species produced in a CH_4 matrix (Table I), with a small amount of $Cp(CO)_2Mo{=}SbMe_2$ (**5e**). Reversal with long-wavelength radiation (λ > 490 nm) resulted in the appearance of three new bands at 2183.6, 1942.6, and 1883.0 cm^{-1}, while bands due to **4e** and **5e** decreased in intensity. The band at 2183.6 cm^{-1} is in the region typical for NN terminal stretching modes, e.g., $CpCo(CO)(N_2)$ (ν_{NN} at 2164.6 cm^{-1} in N_2 matrix),[9] $CpMn(CO)_2(N_2)$ (ν_{NN} at 2175 cm^{-1} in N_2 matrix[10] and at 2169 cm^{-1} in *n*-hexane solution[11]), and $Cp(CO)_2(N_2)Mo{-}CH_3$ (ν_{NN} at 2191 cm^{-1} in N_2 matrix[7]). The bands at 1942.6 and 1883.0 cm^{-1} are terminal CO stretching modes, and, therefore, the product can be identified as $Cp(CO)_2(N_2)Mo{-}SbMe_2$ (**6e**). Calculation[12] of the OC–Mo–CO bond angle ($\theta = 83°$) from relative band intensities and the energy-factored CO interaction force constant ($k_i = 46.0$ N m^{-1}) and comparison with data for *cis*-$Cp(CO)_2(N_2)Mo{-}CH_3$ ($\theta = 82°$ and $k_i = 43.3$ N m^{-1})[7] and $Cp(CO)_3Mo{-}SbMe_2$ (**3e**) ($k_{cis} = 37.3$ and $k_{trans} = 55.0$ N m^{-1}) suggest cis stereochemistry for the CO ligands in **6e**. The arsenic analogue, **3a**, also gave a dinitrogen complex (**6a**), but under these conditions the W compounds **3b–d** produced only the 16-electron and the double-bonded species.

The observation of high yields of the 16-electron species **4a–c** in matrices, even N_2 matrices, suggests strongly that the M=As complexes in eq 1 are generated via the coordinatively unsaturated species $Cp(CO)_2M{-}As(t\text{-}Bu)_2$ (M = Mo, W). Future work will seek to establish (a) whether a CO ligand cis or trans to E is ejected in complexes of the type **3a–e** and (b) whether the arsanes and stibanes $Cp(CO)_2(L)M{-}ER_2$ (L = MeNC, Me_3P, $(MeO)_3P$)[13a–c] can be converted into the double-bonded complexes $Cp(CO)(L)M{=}ER_2$.

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Registry No. **3a**, 52456-34-5; **3b**, 52456-36-7; **3c**, 88669-43-6; **3d**, 80977-53-3; **3e**, 88685-54-5; **4a**, 88669-44-7; **4b**, 88669-45-8; **4c**, 88669-46-9; **4d**, 85442-86-0; **4e**, 88685-55-6; **6a**, 88669-47-0; **6e**, 88685-56-7.

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Synthesis and Crystal and Molecular Structure of Trimethylammonium *anti*-7,7′:8,8′-Bis(dithio)bis(7,8-dicarbaundecaborate(10))

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Summary: In refluxing ethanol, ammonium 7,8-dimercapto-7,8-dicarbaundecaborate(10) is formed from ammonium 1,2-disulfido-1,2-dicarbadodecaborane. Oxidation of 7,8-dimercapto-7,8-dicarbaundecaborate(10) with I_3^- in water yields 7,7′:8,8′-bis(dithio)bis(7,8-dicarbaundecaborate(10)). The structure of this salt, as determined by single-crystal X-ray diffraction methods ($P2_1/a$; $a = 13.318$ (4) Å, $b = 15.432$ (5) Å, $c = 7.084$ (2) Å, $\beta = 100.45$ (2)°, $D_{calcd} = 1.186$ g cm^{-3}, $Z = 2$), consists of two 7,8-dicarbaundecaborate(10) units bonded by two –S–S– bridges in such a way that the two cages are placed in an anti fashion. The ^{11}B NMR spectrum of the salt in $Me_2CO\text{-}d_6$ is in accord with the structure established by X-ray diffraction and indicates the isomeric purity of the salt.

It is well-known that removal of the most positive boron atoms, B(3) or B(6), in the *o*-/*m*-dicarbadodecaborane cage (*o*-/*m*-$HCB_{10}H_{10}CH$) may be achieved with strong bases such as methoxide ion yielding $[HCB_{H10}CH]^-$.[1,2] Many *o*/*m*-dicarbadodecaborane derivatives are known to contain more than one cluster unit arranged either linearly as in $RCB_{10}H_{10}CN{=}NCB_{10}H_{10}CR$[3] or cyclically as in $\overbrace{CB_{10}H_{10}CCOCB_{10}H_{10}C}^{CO}$.[4] Although many such compounds are known, the geometry (syn or anti) of partially degraded bis(*o*-/*m*-dicarbadodecarborane) clusters, where there is restricted rotation of the cages, has not been established. We recently found that salts of 1,2-dimercapto-*o*-dicarbadodecaborane unexpectedly undergo partial degradation without the involvement of a base when they are reacted with CH_2Cl_2 or $BrCH_2CH_2Br$ to produce dimers with 7,8-dicarbaundecaborate(10) cages symmetrically placed.[5] No indication of the geometry was then obtained. In this report we present the unexpected syntheses of 7,8-dimercapto-7,8-dicarbaundecaborate(10) and 7,7′:8,8′-bis(dithio)bis(7,8-dicarbaundecaborate(10)) anions and the molecular structure of the latter which shows an anti geometry.

The syntheses of the title compounds was via the route[6,7] shown in eq 1–4. Compounds **3** and **5** are stable in air.

$$\underset{\mathbf{1}}{o\text{-}HSCB_{10}H_{10}CSH} \xrightarrow{NH_3\ \text{liquid}} \underset{\mathbf{2}}{(NH_4)_2[o\text{-}SCB_{10}H_{10}CS]} \tag{1}$$

$$\mathbf{2} \xrightarrow[\text{48-h reflux}]{EtOH} \underset{\mathbf{3}}{(NH_4)[7,8\text{-}HSCB_9H_{10}CSH]} \tag{2}$$

$$\mathbf{3} + NMe_3HCl \xrightarrow{\text{water}} \underset{\mathbf{4}}{(NMe_3H)[7,8\text{-}HSCB_9H_{10}SH]} \tag{3}$$

$$\mathbf{4} + I_3^- \xrightarrow{\text{water}} \underset{\mathbf{5}}{(NMe_3H)_2\ [\overline{SCB_9H_{10}CS\text{-}SCB_9H_{10}CS}]} \tag{4}$$

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‡ Deceased May 11, 1981.

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(2) This boron removal, also known as partial degradation, is also effective for most *o*-/*m*-dicarbadodecaborane derivatives. See, for example: Totani, T.; Aono, K.; Yamamoto, K.; Tawara, K. *J. Med. Chem.* **1981**, *24*, 1492–1499 or ref 3.

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(6) Compound **1** was synthesized according to: Smith, H. D.; Oberland, C. O.; Papetti, S. *Inorg. Chem.* **1966**, *5*, 1013.

(7) Details will be the subject of a full paper.

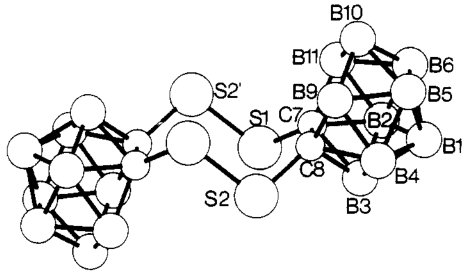

Figure 1. Perspective drawing of the anion 7,7′:8,8′-bis(dithio)bis(7,8-dicarbaundecaborate(10)). Hydrogen atoms have been omitted for clarity. Some significant interatomic distances and angles are as follows: S1–S2′, 2.061 (1) Å; S1–C7, 1.774 (3) Å; C7–C8, 1.594 (4) Å; C7–B11, 1.634 (5) Å; B10–B11, 1.838 (7) Å; S'_1–S_2–C_8, 102.95 (11)°, C8–C7–B11, 110.72 (26)°.

It is important to point out that partial degradation and protonation of both sulfurs has taken place in the step indicated in eq 2. The structure of compound **5** has been solved by single-crystal X-ray diffraction and is illustrated in Figure 1, which shows the molecular geometry and atom numbering convention. The crystals of **5** belong to the monoclinic system, space group $P2_1/a$, with unit cell dimensions a = 13.318 (4) Å, b = 15.432 (5) Å, c = 7.084 (2) Å, and β = 100.45 (2)°; D_{calcd} = 1.186 g cm^{-3} for Z = 2.[8] In this space group this requires that the center of symmetry of each molecule reside at a special position. The molecule consists of two 7,8-dicarbaundecaborate(10) moieties bridged by two –S–S– units in such a way that there is an inversion center in the middle of the molecule. As a consequence the two cluster units are relatively placed in an anti fashion.[9] The cations NMe$_3$H (not represented in Figure 1) are placed sideways to the anionic moiety, not above the pentagonal faces with the missing borons. Some selected distances are indicated in Figure 1. It is interesting to comment on the C-S bond lengths. A C–S distance of 1.774 (3) Å is found in **5**, which is slightly shorter than the C–S bond length of 1.82 (4) Å reported for the disulfide [C$_5$H$_9$NMeHS]$_2$CuCl$_4$[10] while being slightly longer than the C–S distance of 1.737 (5) Å in the copper thiolato complex [Cu(cyclam)(SC$_6$F$_5$)$_2$].[11] Accordingly, there is an apparent relationship between the carbon hybridization and the C–S distances, with C(sp^2) < C(5) < C(sp^3), which could imply a certain C═S double bond character in **5** through delocalization of the sulfur lone pair into the cluster open-face orbitals. The ^{11}B NMR spectrum at 115.5 MHz in the Me$_2$CO-d_6 shows six regions of resonance at –4.23 (d, 142), –9.35 (d, 168), –15.01 (d, 139), –17.14 (d, 146), –32.49, (d, 122), and –34.55 ppm (d, 125) with relative intensities 2:1:2:2:1:1. There is an additional splitting of each of the resonances at –32.49 ppm of 49 Hz attributed to bridge hydrogen.[12] All these data are consistent with the structure stablished by X-ray diffraction. The {^{1}H} ^{11}B NMR spectrum displays only five well-defined signals, which indicate fairly clearly the isomeric purity of compound **5**.

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Supplementary Material Available: Table of structure factors for **5** (9 pages). Ordering information is given on any current masthead page.

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[8] A crystal with approximate dimensions 0.21 × 0.19 × 0.18 mm was selected for X-ray analysis. Intensity measurements were carried out on a Syntex P2$_1$ automated four-circle diffractometer using graphite monochromatized Mo Kα radiation. Reflections with 2θ up to 55° were collected by the θ–2θ scan technique. A total of 3970 unique data was collected, of which 1935 had $I < 3\sigma(I)$. The structure was solved by direct methods using standard procedures (cf.: Hilty, T. K.; Thompson, D. A.; Butler, W. M.; Rudolph, R. W. *Inorg. Chem.* **1979**, *18*, 2642) to give an R_1 value of 0.047 and R_2 value of 0.053.

[9] A priori, it would have been expected that in order to minimize the electrical repulsions an anti geometry would be favored when the cages occupy nearby spatial positions, and a mixture of syn and anti isomers would appear when they were placed in noninteracting positions.

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[12] (a) This resonance is attributed to B(10). (b) Siedle, A. R.; Bodner, G. M.; Todd, L. J. *J. Organomet. Chem.* **1971**, *33*, 137. (c) The ^{11}B NMR data for compound 4 in Me$_2$CO-d_6 is as follows: –5.90 (d, 140), –7.48 (d, 165), –16.20 (d, 142), –33.02 (d, 124), and –34.20 ppm (d, 127), with relative intensities 2:1:4:1:1. There is an additional splitting of each of the resonances at –33.02 ppm of 41 Hz which is attributed to bridge hydrogen.

(C$_5$H$_5$)$_2$Zr[Ru(CO)$_2$C$_5$H$_5$]$_2$. A Metal–Metal Bonded Zirconium–Diruthenium Complex

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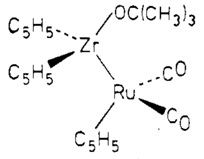
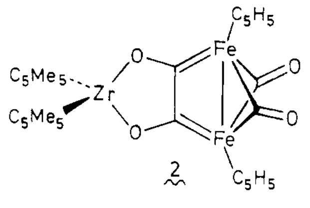
Summary: K[(C$_5$H$_5$)Ru(CO)$_2$] reacts with (C$_5$H$_5$)$_2$ZrI$_2$ to give (C$_5$H$_5$)$_2$Zr[Ru(CO)$_2$(C$_5$H$_5$)]$_2$ (**3**). A single-crystal X-ray structural analysis of **3** establishes the metal–metal bonded nature of the complex. The space group is *Pbca*; the cell dimensions are a = 15.000 (4) Å, b = 17.425 (3) Å, c = 16.957 (4) Å, and Z = 8.

We have become interested in synthesizing heterobimetallic complexes in which an early transition metal is directly bonded to a late transition metal because we believe such compounds might be good precursors for new types of hydrogenation catalysts. Recently we reported the synthesis of a series of metal–metal bonded zirconium-iron and zirconium–ruthenium complexes such as (C$_5$H$_5$)$_2$[(CH$_3$)$_3$CO]Zr–Ru(CO)$_2$C$_5$H$_5$ (**1**) by reaction of



1



2

K[(C$_5$H$_5$)M(CO)$_2$] (M = Fe, Ru) with bis(cyclopentadienyl)zirconium chloride complexes.[1] We were interested to see if we could extend this method to the

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[1] Casey, C. P.; Jordan, R. F.; Rheingold, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 665 and references therein.