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Preliminary communication

Metal atoms in the synthesis of metal clusters

III *. $HFe_3(CO)_9(C{\equiv}CSiMe_3)$, synthesis and crystal structure

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Abstract

Vaporization of nickel atoms into a solution of bis(trimethylsilyl)acetylene and $Fe(CO)_5$ in methylcyclohexane at −120 °C unexpectedly affords (after chromatographic work-up and crystallization) deep red crystals of the new triangular cluster μ_3-(δ,2π-trimethylsilylacetylene)tris[(tricarbonyl)iron]hydride **1** in low yield.

Reactions of vaporized free metal atoms offer some new routes for the synthesis of metal cluster compounds. As shown previously the interaction of metal atoms with suitable organic ligands (e.g. Cp*H, mesitylene) and an appropriate organometallic compound can afford new heteronuclear cluster compounds that are not normally obtained by conventional cluster synthesis [1,2]. To gain further insight into the cluster formation via the use of metal atoms we now wish to report the unexpected product in the reaction of an alkyne with nickel atoms and $Fe(CO)_5$. As the alkyne we used the sterically demanding bis(trimethylsilyl)acetylene (btmsa) in order to avoid the trimerization of the ligand that is often observed in reactions of metal atoms with alkynes [3]. A product from the reaction of Ni atoms with btmsa has been reported previously, but it was not completely characterized owing to its oligomeric nature [4].

Vaporization of nickel atoms (ca. 0.03 mol) into a solution of btmsa (0.05 mol) and $Fe(CO)_5$ (0.05 mol) at −120 °C forms a bright red-brown colored solution under the conditions used. Subsequent work-up (filtration followed by evaporation of the solvent and unchanged reactants) followed by chromatography (Al_2O_3/5% H_2O, pentane) yielded a red crystalline material (600 mg), from which deep red crystals of **1** (420 mg, 0.81 mmol, 3.7%) were obtained by crystallization (pentane/ − 6 °C) **. However, during the chromatographic work-up a considerable amount of the primary product formed during the metal-atom reaction decomposed on the

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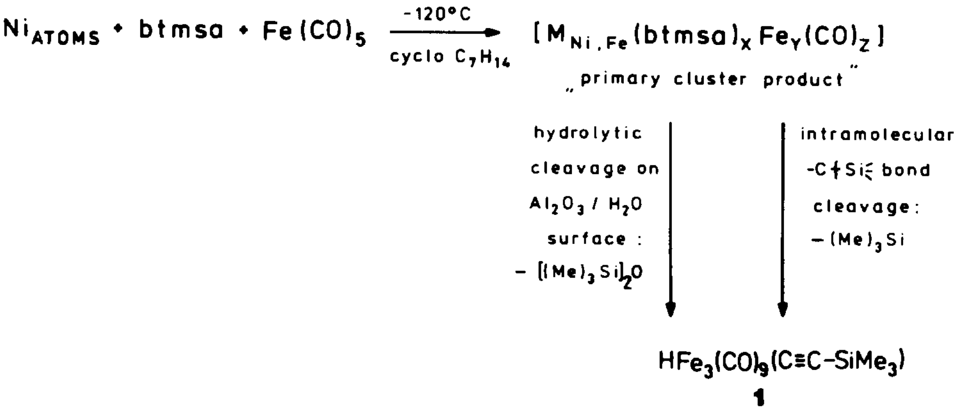
* For Part II see ref. 1.



Scheme 1. Formation pathways for the synthesis of **1**, starting from Fe(CO)$_5$, Ni-atoms and btmsa.

column, and this accounts for the low yield. The only isolated organometallic material **1** contained no nickel, which was surprising since we expected to isolate a heteronuclear cluster compound. Inspection of the ^{13}C-NMR data show the presence of two different tertiary carbon atoms. The strongly deshielded signal at 203.4 ppm is in the range of a "carbene like" carbon atom, indicating a direct metal to ligand bond and the loss of one trimethylsilyl group from the btmsa ligand in **1**. Furthermore the large downfield shift is characteristic of both σ- and π-bonding to the metal framework [5]. This cleavage must have occurred during the work-up procedure, since in a control experiment in which trimethylsilylacetylene (tmsa) was treated with nickel atoms and Fe(CO)$_5$ under similar conditions no **1** was formed. Instead we isolated compound **2** as bright yellow needles, also containing no Ni ***. In contrast to btmsa the tmsa ligand seems to remain intact in this metal-atom reaction. The nature of compound **2** is under investigation.

Since we used H$_2$O-deactivated alumina for the chromatographic work-up of **1** a hydrolytic cleavage of a coordinated but still intact btmsa ligand followed by a subsequent take-up of H seems possible. No attempts were made to identify hexamethyldisiloxane as a possible reaction product. Another explanation for the formation of **1** (Scheme 1) might lie in the desilylation of a coordinated btmsa ligand in this primary cluster product brought about by Fe–CO fragments, as recently suggested by Vahrenkamp [6], but it remains unclear why complete desilylation of coordinated btmsa does not occur. Further investigations aimed at eluci-

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** Spectroscopic data for **1**: IR (KBr, ν(C≡C) cm^{-1}) 1580 s; terminal carbonyl region (ν cm^{-1}, hexane); 2090 w, 2053 s, 2039 s, 2017 s 2002 sh, 1984 w, 1968 w; ^{1}H-NMR (toluene-d_8, 200 MHz, δ ppm) −26.7 (s 1H), 0.1 (s 9H); ^{13}C-NMR (toluene-d_8, 75.5 MHz, δ ppm, 30 °C) 0.75(s), 89.36(s), 203.44(s), δ(CO) (−30 °C), 213.48, 206.23, 204.74; MS (EI) m/z (rel. int.) 518 (M^+ 37%), 490 (8), 462 (18), 434 (47), 406 (43), 378 (100), 350 (49), 322 (27), 294 (58), 266 (48). Anal. Found C, 33.32; H, 2.19; Si, 6.09. $C_{14}H_{10}O_9SiFe_3$ (517.88) calc. C, 32.35; H, 1.95; Si, 5.42%.

*** Spectroscopic and analytical data for **2**: IR (KBr, ν(C≡C) cm^{-1}) 1603 vs, terminal carbonyl region (ν cm^{-1}, hexane) 2017 s, 2015 s, 1995 s; ^{1}H-NMR (CDCl$_3$, 200 MHz) 0.2 (s 9H), 5.45 (s, 1H); ^{13}C-NMR (toluene-d_8, 75.5 MHz, δ ppm, 30 °C) −1.1 (qui), 76.7 (mult.), 90.2 (d(d)), 182 (s(t)), 209 (s); MS (EI) m/z (rel. int.) 364 (M^+ 25%), 336 (42), 308 (100), 280 (65), 254 (52), 252 (53), 250 (35), 193 (24), 154 (25), 83 (20), 73 (51), 45 (22). Anal. Found: C, 45.39; H, 5.20; Si, 15.20; Fe, 12.63%.

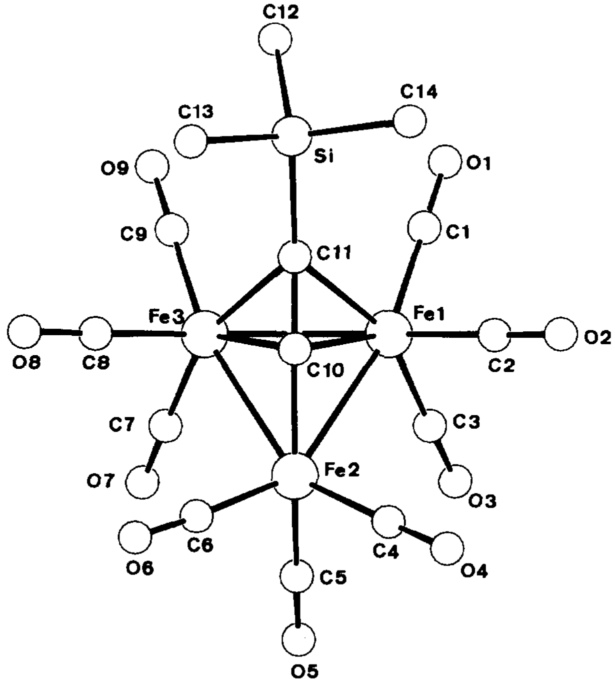

Fig. 1(a). Crystal structure of 1 with numbering of the atoms and important bond lengths (Å) and angles (°): Fe(1)–Fe(2) 2.654(1); Fe(1)–Fe(3) 2.558(1), Fe(2)–Fe(3), 2.650(1); Fe(1)–C(10) 2.026(3); Fe(1)–C(11) 2.139(3); Fe(3)–C(10) 2.030(3); Fe(3)–C(11) 2.145(3); Fe(2)–C(10), 1.807(3); C(10)–C(11) 1.296(4); C(11)–Si 1.866(3); Fe(2)–C(10)–C(11) 159.3(2); Fe(1)–C(10)–Fe(3) 78.2(1); Fe(1)–C(10)–Fe(2) 87.4(1); Fe(2)–C(10)–Fe(3) 87.2(1); Fe(1)–C(11)–Fe(3) 73.3(1); Fe(1)–C(11)–C(10) 67.2(2); Fe(3)–C(11)–C(10) 67.1(2) Fe(2)–Fe(1)–Fe(3) 61.1(1); Fe(1)–Fe(2)–Fe(3) 57.7(1); Fe(1)–Fe(3)–Fe(2) 61.2(1);

dating the reaction pathway to 1 are underway. The structure of 1 was determined by an X-ray diffraction study of crystals obtained from a concentrated pentane solution at 0 °C *. The molecular structure is depicted in Fig. 1. The cluster framework is formed by an unsymmetrical triangle of iron atoms in which the bond Fe(1)–Fe(3) is considerably shorter than the remaining two (Fe(1)–Fe(3), 2.558(1); Fe(1)–Fe(2), 2.654(1); Fe(2)–Fe(3), 2.650(1) Å). Each iron atom is bonded to three terminal CO groups, two in an equatorial and one in an axial position to the metal. The iron triangle is capped by an $-C{\equiv}CSiMe_3$ end-on as well as side-on bonded fragment, thus providing a rare example among structurally characterized alkyne

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* *Crystal data.* $C_{14}H_9O_9Fe_3Si$, triclinic, space group $P\bar{1}$, M 516.8, a 9.122(1), b 9.664(1), c 11.679(1) Å, α 101.90(1), β 97.96(1), γ 92.62(1)°, V 994.8 Å^3, $Z = 2$, μ(Mo-K_α) 22.58 cm^{-1}, d_{calc} 1.73 g cm^{-3}, 4785 independent and 4107 observed reflections, 244 refined parameters, $R = 0.039$, $R_w = 0.047$, final difference Fourier 0.35 e Å^{-3}. Intensity data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer by the ω–2θ method. The structure was solved by heavy-atom methods, the H-atom positions were calculated and kept fixed in the final refinement stage. Further details of the crystal structure investigation, e.g. full listings of atomic coordinates and bond lengths and angles, are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD 54959, the names of the authors, and the journal citation.

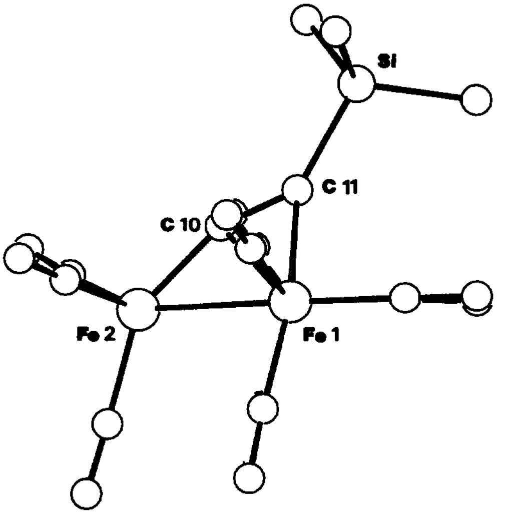

Fig. 1(b). View onto the Fe(1)–Fe(2) bond of **1**, showing the tilted arrangement of the bridging alkyne fragment.

trimetallic clusters of a species in which the alkyne ligand acts as a five-electron donor [7]. The distance (Fe(2)–C(10), 1.807(3) Å) is typical for a Fe–C_{sp} bond length, whereas two sets of longer bonds are observed (set 1: Fe(1)–C(11), 2.139(3); Fe(3)–C(11), 2.145(3) Å); set 2: Fe(1)–C(10), 2.026(3); Fe(3)–C(10), 2.030(3) Å) for the π-bonds to Fe(1) and Fe(3). The C≡C triple bond of **1** is slightly elongated compared with that in uncoordinated acetylenes [8]. Whereas in clusters containing μ_3-acetylenic ligands the triple bond length is rather insensitive to variation of the substituents on the alkyne or of the cluster metals, the observed coordination mode of the alkyne as a five-electron donor offers a wide variation of C≡C bond lengths. Two categories can be defined. In clusters formed by the first row transition metals (C≡C bond distances: $CoFe_2(CO)_9(C{\equiv}CSiMe_3)$, 1.289(6) [10], 1.296(4) Å this work), the C–C distances are shorter than those in compounds with second and third row transition metals ($HOs_3(CO)_9(C{\equiv}CCF_3)$, 1.331(13) [11]; $HRu_3(CO)_9(C{\equiv}CBu^t)$, 1.315(3) [12] $HOs_3(CO)_9(C{\equiv}CSiMe_3)$, 1.31(1) [13]). The presence of a hydridic hydrogen atom in **1** is indicated by ^{1}H-NMR as well as by mass spectroscopy. This atom could not be located directly by the X-ray investigation, but comparison with $HRu_3(CO)_9(C{\equiv}CBu^t)$, in which the hydrogen atom was located unambiguously by neutron diffraction [12], indicates that it is in a position bridging the slightly elongated bond Fe(1)–Fe(3) (2.558(1) Å).

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