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[11] Determination of conversion by ESI-MS using an internal standard: a) S. Takayama, S. T. Lee, S.-C. Hung, C.-H. Wong, *Chem. Commun.* **1999**, 127 – 128; b) S. A. Gerber, C. R. Scott, F. Turecek, M. H. Gelb, *J. Am. Chem. Soc*. **1999**, *121*, 1102 – 1103.

[12] Aliquots (10 μL) of 1 mM 1:1 mixtures of **15** and **16** in CH_3OH were injected into a Rheodyne port of an ESI-MS system (ESI-MS conditions: MS: Hewlett Packard 5989B MS engine quadrupole mass spectrometer equipped with a Hewlett Packard 59987A API electrospray source II with hexapole ion guide (Analytica of Branford) and ChemStation data system; data acquisition: positive-ion mode scan spectra; *m*/*z* 90 – 300; step size *m*/*z* 0.1, unit resolution, gaussian mass filter *m*/*z* 0.3; gaussian time filter 0.05 min; API source conditions: potential difference between spray needle and first electrode – 5250 V, pressure of N_2 nebulization gas: 4140 Torr, flow of N_2 drying gas ca. 9 L min^{-1} (150 °C), solvent flow 0.06 mL min^{-1}, CH_3OH/H_2O 8/2). ESI mass spectra were collected, and the ratios of **15** and **16** were determined on the basis of absolute intensities of the peaks of the corresponding sodium adducts ([**15**+Na]$^+$ and [**16**+Na]$^+$, Figure 1). The ratios of the peak intensities (and thus the *ee* values of the synthetic mixtures of **15** and **16**) were obtained automatically using a macro to submit the data from the *m*/*z* intensity table of each measurement to an Excel spread sheet.

[13] All enzyme-catalyzed hydrolytic reactions and esterifications were performed in deep-well microtiter plates (total volume 1.2 mL). For ESI-MS analysis a defined volume of the resulting product mixtures was extracted with diethyl ether. The extracts were automatically transferred in microtiter plates and diluted with methanol to a final concentration of 0.5 – 2.0 mM. The microtiter plates were placed in an automated sample manager (Scheme 2) equipped with a Rheodyne port for the injections.

[14] M. T. Reetz, M. H. Becker, H.-W. Klein, D. Stöckigt, **1999**, patent application submitted.

[{[(η^7-$C_2B_{10}H_{12}$)(η^6-$C_2B_{10}H_{12}$)U][K_2(thf)$_5$]}$_2$]: A Metallacarborane Containing the Novel η^7-$C_2B_{10}H_{12}^{4-}$ Ligand**

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It has been well-documented that $C_2B_{10}H_{10}R_2$ (R = H, alkyl, aryl) can be reduced by alkali metals to form the *nido*-$C_2B_{10}H_{10}R_2^{2-}$ dianion, which can be bound in a η^6 manner to transition metals to afford a series of 13-vertex *closo*-metallacarboranes.[1] Treatment of [(η^6-$C_2B_{10}H_{12}$)Co(η^5-C_5H_5)] with Na/naphthalene followed by reaction with C_5H_5Na and $CoCl_2$ gave the 14-vertex *closo*-metallacarborane [(η^6:η^6-$C_2B_{10}H_{12}$)-{Co(η^5-C_5H_5)}$_2$].[2] The proposed geometry of the cage is the bicapped hexagonal antiprism; X-ray confirmation of this species has not been reported. We are interested in this tetraanion ligand and its bonding mode to transition metals, and describe herein the isolation and structural characterization of the first metallacarborane bearing a η^7-$C_2B_{10}H_{12}^{4-}$ ligand.

Interaction between *o*-$C_2B_{10}H_{12}$ and excess K metal in THF at room temperature followed by treatment with a suspension of UCl_4 in THF gave, after workup, **1** as deep red crystals in 58% yield [Eq. (a)]. Compound **1** is extremely air- and

$$4\,o\text{-}C_2B_{10}H_{12} + 12\,K + 2\,UCl_4 \xrightarrow{THF} \underset{\mathbf{1}}{[\{[(\eta^7\text{-}C_2B_{10}H_{12})(\eta^6\text{-}C_2B_{10}H_{12})U][K_2(thf)_5]\}_2]} + 8\,KCl \quad (a)$$

moisture-sensitive, but remains stable for months at room temperature under an inert atmosphere. Contact with traces of air immediately results in conversion of the intensely colored **1** into a yellow powder. Compound **1** is soluble in polar organic solvents such as THF and pyridine, sparely soluble in toluene, and insoluble in hexane.

An X-ray diffraction study[3] reveals that **1** is a centrosymmetric dimer with a bent sandwich structural motif. As shown in Figure 1, each U atom is η^6-bound to *nido*-$C_2B_{10}H_{12}^{2-}$, η^7-bound to *arachno*-$C_2B_{10}H_{12}^{4-}$, and coordinated to two B–H bonds from the C_2B_5 bonding face of the neighboring *arachno*-$C_2B_{10}H_{12}^{4-}$ ligand. This results in a highly distorted tetrahedral geometry at U with a cent(S)–U–cent(L) angle of 136.3° (cent(S) and cent(L) are the centroids of the C_2B_4 and C_2B_5 bonding faces, respectively). Compound **1** represents not only the first metallacarborane containing a novel η^7-$C_2B_{10}H_{12}^{4-}$ ligand, but also the first organoactinide compound bearing a η^6-$C_2B_{10}H_{12}^{2-}$ ligand.

The average distance between U and a cage atom of the C_2B_4 bonding face in **1** (2.867(7) Å) is longer than that between U and a cage atom of the C_2B_3 bonding face in

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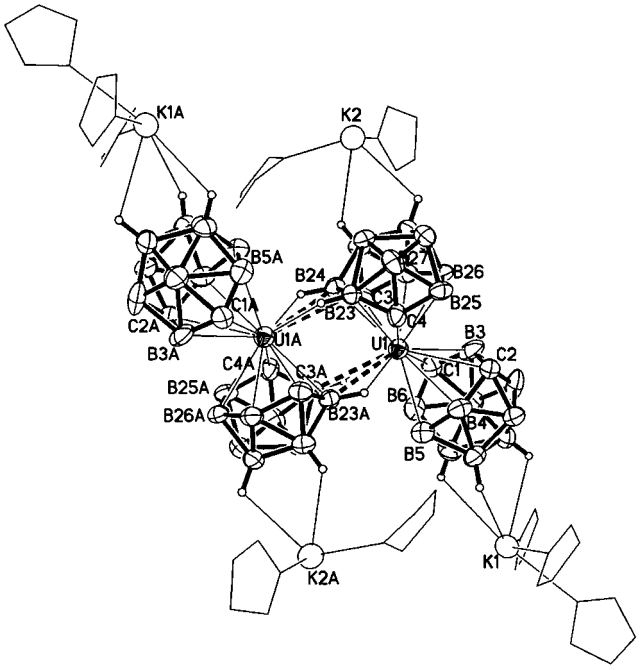

Figure 1. Molecular structure of **1**. Selected distances [Å]: U1–C1 2.744(6), U1–C2 2.958(5), U1–B3 2.969(7), U1–B4 2.702(7), U1–B5 2.840(7), U1–B6 2.991(7), U1 ··· B23A 2.980(6), U1 ··· B24A 2.989(6).

$[Li(thf)_4]_2[(\eta^5\text{-}C_2B_9H_{11})_2UCl_2]$ (2.73(2) Å)[4] and $[Li(thf)_4]_2[(\eta^5\text{-}C_2B_9H_{11})_2UBr_2]$ (2.72(2) Å).[5] This measured distance can be compared with the values of 2.841(3) Å in $[\{Me_2Si(\eta^6\text{-}C_2B_{10}H_{11})(\eta^5\text{-}C_5H_4)\}Sm^{III}(thf)_2]$,[6] 2.976 Å in $[\{(\eta^6\text{-}C_2B_{10}H_{12})Eu^{II}(MeCN)_3\}_n]$, and 3.03 Å in $[(\eta^6\text{-}C_2B_{10}H_{12})_2Eu^{II}(thf)_2]^{2-}$.[7] The Shannon radius for U^{IV} is 0.079 and 0.25 Å smaller than that of Sm^{III} and Eu^{II}, respectively.[8] The distances from the U atom to the five B atoms of the C_2B_5 bonding face from the $\eta^7\text{-}C_2B_{10}H_{12}{}^{4-}$ ligand range from 2.772(6) to 2.791(6) Å with an average value of 2.780(6) Å, which is close to those in $[(\eta^5\text{-}C_2B_9H_{11})_2UX_2]^{2-}$ (X = Cl,[4] Br[5]) but shorter than the average distance between U and a cage atom of the C_2B_4 bonding face of the $\eta^6\text{-}C_2B_{10}H_{12}{}^{2-}$ ligand (2.867(7) Å). The U ··· B distances in the two U-H-B units are 2.980(6) Å and 2.989(6) Å, which can be compared with the Sm^{II} ··· B distances of 3.025(8) to 3.058(8) Å found in $[\{[C_2B_9H_9(CH_2C_6H_5)_2]Sm(dme)_2\}_2]$ (dme = 1,2-dimethoxyethane),[9] and the Th^{IV} ··· B distances of 3.086(3) and 3.101(3) Å observed in $[(C_5Me_5)_2ThMe]_2[(C_2B_9H_{11})_2Fe]$.[10] Further comparisons are difficult due to the lack of other related compounds.

The most interesting features of this structure are the boat shape of the C_2B_5 bonding face, the coordination environment of each cage atom of the novel $\eta^7\text{-}C_2B_{10}H_{12}{}^{4-}$ ligand, and the unexpectedly short U–C3 and U–C4 bond distances of 2.414(5) and 2.443(5) Å (Figure 2). These values are very close to those of U–C σ bonds normally observed in organouranium compounds, for instance, 2.43(2) Å in $[(C_5H_5)_3U(n\text{Bu})]$,[11] 2.56(1) Å in $[(C_5H_5)_3U(n\text{Bu})]^-$,[12] 2.48(3) Å in $[(C_5H_5)_3U\{CH_3C(CH_2)_2\}]$,[13] 2.54(2) Å in $[(C_5H_5)_3U(p\text{-}CH_2C_6H_4CH_3)]$,[11] and 2.436(4) Å in $[(Me_3SiC_5H_4)_3U(CH{=}CH_2)]$.[14] The five B atoms of the C_2B_5 bonding face are almost coplanar, and the two C atoms

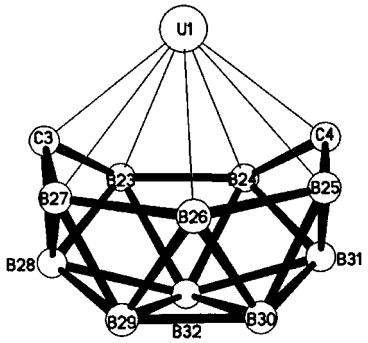

Figure 2. Interaction between the U atom and the $C_2B_{10}H_{12}{}^{4-}$ ligand in **1**. Selected distances [Å]: U1–C3 2.414(5), U1–C4 2.443(5), U1–B23 2.772(6), U1–B24 2.785(6), U1–B25 2.777(6), U1–B26 2.776(6), U1–B27 2.791(6).

are about 0.6 Å above this plane. The coordination number for the C atoms is one less than those of B atoms in this bonding face.[15] Based on the above-mentioned findings, the U–C3 and U–C4 bonds are best described as σ bonds.

The mechanism of the formation of **1** might be proposed as follows: In the presence of excess K metal, $[C_2B_{10}H_{12}]K_2$[1, 7] reacts with UCl_4 in THF to give the presumable intermediate $[(C_2B_{10}H_{12})_2U(thf)_2]$. Further reduction of the *nido*-$C_2B_{10}H_{12}{}^{2-}$ ligands by K metal to *arachno*-$C_2B_{10}H_{12}{}^{4-}$ affords **1**. Direct reduction of $C_2B_{10}H_{12}$ to $C_2B_{10}H_{12}{}^{4-}$ by excess K metal seems very unlikely.[2, 16]

Experimental Section

1: A mixture of *o*-$C_2B_{10}H_{12}$ (0.145 g, 1.0 mmol) and K (0.98 g, 25.0 mmol) in THF (40 mL) at room temperature was stirred overnight. To this pale yellow suspension was added UCl_4 (0.19 g, 0.50 mmol), and the mixture was stirred at room temperature for 4 d to afford a dark red suspension. After removal of excess K metal and precipitates, the dark red solution was evaporated to give a very dark red solid. Recrystallization from toluene/THF afforded **1** as very dark red crystals (0.278 g, 58 %). ^{1}H NMR (300 MHz, [D$_5$]pyridine, 25 °C, TMS): $\delta = 1.55$ (brs, thf), 3.59 (brs, thf), 27.78 (brs, cage CH), 52.62 (brs, cage CH); ^{11}B NMR (160 MHz, [D$_5$]pyridine, 25 °C, $BF_3 \cdot OEt_2$): $\delta = -3.5$ (4B), -9.0 (2B), -9.9 (4B), -14.0 (4B), -14.6 (2B), -21.5 (2B), -36.9 (2B); IR (KBr): $\tilde{\nu} = 3075$ (w), 2969 (m), 2870 (m), 2490 (vs), 2278 (m), 1049 (s), 902 cm^{-1} (m); elemental analysis calcd for $C_{40}H_{112}B_{40}K_4O_8U_2$ (**1** – 2 thf): C 26.89, H 6.32; found: C 26.48, H 6.21.

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$R_1 = 0.0778$, wR_2 $(F^2) = 0.1857$. This structure was solved by direct methods and refined by full-matrix least squares on F^2 by using the Siemens SHELXTL/PC package of crystallographic software.[18] All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were geometrically fixed using the riding model. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-112284. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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ESI Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (ESI-FT-ICR-MS): A Rapid High-Resolution Analytical Method for Combinatorial Compound Libraries**

Tilmann B. Walk, Axel W. Trautwein, Hartmut Richter, and Günther Jung*

Test systems for the search for active materials are largely automated and designed for the reliable recognition of in vitro activity with minimal sample consumption (high-throughput screening). Compound collections for mass screening are nowadays prepared by the methods of combinatorial chemistry.[1, 2] The parallel synthesis of hundreds and thousands of compounds per day is state of the art (high-throughput synthesis). The requirement for rapid characterization of the compounds (high-throughput analysis) arises from this development. An increase in the efficiency of "off-bead" analysis by ESI/MALDI-TOF/quadrupole-MS[3, 4] and reverse-phase HPLC[5] as well as "on-bead" analysis by NMR[6] and FT-IR spectroscopy[7] has been rapidly achieved. Previously less utilized methods such as FT-IR microscopy even allow simultaneous "on-bead" analysis of polymer-bound compound collections on hundreds of resin beads.[8]

FT-ICR mass spectrometry[9] sets new standards with respect to effectiveness, informative value, and sample consumption. In Figure 1, measurements obtained by ESI-quadrupole (A) and ESI-FT-ICR mass spectrometry (B) on a compound prepared by solid-phase organic synthesis[10] are superimposed. The ESI-FT-ICR measurement gives a mass accuracy which is greater by a factor of about 550 (A: $\delta = 221$ ppm; B: $\delta = 0.4$ ppm). Accordingly, the difference between calculated and measured mass of the FT-ICR determination corresponds to 0.00018 Da in this example. The resolution is about a factor of 15 better than for the comparable measurement with a quadrupole analyzer (A: 4500; B: 70000). The FT-ICR measurement was taken in the broad-band mode with a scanned mass range of 1400 Da. This measurement mode is not designed for the highest resolutions, but nevertheless a resolution of 70000 was obtained. The corresponding measurement in the high-resolution mode at a scanned mass range of 100 Da gave a resolution of 350000 (data not shown).

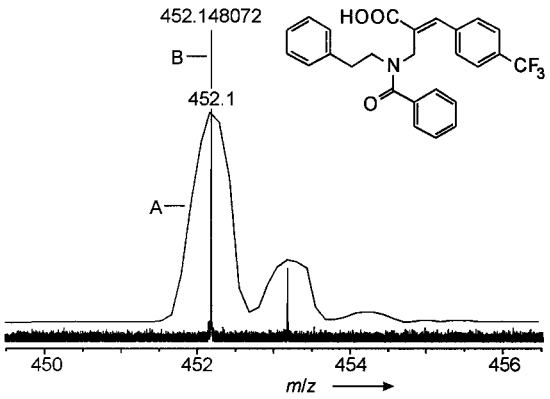

Figure 1. Superimposed measurements of a compound obtained by solid-phase synthesis with ESI-quadrupole (A) and ESI-FT-ICR mass spectrometry (B). Starting points for elemental analysis: $[M-H]^-$ measured: 452.1480720 Da, charge -1, min./max. double bond equivalents (DBE) 0.5/30, tolerance ± 0.0005 Da. Elemental analysis for $M_r = 452.1480720$: C 26, O 3, N 1, S 0, H 21, F 3; $[M-H]^-$ calculated: 452.1478911, 15.5 DBE, deviation 0.4 ppm. The calculation of possible molecular formulas on the basis of the very precise ESI-FT-ICR measurement thus gave solely the correct composition.

The amount of sample required for an FT-ICR measurement is 10 times less than for the quadrupole measurement (A: 40 pmol; B: 4 pmol). The tolerance of the FT-ICR measurement resulting from the mean accuracy of the

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