function by Friedel–Crafts acetylation of the iron diene moity. Compound **5**, the derivative cluster of the ketone, was obtained in 23% yield [5*]. **5** was crystallized from dichloromethane/hexane at $-20°C$. The spectroscopic and analytical data were in good agreement with the proposed structure, which was finally established by an X-ray diffraction study [6*]. As in complex **3**, the diene moiety of the hydrocarbon chain in **5** is bound to an iron tricarbonyl group. The diene-one is coordinated in its *cis*-configuration, with the oxygen atom of the carbonyl group considerably tilted away from the metal center. The two carbon atoms of the acetylenic portion together with the two cobalt atoms form the trapezoid base of a pyramid. Its apex is occupied by a second iron tricarbonyl fragment. Thus the alkyne is bound to the triangular metal framework in the common μ^3,η^2-|| binding mode, with the C–C bond parallel to the Co–Co vector. When compared with known FeCo$_2$C$_2$-cluster compounds, **5** can be seen to show normal bond lengths and bond angles within its pyramidal framework [2].
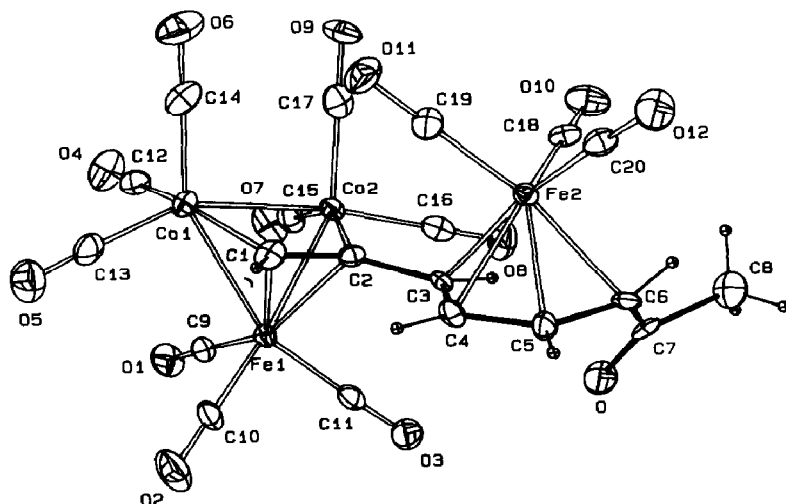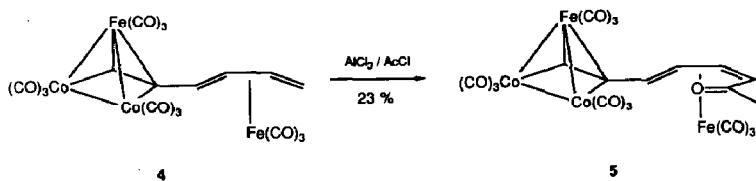

Fig. 1. ORTEP plot of one molecule of **5** showing the numbering scheme used. Ellipsoids are scaled to enclose 50% of the electronic density.

Due to the unsymmetric substitution of the triple bond the $FeCo_2C_2$-cage in **5** is chiral, and so should exist in two diastereomeric forms. The structure reveals only one of these configurations, which is probably the more stable one. Evidence for the second diastereomer comes from low temperature ^{1}H-NMR spectra in acetone-d_6, which below $-60\,^\circ$C show a small peak at 8.8 ppm. At room temperature the two diastereomers are rapidly interconverted by a formal rotation of the alkyne over the metal triangle as previously described for various M_3C_2-cluster molecules [7–9]. Because of the unfavourable equilibrium constant ($\Delta_R G \approx 5$ kJ/mol) of the interconversion it is difficult to determine the coalescence temperature and thus the exact rate constant of the interconversion process.

The condensation of $Fe(CO)_3$-fragments with $Co_2(CO)_6$-alkyne molecules to form $FeCo_2C_2$-clusters has been described by Vahrenkamp et al., who used iron enneacarbonyl as source of the iron fragments. The components are stirred in hexane at room temperature for 24 h to give the heterometallic cluster molecules in moderate yields [3]. Although the formation of **4** described above also involves a metal fragment condensation, the conditions under which **4** is obtained are milder ($-40\,^\circ$C–$0\,^\circ$C) and the reaction is much faster (1–2 h). At first sight this could be attributed to the higher reactivity of the Grevels reagent as source of $Fe(CO)_3$-fragments, but the dicobalt alkyne complex **3** and the corresponding compound of phenylacetylene do not react with the Grevels reagent at all, only the starting dicobalt complexes being recovered. This demonstrates that the formation of **4** in the reaction of complex **2** with (biscyclooctene)(tricarbonyl)iron is not due to the high reactivity of the $Fe(CO)_3$ source, which in the presence of simple dicobalt

alkyne complexes decomposes much faster than it could react to give the $FeCo_2C_2$-clusters. Since **3** does not react with an excess of Grevels reagent to give **4**, it follows that the metal fragment condensation takes place before the diene substituent in **2** is bound to the $Fe(CO)_3$-fragment. This led us to suspect that a free double bond in the vicinity of the Co_2C_2-cage of the starting complex could facilitate the incorporation of an incoming metal fragment, and the dicobalt ene-yne complex **6** did, in fact, give the corresponding $FeCo_2$-ene-yne cluster **8** in almost quantitative yield. Similarly, the heterometallic cluster **9** was formed from the Co_2-complex **7** of propiolaldehyde in more than 50% yield [10*].
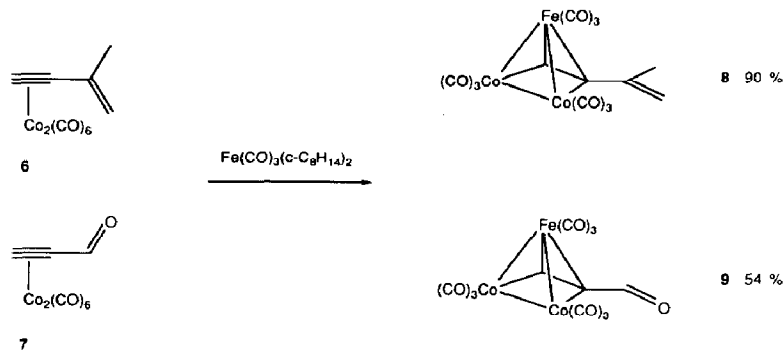
These results show that the outcome of metal fragment condensation reactions with alkyne complex precursors may depend on the organic substituents on the alkyne. Functional groups which can interact with the incoming metal fragment by some kind of precoordination can increase the rate of the condensation reaction.

References and notes

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5 Friedel–Crafts acetylation of **4**: A solution of **4** (360 mg, 0.56 mmol) in 5 ml of dichloromethane was added to a stirred solution of $AlCl_3$ (140 mg, 1.05 mmol), and acetylchloride (100 µl, 1.4 mmol) in 4 ml of CH_2Cl_2 at 0°C. The mixture was then stirred for 20 min at 0°C and for 1 h at room temperature, then treated with ice water. The product was extracted with ether and purified by column chromatography on silica gel (25 g silica gel 60, Merck, 230–400 mesh) with a mixture of 20% ether in hexane as eluent. After the starting complex (50 mg, 13%) the product **5** was eluted. Yield: 90 mg (23%). Analysis: found, C, 35.04%; H, 1.15%. Calc. $C_{20}H_8O_{13}Co_2Fe_2$: C, 35.03%; H, 1.18%. ^1H-NMR($CDCl_3$): 8.94 (s, 1H); 5.95 (dd, $^3J = 8.9$ Hz, 5.6 Hz, 1H); 5.34 (tr, $^3J = 6.4$ Hz, 1H); 3.28 (d, $^3J = 6.4$ Hz, 1H); 3.10 (d, $^3J = 8.8$ Hz, 3H); 2.17 (s, 1H). IR(CCl_4): 2100(m); 2060(s); 2040(s); 1995(s); 1655(s) cm^{-1}.
6 Crystal data for $C_{20}H_8O_{13}Fe_2Co_2$ (**5**): $M = 685.84$, monoclinic, space group $C2/c$, a 36.841(10), b 9.814(3), c 13.163(4) Å, β 100.45(2)°, V 4680.2 Å^3, $Z = 8$, $d_{calc} = 1.947$ g cm^{-3}, $F(000) = 2704$, μ(Cu-K_α) = 219.165 cm^{-1}, λ(Cu-K_α) = 1.5418 Å. A crystal of $0.16 \times 0.18 \times 0.22$ mm was used.

Intensities of 2951 independent reflections with θ in the range 3–52° were measured on a Philips PW1100/16 diffractometer at −100°C, this temperature being maintained by use of a locally built gas-flow system. A $\theta/2\theta$ flying step-scan mode was used. The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares [11] first with isotropic and then with anisotropic thermal parameters for all non-hydrogen atoms using 1775 observed reflections [$I > 3\sigma(I)$]. Empirical absorption corrections were made (abs min/max 0.81/1.33) [12]. The hydrogen atoms were placed in their geometrically calculated positions and included in structure factor calculations (C–H = 0.95 Å, isotropic temperature factor as $B(H) = 1.3B$eqv(C)) but not refined. Final R and R_w values were 0.032 and 0.050, GOF = 1.133 for $p = 0.08$ in $\sigma^2(F_o) = \sigma^2$count + $(pI)^2$. Scattering factors were taken from ref. 13. All calculations were performed on a MicroVax II computer. Tables of atomic coordinates, a list of bond distances and angles, a list of thermal parameters and a list of observed and calculated structure factors have been deposited with the Cambridge Crystallographic Data Center, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. They may be obtained on request from the Director by citing the full reference to this communication.

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10 General procedure for the preparation of clusters 4, 8 and 9: A solution of the appropriate dicobalt complexes 2, 6, or 7, in pentane or ether was added to a solution of the Grevels reagent in the same solvent cooled to −78°C in a dry ice/acetone bath. The mixture was stirred as it warmed up from −78°C to room temperature. In the case of the aldehyde 9 the mixture was stirred at room temperature for 24 h, whereas the other cluster compounds were isolated immediately after warming up. The mixture was filtered, and the products separated by column chromatography on silica gel (silica gel 60, Merck, 230–400 mesh) with hexane, or in the case of 9, a mixture of 5% ether in hexane as eluant.

4 (by-product of 3): From 1.70 g (4.7 mmol) 2 and 1.72 g (4.8 mmol) Fe(CO)$_3$(c-C$_8$H$_{14}$)$_2$. Yield: 150 mg (5%). ^{1}H-NMR(CDCl$_3$): 8.85 (s, 1H); 5.77 (dd, ^3J = 8.5 Hz, 5.1 Hz, 1H); 5.34 (m, 1h); 2.02 (dd, ^3J = 6.6 Hz, ^2J = 3.3 Hz, 1H); 1.83 (d, ^3J = 8.4 Hz, 1H); 0.73 (dd, ^3J = 9.5 Hz, ^2J = 2.0 Hz, 1H). IR(CCl$_4$): 2100(m); 2050(s); 2040(s); 2020(m); 1980(s,br) cm^{-1}.

8: From 884.2 mg (2.51 mmol) 6 and 1.19 g (3.3 mmol) Fe(CO)$_3$(c-C$_8$H$_{14}$)$_2$. Yield: 1115.3 mg (90.3%). Analysis: found, C, 34.30%; H, 1.40%. Calc. C$_{14}$H$_6$O$_9$Co$_2$Fe: C, 34.18%; H, 1.23%. ^{1}H-NMR(CDCl$_3$): 9.17 (s, 1H); 5.04 (m, 2H); 2.08 (s, 3H). IR (CCl$_4$): 2095(m); 2055(s); 2040(s); 2020(sh); 1975(s); 1615(w) cm^{-1}.

9: From 182.7 mg (0.4 mmol) 7 and 223.3 mg (0.62 mmol) Fe(CO)$_3$(c-C$_8$H$_{14}$)$_2$. Yield: 139.1 mg (53.7%). Analysis: found, C, 30.33%; H, 0.64%. Calc. C$_{12}$H$_2$O$_{10}$Co$_2$Fe: C, 30.04%; H, 0.42%. ^{1}H-NMR(CDCl$_3$): 10.00 (s, 1H); 9.72 (s, 1H). IR(CCl$_4$): 2100(m); 2070(s); 2050(s); 2030(sh); 1985(s); 1675(s) cm^{-1}.

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