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Ten Vertex {*closo*-2,1,10-FeC_2B_7} Clusters with Intramolecular Imidate Linkages: Anchors for Supramolecular Construction

Andreas Franken, Thomas D. McGrath and F. Gordon A. Stone

Experimental

General Considerations. All reactions were carried out under an atmosphere of dry nitrogen using Schlenk line techniques. Solvents were distilled from appropriate drying agents under nitrogen prior to use. Petroleum ether refers to that fraction of boiling point 40–60 °C. Chromatography columns (ca. 20 cm in length and ca. 2 cm in diameter) were packed with silica gel (Acros, 60–200 mesh). NMR spectra were recorded (298 K) from CD_2Cl_2 solutions at the following frequencies (MHz): ^{1}H, 360.13; ^{13}C, 90.56 and ^{11}B, 115.5. Compound **1a** was synthesized following the literature procedure.[1]

Synthesis of 3 and 4. (i) Compound **1a** (0.13 g, 0.5 mmol) was dissolved in CH_3CN (20 cm^3), Me_3NO (0.08 g, 1.0 mmol) was added, and the mixture stirred at ambient temperature for 18 h. Solvent was removed under reduced pressure, and the residue was dissolved in CH_2Cl_2–petroleum ether (1:1, 5 mL) and transferred to the top of a chromatography column. Eluting with the same mixture gave an orange fraction, removal of solvents from which yielded orange microcrystals of **3** (0.09 g, 63 %). IR (CH_2Cl_2) ν_{max}(CO): 2039 s, 1993 s cm^{-1}. NMR: ^{1}H δ 7.38 (br s, 1H, cage CH), 5.81 (br s, 1H, NH), 2.64 (s, 3H, CH_3); $^{13}C\{^1H\}$ δ 210.2 (CO), 191.3 (br,

cage CO), 181.6 (C=N), 70.9 (br, cage CH); $^{11}B\{^1H\}$ δ –2.6 (1B), –12.5 (2B), –19.1 (2B), –20.5 (2B).

(ii) Similarly, compound **1a** (0.13 g, 0.5 mmol) in CH_2Cl_2 (20 cm^3) with *p*-NC-C_6H_4-C≡CH (0.26 g, 2 mmol) and Me_3NO (0.08 g, 1 mmol) with identical work-up yielded orange microcrystals of **4** (0.13 g, 72 %). IR (CH_2Cl_2) ν_{max}(CO): 2041 s, 1997 s cm^{-1}. NMR: ^1H δ 8.24 (br s, 1H, cage CH), 8.01–7.76 (m, 5H, C_6H_4), 5.89 (br s, 1H, NH), 3.46 (s, 1H, ≡CH); $^{13}C\{^1H\}$ δ 210.3 (CO), 191.1 (br cage CO), 177.9 (C=N), 132.9–125.5 (C_6H_4), 81.9 (*C*≡CH), 81.4 (C≡*C*H), 70.6 (br, cage CH); $^{11}B\{^1H\}$ δ –2.6 (1B), –12.4 (2B), –19.2 (2B), –20.4 (2B).

Synthesis of 5. Compound **4** (0.13 g, 0.35 mmol) was dissolved in CH_2Cl_2 (20 cm^3), [CuCl(TMEDA)] (0.13 g, 0.60 mmol) was added, and air was passed through the stirred suspension for 3 h. Volatiles were removed under reduced pressure, and the residue was dissolved in CH_2Cl_2/petroleum ether (3:2, 5 cm^3) and applied to a chromatography column. Eluting with CH_2Cl_2/petroleum ether (1:1) gave an orange fraction, removal of solvents from which yielded orange microcrystals of **5** (0.10 g, 82 %). IR (CH_2Cl_2) ν_{max}(CO): 2041 s, 1997 s cm^{-1}. NMR: ^1H δ 8.24 (br s, 2H, cage CH), 8.04–7.72 (m, 10H, C_6H_4), 5.90 (br s, 2H, NH) 210.0 (CO), 184.0 (br, cage CO), 177.7 (C=N), 133.0–125.5 (C_6H_4), 81.6 , 76.8 (C≡C), 70.5 (br, cage CH); $^{11}B\{^1H\}$ δ –2.5 (1B), –12.4 (2B), –19.1 (2B), –20.3 (2B)

Synthesis of 6. Compound **5** (0.09 g, 0.13 mmol) was dissolved in CH_2Cl_2 (20 cm^3), and [$Co_2(CO)_8$] (0.17 g, 0.5 mmol) was added and the mixture stirred at ambient temperature for 18 h. The CH_2Cl_2 was removed under reduced pressure, and the residue was dissolved in CH_2Cl_2/petroleum ether (3:2, 5 cm^3) and subjected to column chromatography. Eluting with

petroleum ether yielded a yellow-brown band identified as [$Co_2(CO)_8$] which was discarded. Thereafter, elution with CH_2Cl_2/petroleum ether (1:1) gave another yellow- brown fraction, from which was obtained red microcrystals of **6** (0.15 g, 87 %) after evaporation *in vacuo*. IR (CH_2Cl_2) ν_{max}(CO): 2104 m, 2085 s, 2056 s, 2040 s, 1997 w cm^{-1}. NMR: ^{1}H δ 8.25 (br s, 2H, cage CH), 8.08–7.78 (m, 10H, C_6H_4), 5.91 (br s, 2H, NH); ^{13}C{^{1}H} δ 210.3 (Fe−CO), 196.2 (Co−CO), 184.0 (br, cage CO), 178.1 (C=N), 145.3–124.6 (C_6H_4), 96.4, 92.5 (C_2Co_2), 70.6 (br, cage CH); ^{11}B{^{1}H} δ –2.5 (1B), –12.4 (2B), –19.2 (2B), –20.3 (2B).

X-Ray Diffraction Studies

X-ray intensity data were collected at 110(2) K on a Bruker-Nonius X8 APEX CCD area-detector diffractometer using Mo-Kα X-radiation. Several sets of narrow data 'frames' were collected at different values of θ, for various initial values of ϕ and ω, using 0.5° increments of ϕ or ω. The data frames were integrated using SAINT;[2] the substantial redundancy in data allowed an empirical absorption correction (SADABS[2]) to be applied, based on multiple measurements of equivalent reflections.

All structures were solved using conventional direct methods[2] and refined by full-matrix least-squares on all F^2 data using SHELXL-97.[3] The locations of the cage-carbon atoms were verified by examination of the appropriate internuclear distances and the magnitudes of their isotropic thermal displacement parameters. All non-hydrogen atoms were assigned anisotropic displacement parameters. All B–H and C–H hydrogen atoms were included in calculated positions and allowed to ride on their parent atoms. All hydrogen atoms had fixed isotropic thermal parameters, calculated as U_{iso}(H) = 1.2 × U_{iso}(parent), or U_{iso}(H) = 1.5 × U_{iso}(parent) for methyl hydrogens.

Note that crystals of 6 contain only one half molecule of compound **6**, plus one molecule of Et_2O as solvate, per asymmetric unit. Thus, whole molecules of **6** have crystallographically imposed C_2 symmetry. One of the solvate methyl groups was modeled as being disordered over two positions, with refining complementary occupancies of 59:41 at convergence.

References

1. A. Franken, T. D. McGrath and F. G. A. Stone, *Organometallics*, 2008, **27**, 908.
2. *APEX* 2. Version 1.0. Bruker AXS, Madison, WI, USA.
3. *SHELXTL-PC*. Version 6.12. Bruker AXS, Madison, WI, USA.