were added, and the mixture was stirred until the orange color was discharged and replaced by a pale yellow color. For compounds **5** and **6**, this required ca. 3 h of stirring at room temperature, but the preparation of **7** required 3 h of heating to reflux. A saturated NaCl solution was added to the reaction mixture. Extraction with toluene (**5**, **6**) or CH_2Cl_2 (**7**), filtration, and drying of the organic layer followed by removal of solvent gave the dihydride complexes as colorless solids. Yield: **5** (88%), **6** (80%), **7** (84%). See Table I.

Synthesis of Trihydride Cations. A typical preparation is as follows: A 100-mg quantity of **5** was dissolved in 5 mL of CH_2Cl_2 and cooled to −40 °C. One equivalent of $HBF_4{\cdot}Et_2O$ was added, and the trihydrido cation was precipitated with the addition of 10 mL of Et_2O. The solid was allowed to settle, and the supernatant was removed. The precipitate was washed with 2 × 10 mL of Et_2O and dried in vacuo at room temperature to afford 45 mg of **8** (39%). A similar procedure gave **9** (89%) and **10** (69%). See Table I.

^{1}H NMR Studies. A 10–15-mg quantity of the trihydride was loaded into an NMR tube in the inert atmosphere drybox. The sample was degassed under vacuum and $CDFCl_2$ was condensed in. The samples were freeze/pump/thaw/degassed and sealed under dynamic vacuum. During the thaw portion of the cycle, the samples were warmed only to −78 °C and were kept at that temperature until use.

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Metallacarborane Complexes as Guests for Cyclodextrins. Molecular Structure of the Inclusion Complex $Cs[\mathit{closo}\text{-}3,3,3\text{-}(CO)_3\text{-}3,1,2\text{-}ReC_2B_9H_{11}{\cdot}\alpha\text{-}CD]{\cdot}8H_2O$

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Inclusion complexes of the metallacarboranes $Cs[\mathit{closo}\text{-}3,3,3\text{-}(CO)_3\text{-}3,1,2,\text{-}MC_2B_9H_{11}]$ (M = Mn, Re) with α- and β-cyclodextrin have been prepared in aqueous solution to yield $Cs[\mathit{closo}\text{-}3,3,3\text{-}(CO)_3\text{-}3,1,2\text{-}MC_2B_9H_{11}{\cdot}\alpha\text{-}CD]$ [M = Mn (**1a**), M = Re (**2a**)] and $Cs[\mathit{closo}\text{-}3,3,3\text{-}(CO)_3\text{-}3,1,2\text{-}MC_2B_9H_{11}{\cdot}\beta\text{-}CD]$ [M = Mn (**1b**), M = Re (**2b**)]. The binding constants of these inclusion complexes have been determined by NMR studies. Very strong binding was observed in aqueous solution with β-cyclodextrin as host, and the binding constants obtained for **1b** and **2b** were 1080 (±150) and 942 (±73) M^{-1}, respectively, in D_2O/DMSO-d_6 (50:50 volume ratios). The single-crystal X-ray diffraction study of **2a**·8H_2O is reported. Crystal data for **2a**·8H_2O: $C_{41}H_{71}B_9CsReO_{33}$ + 8H_2O, orthorhombic, $P2_12_12_1$, a = 13.705 (1) Å, b = 20.280 (2) Å, c = 23.384 (2) Å, V = 6499 Å^3, Z = 4, D(calcd) = 1.689 g cm^{-3}, T = 188 K, λ = 0.709 26 Å, crystal size 0.4 × 0.3 × 0.1 mm, μ = 25.29 cm^{-1}. Of the 6432 unique reflections measured, in the range $\theta < 28°$, 3960 were considered observed ($I > 3\sigma(I)$). The final R factor was R = 0.075, R_w = 0.085.

The study of inclusion complexes of cyclodextrins with both organic[1] and organometallic[2] guest molecules has stimulated interest due to their possible application in catalysis[3] and as enzyme models.[4] A number of inclusion complexes have been prepared with organometallic compounds as guests;[5] adduct formation results from insertion of a hydrophobic moeity such as a cyclopentadienyl, arene, or diene ligand on the metal into the cyclodextrin cavity.[6] In most cases the structures of these ligands do not allow for optimal host–guest interaction within the cyclodextrin

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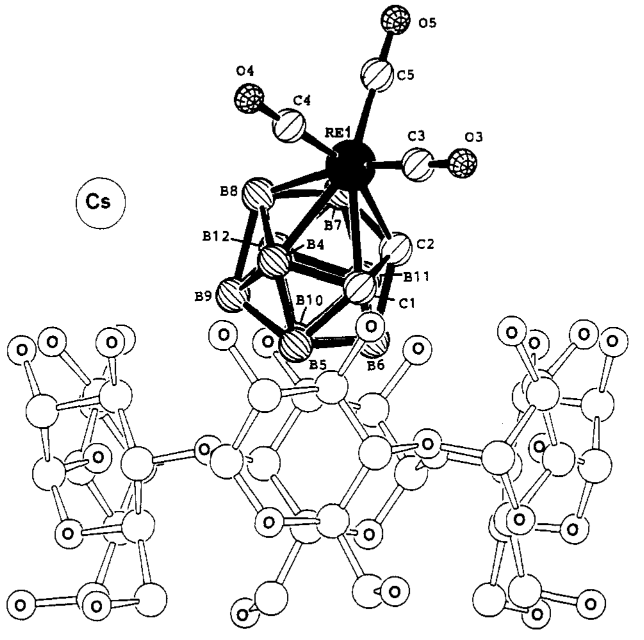

Figure 1. Molecular structure of the inclusion complex Cs[*closo*-3,3,3-$(CO)_3$-3,1,2-$ReC_2B_9H_{11}$·α-CD]·$8H_2O$ (**2a**). Hydrogen atoms and water molecules have been omitted for clarity.[13]

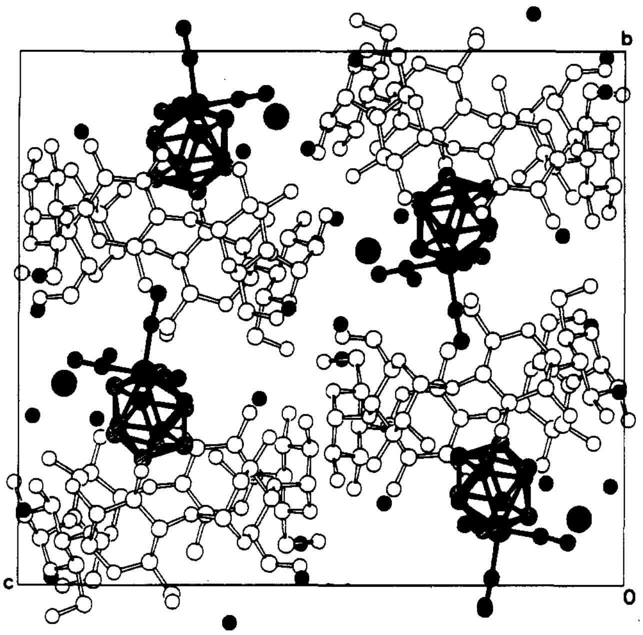

Figure 2. Molecular packing of Cs[*closo*-3,3,3-$(CO)_3$-3,1,2-$ReC_2B_9H_{11}$·α-CD]·$8H_2O$ (**2a**). The atoms of the guest molecules are shaded, and water molecules are represented by black circles. Hydrogen atoms have been omitted for clarity.

cavity, resulting in a relatively weak binding of the metal complex to the cyclodextrin.[7] The formation of inclusion complexes between *o*-carborane and cyclodextrins[8] suggested that transition-metal dicarbollide complexes should readily form inclusion compounds with these hosts, allowing for the formation of a new class of transition-metal inclusion complexes. The shape and dimension of the dicarbollide ligand would be expected to maximize the important van der Waals contribution[9] to the interaction between host and guest and strongly bind the metal fragment to the cyclodextrin. In this report we describe the formation of the first metallacarborane inclusion complexes of Cs[*closo*-3,3,3-$(CO)_3$-3,1,2-$MC_2B_9H_{11}$] [M = Mn (**1**), M = Re (**2**)][10] as guests with α-cyclodextrin to yield Cs[*closo*-3,3,3-$(CO)_3$-3,1,2-$MC_2B_9H_{11}$·α-CD] [M = Mn (**1a**), M = Re (**2a**)]. With β-cyclodextrin the complexes Cs[*closo*-3,3,3-$(CO)_3$-3,1,2-$MC_2B_9H_{11}$·β-CD] [M = Mn (**1b**), M = Re (**2b**)] were obtained. The molecular structure of Cs[*closo*-3,3,3-$(CO)_3$-3,1,-2-$ReC_2B_9H_{11}$·α-CD]·$8H_2O$ (**2a**) was determined by X-ray crystallography, and the binding constants of complexes **1a** and **2a** in D_2O and of **1b** and **2b** in D_2O/DMSO-d_6 (50/50) are reported.

The syntheses of the inclusion complexes were carried out by directly adding the guest to hot aqueous solutions of the cyclodextrin. Slow cooling of the filtered solutions resulted in well-defined crystals for the α-cyclodextrin inclusion complexes whereas with β-cyclodextrin as host microcrystalline solids were obtained. All the complexes were obtained as hydrates and analyzed correctly for a 1:1 host–guest stoichiometry.[11]

An X-ray diffraction study of **2a**[12] was undertaken, and the molecular structure (Figure 1) revealed that the guest anion only just penetrates into the cyclodextrin cavity such that the B(5) and B(6) atoms lie 0.11 and 0.02 Å, respectively, below the plane defined by the 12 secondary hydroxy oxygens of the cyclodextrin; the B(10) atom lies 0.02 Å above this plane. The guest is oriented such that the plane including the B(5), B(6), and B(10) atoms is nearly parallel (4°) to the plane containing the 12 secondary hydroxy oxygens of the cyclodextrin. The non-hydrogen intermolecular distances between the boron atoms B(5), B(6), B(9), and B(10) and their closest contact atoms of the host are the sum of their van der Waals radii, indicating that further penetration into the cavity is not possible. Interestingly, the pentagon incorporating atoms B(5), B(6), B(11), B(12), and B(9) subtends an angle of 41° to the best plane through the 12 secondary hydroxy oxygens of the cyclodextrin. This is nearly the same value which the cyclopentadienyl ligands of ferrocene[6a] (42°) and

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(7) The highest K_a value reported in aqueous solution for a transition-metal complex with underivatized cyclodextrin is 2950 kg mol^{-1} for the complex *trans*-$[Pt(PMe_3)Cl_2(NH_3)]$ with β-cyclodextrin.[6d] The PMe_3 ligand penetrates the cyclodextrin cavity, providing a strong binding interaction.

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(11) Anal. found (calcd) for **1a** ($C_{41}H_{71}B_9CsMnO_{33} + 2H_2O$): C, 34.88 (34.83); H, 5.35 (5.35); B, 7.10 (6.88); Cs, 9.21 (9.40); Mn, 3.95 (3.85). Found (calcd) for **1b** ($C_{47}H_{81}B_9CsMnO_{38} + 5H_2O$): C, 35.87 (34.64); H, 5.68 (5.64); B, 5.70 (5.97); Cs, 7.46 (8.16); Mn, 3.30 (3.37). Found (calcd) for **2a** ($C_{41}H_{71}B_9CsReO_{33} + 3H_2O$): C, 31.92 (31.51); H, 5.03 (4.98); B, 6.40 (6.23); Cs, 8.55 (8.51); Re, 12.05 (11.92). Found (calcd) for **2b** ($C_{47}H_{81}B_9CsReO_{38} + 5H_2O$): C, 31.26 (32.06); H, 5.06 (5.22); B, 5.60 (5.52); Cs, 7.30 (7.55); Re, 10.55 (10.58).

(12) Crystal data: $C_{41}H_{71}B_9CsReO_{33} + 8H_2O$, orthorhombic, $P2_12_12_1$, a = 13.705 (1) Å, b = 20.280 (2) Å, c = 23.384 (2) Å, V = 6499 $Å^3$, Z = 4, D(calcd) = 1.689 g cm^{-3}, T = 188 K, λ = 0.709 26 Å, crystal size 0.4 × 0.3 × 0.1 mm, μ = 25.29 cm^{-1}. Data were collected on a Philips PW100 diffractometer at 188 (2) K in the θ–2θ mode. Of the 6432 unique reflections measured, in the range $\theta < 28°$, 3960 were considered observed ($I > 3\sigma(I)$). The final *R* factor was $R = 0.075$, $R_w = 0.085$. The cesium atom and the primary hydroxy group of G2 are disordered. The cesium cation could be located at two positions having an occupancy ratio of about 4:1. In the position of high occupancy, the cesium is coordinated to three hydroxy groups and two water molecules at distances of 2.90 and 3.22 Å, respectively. Due to the small number of observed reflections, only Re was refined anisotropically and hydrogen atoms could not be localized.

(13) Fortran program (SCHAKAL 88B/V16) for the graphic representation of molecular and crystallographic models by E. Keller, Kristallographisches Institut der Universität, D-7800 Freiburg, FRG.

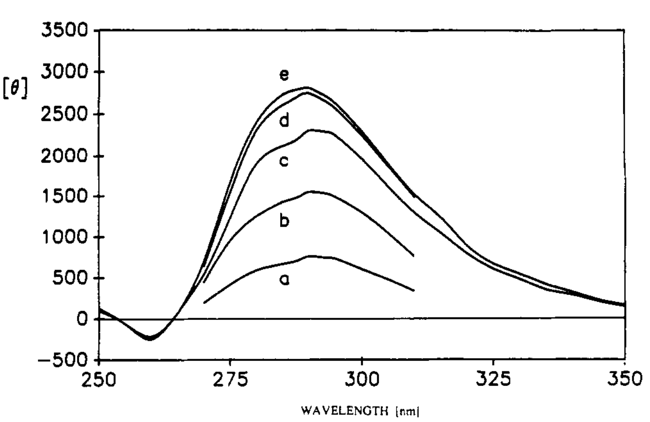

Figure 3. Induced circular dichroism spectra of aqueous solutions of **2** (3.0×10^{-4} M) in the presence of (a) 0.33, (b) 0.67, (c) 1.0, (d) 1.5 and (e) 2.0 equiv β-cyclodextrin.

the cyclopentadienyl and arene groups of $(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}C_6H_6)PF_6$[6b] (39° and 40°, respectively) subtend with the same plane of α-cyclodextrin.[14] The cyclodextrin units pack in a head to tail manner, forming a channel structure. Each cyclodextrin is hydrogen bonded to its adjacent neighbors in the channel either indirectly via water molecules or directly through its primary or secondary hydroxy groups (Figure 2). None of the three guest carbonyl oxygens is involved in any hydrogen-bonding interactions with the cyclodextrin or water molecules. One carbonyl ligand, C(5)–O(5), penetrates the cavity of the adjacent cyclodextrin molecule in the channel such that the O(5) atom is 0.48 Å above the best plane incorporating the six primary hydroxy oxygens of the adjacent cyclodextrin. The guest anions lie in the cyclodextrin channels, with their axis being alternatively tilted in a positive and negative sense relative to the channel axis. Another interesting feature of the packing is that adjacent channels run antiparallel to one another so that the guests of one channel are aligned in the opposite sense to those in the adjacent channel.

The ^{1}H NMR spectrum of a 6 mM solution of **2a** in D_2O at room temperature showed a downfield chemical shift, relative to the chemical shift of free α-cyclodextrin, of 36.6 Hz at 250 MHz for the H(3) protons of the α-cyclodextrin. No shift was observed for the H(5) protons of the cyclodextrin or for the carboranyl C–H groups of the guest anion, implying little penetration of the guest into the cavity occurs in solution, as expected from the molecular structure. The same changes were observed in the ^{1}H NMR spectrum of **1a** in D_2O, suggesting that the mode and degree of penetration of the guest anion into the α-cyclodextrin cavity are similar to that of **2a**. The binding constants (K_a) for **1a** and **2a** were determined by the chemical shift dependence of the H(3) protons on concentration,[15] yielding values of 426 (±17) and 329 (±16) M^{-1}, respectively. The room-temperature ^{1}H NMR spectrum of **2b** in D_2O (3 mM) at 250 MHz shows an upfield shift for the carboranyl C–H groups of 54.4 Hz relative to the chemical shift of free **2**, suggesting that the dicarbollide ligand penetrates deeply into the cavity of the cyclodextrin.

Induced circular dichroism (ICD) spectra of solutions of **2** with varying concentrations of β-cyclodextrin showed a positive Cotton effect, which could already be observed in a solution of the preformed complex (Figure 3). Due to a very strong binding interaction and a relatively weak Cotton effect, the solution of **2** could not be titrated in the concentration range allowing for quantitative assessment of K_a. A similar attempt to obtain the binding constant using the decrease in the ultraviolet absorption intensity of **1** with increasing β-cyclodextrin concentration was unsuccessful for the same reasons. The concentration-dependent ICD spectra (Figure 3) suggest a very strong host–guest binding interaction, since saturation binding was achieved with the addition of 2 equiv of β-cyclodextrin in a 3.0×10^{-4} M aqueous solution of **2**.[7,16] The K_a values for **1b** and **2b** were measured in D_2O/DMSO-d_6 (50:50 volume ratios)[17] by ^{1}H NMR[15] spectroscopy using the carboranyl C–H as a probe. In this solvent mixture values of 1080 (±150) and 942 (±73) M^{-1} were obtained for **1b** and **2b**, respectively.[18] These values, when compared to the binding constant of a strongly interacting guest molecule such as *m*-*tert*-butylphenyl acetate with β-cyclodextrin[19] (K_a = 500 M^{-1} in the same solvent mixture[17]), demonstrate a very strong interaction between **2** and β-cyclodextrin and emphasize the optimal fit of the dicarbollide ligand in the cavity of β-cyclodextrin.

Acknowledgment. We thank T. Lochmann, K. Jäkel, and H. R. Walter for technical assistance and Dr. A. Alder for helpful discussions.

Supplementary Material Available: Listings of bond distances and bond angles and positional and thermal parameters (9 pages); a listing of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

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(17) The binding of substrates to cyclodextrins is substantially weakened in the presence of nonaqueous solvents. See ref 16b and: Breslow, R.; Siegel, B. *J. Am. Chem. Soc.* **1975**, *97*, 6869–6870.

(18) The complexes $(\eta^5\text{-}C_5H_5)_2M$ (M = Fe, Ru, Os) have been shown to interact strongly with β-cyclodextrin in ethylene glycol. K_a values between 510, 660, and 790 M^{-1}, respectively, have been reported. Sokolov, V. I.; Bondareva, V. L.; Golovaneva, I. F. *Metallorg. Khim.* **1989**, *2*, 1252–1255.

(19) The binding constant between *m*-*tert*-butylphenyl acetate and β-cyclodextrin in aqueous solution is 1×10^4 M^{-1} (see ref 9c).