Carbon–Carbon Triple Bond Cleavage at Room Temperature with Nonacarbonyldi-iron: Synthesis of $[Fe_3(CO)_9(\mu_3\text{-}CMe)(\mu_3\text{-}CNEt_2)]$

E. Cabrera, J. C. Daran, and Yves Jeannin

Laboratoire de Chimie des Métaux de Transition, UA-CNRS 419, Université P. et M. Curie, 4 Place Jussieu, 75252 Paris Cedex 05, France

An aminoalkyne C≡C triple bond has been cleaved at room temperature in the presence of $[Fe_2(CO)_9]$ using a sodium diphenylketyl catalyst; a di-μ_3-carbyne cluster is formed.

Although the alkyne R–C≡C–R′ triple bond is known to be strong, some examples of its scission have now been reported. In addition to the well-known metathesis reactions, a special case is the alkyne cleavage which yields two carbyne fragments stabilized by bonding to an organometallic triangular framework. R. B. King and coworkers[1] have described the cleavage of a symmetrical aminoalkyne by a rhodium complex $[C_5H_5Rh(CO)_2]$. Their conclusion was based on general considerations, on n.m.r. studies, and on preliminary unpublished *X*-ray work. Well characterized C≡C cleavages were described later on by Vollhardt and coworkers,[2,3] by King and coworkers,[4] by Yamasaki and coworkers,[5] and by Shapley and coworkers[6,7] using various metal compounds; all these reactions were carried out in the 100—195 °C temperature range. In the course of our study of the reaction of aminoalkynes with iron and ruthenium carbonyls, we tried to improve the yield of the dinuclear monoalkyne derivative[8] by using sodium diphenylketyl as a catalyst.[9] A C≡C cleavage occurred at room temperature with iron in a triangular metal framework.

$[Fe_2(CO)_9]$ (2.8 mmol) was added to $MeC{\equiv}CNEt_2$ (2.8 mmol) in a Schlenk flask using hexane (80 ml) as solvent. A solution of sodium diphenylketyl was added dropwise in a catalytic amount [0.08 mmol in 7 ml tetrahydrofuran (THF)] at 0 °C. After 16 h at room temperature, the reaction mixture was chromatographed on silica gel. A hexane–dichloromethane fraction was crystallized and *ca.* 100 mg (0.19 mmol) of a black compound was obtained as single crystals (yield 7% based on aminoalkyne).†

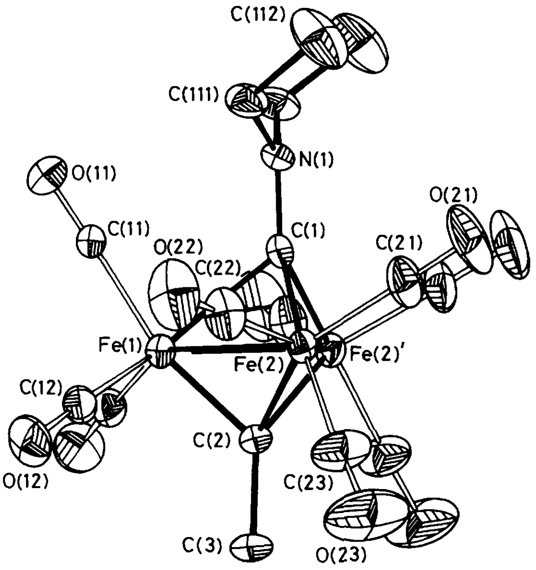

Figure 1. ORTEP view of $[Fe_3(CO)_9(\mu_3\text{-}CMe)(\mu_3\text{-}CNEt_2)]$, showing the atom labelling scheme. Ellipsoids represent 20% probability. Important bond lengths (Å): Fe(1)–Fe(2) 2.5546(6), Fe(2)–Fe(2′) 2.5041(9), Fe(1)–C(1) 2.215(4), Fe(2)–C(1) 1.931(3), C(1)–N(1) 1.317(5), Fe(1)–C(2) 1.853(4), Fe(2)–C(2) 1.999(3), C(2)–C(3) 1.503(7). Important bond angles (°): Fe(1)–C(1)–N(1) 128.1(3), Fe(2)–C(1)–N(1) 136.0(1), Fe(2)–C(1)–Fe(2′) 80.8(1), Fe(1)–C(2)–C(3) 130.5(4), Fe(2)–C(2)–C(3) 131.6(2), C(1)–N(1)–C(111) 120.9(2), C(111)–N(1)–C(111′) 115.6(4).

The molecular structure‡ is based on an Fe_3 triangle capped on each side by a μ_3-carbyne ligand: μ_3-C–Me and μ_3-C=NEt$_2$. These fragments result from the scission of the initial $MeC{\equiv}CNEt_2$ ligand. Few examples of μ_3-aminocarbyne groups can be found in the literature. Two trinuclear cobalt and rhodium complexes containing such a fragment were described by King *et al.*[1] but no *X*-ray structure is included. The crystal structure of a di-iron complex containing two bridging μ_2-CNR$_2$ groups has also been described by this group. As observed in this di-iron complex, the carbon–nitrogen bond length of the title compound is characteristic for a double bond [C=N = 1.317(5) Å] and suggests that nitrogen bears some positive charge. The molecule has a crystallographic mirror plane containing Fe(1), both μ_3-C atoms, and the N atom. It is worthwhile to point out that the μ_3-CNR$_2$ fragment asymmetrically caps the triangular framework with a longer [C(1)–Fe(1) 2.215(4) Å] and two shorter [C(1)–Fe(2) 1.931(3) Å] bond lengths. Similar dissymmetry was observed by Shriver and coworkers in the μ_3-vinylidene triruthenium cluster $[Ru_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}C{=}C(OMe)Me]$[11] with two Ru–C = 2.056 and 2.066 Å, and one Ru–C = 2.161 Å. This dissymmetry is much more pronounced in our case. A capping vinylidene group often behaves as a σ–π ligand; the terminal carbon bridges two metal atoms while the C=C bond is π-ligated to the third metal atom. In the above Ru_3 compound, the capping vinylidene ligand appears (i) to be truly sp^2 with the sum of angles around the terminal C equal to 360°, (ii) to have a nearly planar $Ru_2C{=}C(OMe)Me$ moiety making an angle of 63° with the triangular metal fragment so that the C=C and carbon–ruthenium distances are 2.161(2) and 2.782(2) Å, respectively. This last value is not within usual

---

† *Spectral data:* i.r. in the ν(CO) region: three non-separable peaks at 1975, 2010, and 2035 cm^{-1}; m.s. (measurement carried out using NH_3) highest peak at *m/z* 532 (*M* + 1).

‡ *Crystal data:* $C_{16}H_{13}NO_9Fe_3$, M = 531, space group $P2_1/m$, a = 9.494(3), b = 13.534(3), c = 8.668(3) Å, β = 111.81(2)°, Z = 2, D_c = 1.705 g cm^{-3}. A crystal (0.12 × 0.2 × 0.4 mm) was mounted on a Philips four-circle diffractometer equipped with a graphite monochromator. Unit cell dimensions were obtained by a least-squares fit of 25 reflections. 1757 Reflections were collected at room temperature in the θ range 1.5—25° using Mo-K_α radiation (λ = 0.71069 Å). 1466 Reflections with $I > 3\sigma(I)$ were used for further calculations performed with the CRYSTALS package,[10] The structure was solved using heavy atom methods, and was refined with anisotropic temperature factors for all atoms except hydrogens. Hydrogen atoms except those of the Et methyl group were located on a difference Fourier map. Their atomic co-ordinates were isotropically refined with an overall thermal parameter. The Me hydrogen atom positions were calculated (C–H = 0.96 Å; H–C–H = 109°; U = 0.09) and not refined. Final R 0.031 and R_w 0.039. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

bonding distance; Shriver *et al.* describe this situation as intermediate between a σ–π capping vinylidene and a σ-bound bridging vinylidene. In the title compound, things are different since Fe(1)–C(1) = 2.215(4) and Fe(1)–N(1) = 3.200(3) Å; moreover, the C(1) atom deviates from sp^2 with a sum of angles of 352.8°, and the C=N direction makes an angle of 89.4° with the Fe_3 plane. Therefore we do not consider the C=N bond as π-bonded. The sum of angles around N(1) is 357.4°.

This structure clearly shows that a C≡C cleavage occurred. (i) The reaction was carried out at room temperature using sodium diphenylketyl as a catalyst; it is worthwhile to note that the same reaction without catalyst does not yield any product showing such a cleavage in detectable amounts; (ii) the metal compound involves iron atoms in contrast to the known examples which contain either rhodium or cobalt; (iii) the previously postulated rarely occurring μ_3-CNR_2 ligand is described with an *X*-ray structure for the first time; the Fe_3 triangle is asymmetrically linked.

Received, 26th November 1987; Com. 1719

References

1 R. B. King and C. A. Harmon, *Inorg. Chem.*, 1976, **15**, 879.
2 J. R. Fritch, K. P. C. Vollhardt, and M. R. Thompson, *J. Am. Chem. Soc.*, 1979, **101**, 2768.
3 J. R. Fritch and K. P. C. Vollhardt, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 559.
4 R. B. King, R. M. Murray, R. E. Davis, and P. K. Ross, *J. Organomet. Chem.*, 1987, **330**, 115.
5 H. Yamasaki, Y. Wakatsuki, and K. Aoki, *Chem. Lett.*, 1979, 1041.
6 J. T. Park, J. R. Shapley, M. R. Churchill, and C. Bueno, *J. Am. Chem. Soc.*, 1983, **105**, 6182.
7 Yun Chi and J. R. Shapley, *Organometallics*, 1985, **4**, 1901.
8 E. Cabrera, J. C. Daran, Y. Jeannin, and O. Kristiansson, *J. Organomet. Chem.*, 1986, **310**, 367.
9 M. I. Bruce, D. C. Kehoe, J. G. Matisons, B. K. Nicholson, P. H. Rieger, and M. L. Williams, *J. Chem. Soc., Chem. Commun.*, 1982, 442.
10 J. R. Carruthers and D. J. Watkin, 'CRYSTALS, An advanced Crystallographic Computer Program,' University of Oxford, 1986.
11 M. J. Sailor, C. P. Brock, and D. F. Shriver, *J. Am. Chem. Soc.*, 1987, **109**, 6015.