example has no especially large effect on association constants in chloroform, and we expect that this result will be generally true. Water does, however, have a large effect on ΔH and ΔS of association. Therefore future reports concerning the thermodynamics of host-guest binding in organic solvents should carefully stipulate the amount of water present during binding experiments. Attention to this point would help to reduce the uncertainities that arise when binding data from several different laboratories are compared.

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Supplementary Material Available: Purification methods, spectroscopic data (IR, ^{1}H NMR, ^{13}C NMR, MS) and combustion (elemental) analysis for host **1**, complete binding data for all association constants, and plots of calculated and observed chemical shifts for each binding experiment (12 pages). Ordering information is given on any current masthead page.

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Unusual Organic Chemistry on a Metallacarborane Substrate: Formation of a B-Vinyl Ester from Acetyl Chloride

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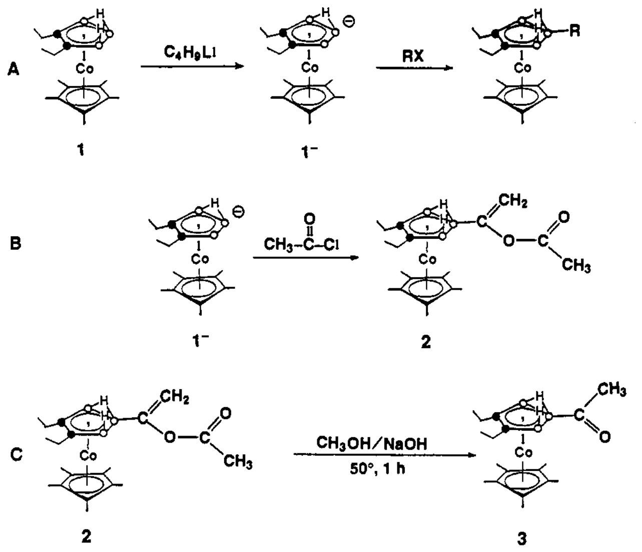
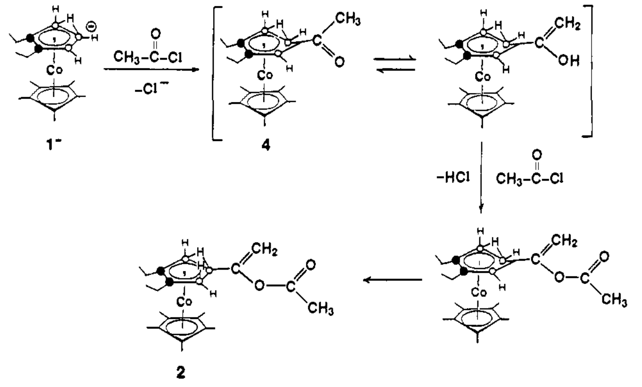
We report an unexpected reaction that has implications for organoborane/organocarborane chemistry, the consequences of which are currently being exploited in our program in transition-metal organometallic synthesis. In developing methods for systematically linking and/or stacking metal-carborane sandwich units such as $(C_5Me_5)Co(Et_2C_2B_3H_5)$ (**1**) as precursors to electron-delocalized oligomers and polymers,[1] we found earlier[1a] that the **1**$^-$ anion (obtained by bridge deprotonation of **1**), when treated with a variety of alkyl and arylalkyl halides, undergoes regiospecific substitution at the middle boron atom [B(5)] to generate the neutral B(5)-alkyl product, as shown in Scheme I (A). (The Fe-arene and Ru-arene analogues of **1** behave similarly[1a]). In the present work, we attempted the analogous synthesis of the B(5)-acetyl derivative via reaction of **1**$^-$ with acetyl chloride in THF at −76 °C, but no acetyl species was detected. Instead, the only identifiable product (55% yield based on **1** consumed) other than the starting material **1** was an air-stable solid (**2**) which has been characterized as the B(5)-(1-vinyl acetate) derivative of **1** [Scheme I (B)].[2] The identity of **2** follows from its 300-MHz ^{1}H, 90-MHz ^{13}C, and 115.8-MHz ^{11}B FT NMR, IR, and mass spectra, supported by X-ray diffraction data. The crystal structure analysis of **2** established the locations of all atoms including hydrogens and confirmed the nature of the vinyl ester (enol acetate) moiety attached to B(5).[3] In a further odd twist of fate, we found that **2** readily undergoes base-catalyzed cleavage to give the B(5)-acetyl derivative **3**, the original target compound, in high yield [Scheme I(C)].[4]

Scheme I[a]



[a] (●) C; (○) B, BH.

Scheme II[a]



[a] (●) C, (○) B.

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(2) A 0.52-5 (1.7 mmol) sample of **1** was deprotonated by treatment with *n*-butyllithium under vacuum in THF at −76 °C as described elsewhere.[1c] To this solution was added, via syringe, 2.1 mmol of acetyl chloride at −76 °C, and the resulting dark orange-brown solution was stirred for 3 days at room temperature, after which the greenish yellow solution was opened to air, the solvent removed by evaporation, and the dark brown solid residue taken up in CH_2Cl_2 and filtered through 2 cm of silica. The filtrate was evaporated, and the dark brown residue was chromatographed on a silica column in 50:50 hexane/CH_2Cl_2, giving two yellow bands, of which the first was **1**, 0.290 g, 0.92 mmol. The second band was yellow-brown **2**, 0.160 g, 0.400 mmol: ^{1}H NMR (δ, ppm, $CDCl_3$) 5.16 (s, $=CH_2$), 5.03 (s, $=CH_2$), 2.14 (s, $COCH_3$), 2.07 (m, CH_2), 1.85 (m, CH_2), 1.70 (s, C_5Me_5), 1.07 (t, CH_3), −4.9 (br s, BHB); ^{13}C NMR (δ, ppm, $CDCl_3$) 169.8 (s, C=O), 160 (br s, CB), 111.8 (t, $=CH_2$), 92.6 (s, C_5 ring), 23.0 (t, CH_2), 21.6 (q, $COCH_3$), 17.6 (q, CH_3), 9.8 (q, C_5Me_5); ^{11}B NMR (δ, ppm, relative to $BF_3{\cdot}OEt_2$, hexane) 11.7 (s, B(5)), −0.8 (d, 125 Hz, B(4,6)); IR (neat, cm^{-1}) 2960 (vs), 2927 (s), 2910 (sh), 2867 (s), 2514 (s), 2358 (w br), 2322 (w br), 1869 (m br), 1750 (vs), 1448 (m), 1379 (vs), 1368 (vs), 1363 (sh), 1237 (vs), 1201 (vs), 1026 (s), 895 (s), 873 (s), 773 (s); exact mass calcd for $^{59}Co^{16}O_2{}^{12}C_{20}{}^{11}B_3{}^1H_{34}{}^+$ 398.2170, found 398.2156.

(3) Crystal data: space group $P2_1/n$; $Z = 4$; $a = 8.368$ (2) Å, $b = 18.757$ (5) Å, $c = 14.234$ (4) Å; $\beta = 97.25$ (2)°; $V = 2216$ (2) Å^3. Data collection parameters: maximum 2θ range 55°, Mo Kα radiation, $\lambda = 0.710\,69$ Å. The structure was solved by heavy-atom techniques (TEXSAN 5.0) and refined to $R = 0.037$ for 3856 absorption-corrected reflections having $F_o{}^2 > 3.0\sigma(F_o{}^2)$. A full report of the structure determination will be given later.

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Although the formation of enol acetates from attack of acyl halides on enolate anions is not uncommon in organic chemistry,[5] reaction B is remarkable in several respects: (i) acetyl chloride is the only source of —(C=O)— in this system; (ii) the acetyl derivative **3** is *not* a precursor to **2**, since treatment of **3** or its deprotonated anion **3**$^-$ with acetyl chloride fails to generate **2**; and (iii) there is no evidence of the existence of **3** in solution under our experimental conditions.[6] Moreover, to our knowledge this type of reaction is unprecedented in boron cluster chemistry. For example, the electrophilic attack of acetyl chloride or benzoyl chloride on *nido*-$C_2B_9H_{12}^-$ carborane ions (which are similar to **1**$^-$ in having an open C_2B_3 face) generates in each case the expected *B*-acyl derivative.[7] Similarly, the interaction of the 1-lithio derivative of the icosahedral 1,2- or 1,7-$C_2B_{10}H_{12}$ carboranes with acetyl chloride proceeds normally to give the respective 1-acetyl carborane.[8]

Reactions of **1**$^-$ with a few other acyl halides have been examined and thus far have not shown behavior of the type seen in reaction B,[9] although studies are continuing. Since the acetyl derivative **3** is not a precursor to **2**, as noted above, a different pathway is involved. Pending the outcome of studies currently under way, we believe it likely that the initial step in reaction B is the attack of an acetyl moiety at the nucleophilic B–B edge of **1**$^-$ to form an acetyl-bridged intermediate **4** containing a B–C–B three-center bond (Scheme II). Such a mechanism would correspond to that proposed earlier for the regiospecific B-alkylation[1a] of **1**, its iron–arene and ruthenium–arene counterparts,[1a] and the *nido*-$R_2C_2B_4H_5^-$ carboranes.[10] Electron withdrawal from the bridging acetyl unit in **4** could be expected to polarize the carboxyl region, favoring the enolate species whose C–O$^-$ group may then undergo O-acetylation and rearrangement to give **2**. At least 50% of the neutral **2** starting material is recovered, attributed to the interaction of **1**$^-$ with protons generated in the formation of the vinyl acetate.

The isolated B(5)-acetyl derivative **3** is itself a remarkable species, manifesting unexpected metal-coordinating properties which have opened a new synthetic route to multidecker sandwich complexes, as described in the accompanying paper,[11] and also is a potentially important precursor to linked metallacarborane oligomers and polymers via acyl polymerization processes.

Acknowledgment. The support of the National Science Foundation (Grant No. CHE 87-21657) and the U.S. Army Research Office is gratefully acknowledged. We thank Professor Frank Carey for enlightening discussions.

Supplementary Material Available: ORTEP diagram of **2** and tables of positional and thermal parameters, bond lengths, and bond angles for **2** (6 pages); listing of observed and calculated structure factors for **2** (26 pages). Ordering information is given on any current masthead page.

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(4) A 0.275-g sample of **2** was dissolved in 50 mL of methanol, 42 mg of NaOH was added, and the solution was heated at 50 °C for 1 h, which produced a color change to pale green. Following addition of excess NH_4Cl, the solution was evaporated, the residue taken up in CH_2Cl_2, the solution filtered, and the filtrate evaporated. The residue was chromatographed on a silica column in 50:50 hexane/CH_2Cl_2, producing several light yellow bands, which were **2** and minor cleavage products, and a major band, which was dark yellow **3**, obtained on evaporation of the solution as a crystalline solid, 0.204 g, 83% yield: ^1H NMR (δ, ppm, $CDCl_3$) 2.17 (s, $COCH_3$), 2.05 (m, CH_2), 1.86 (m, CH_2), 1.66 (s, C_5Me_5), 1.07 (t, CH_3); ^{13}C NMR (δ, ppm, $CDCl_3$) 113 (br s, C_2B_3 ring), 93.1 (s, C_5 ring), 37.2 (q, $COCH_3$), 23.0 (t, CH_2), 17.5 (q, CH_3), 9.9 (q, C_5Me_5); ^{11}B NMR (δ, ppm relative to $BF_3{\cdot}OEt_2$, hexane) 7.8 (s, B(5)), 2.8 (d, 130 Hz, B(4,6)); IR (neat, cm^{-1}) 2961 (vs), 2928 (s), 2912 (sh), 2866 (s), 2520 (s), 1886 (m br), 1851 (m br), 1654 (vs), 1610 (m), 1454 (s), 1446 (s), 1428 (m), 1383 (s), 1340 (m), 1199 (s), 1029 (s), 944 (m), 846 (m), 773 (s); exact mass calcd for $^{59}Co^{16}O^{12}C_{18}{}^{11}B_3{}^{11}H_{32}{}^+$ 356.2064, found 356.2057.

(5) An example of O-acylation in organosilicon chemistry is the reaction of PhCOCl with diethyl (lithio(trimethylsilyl)methyl)phosphonate; the preference for O- over C-acylation was attributed to steric hindrance by the Me_3Si and $P(O)(OEt)_2$ substituents. See: Carey, F. A.; Court, A. S. *J. Org. Chem.* **1972**, *37*, 939. As in most cases, the acylation takes place at an oxygen present in the original substrate, in contrast to the reaction reported here.

(6) The reaction was monitored at room temperature as a function of time, via TLC analysis, with no observable formation of **3** under the conditions employed in the synthesis of **2**.

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(9) Reactions of **1**$^-$ with benzoyl chloride or malonyl chloride yield no identifiable products. Reaction with trimethylacetyl chloride or methyl malonyl chloride forms <5% of the 5-substituted derivative. Trifluoroacetyl chloride yields ~5% of the 4,6-disubstituted metallacarborane.

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Electronic Control of Metallacarborane Stacking Reactions. Directed Synthesis of $Cp^*Co(C_2B_3)M(C_2B_3)CoCp^*$ Tetradecker Sandwiches[1]

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Small metallacarboranes of the type $LM(R_2C_2B_3H_5)$ (**1**), in which LM typically is CpCo, $(C_5Me_5)Co$, (arene)Fe, or (arene)Ru, are versatile building block reagents for the preparation of linked and stacked sandwich complexes, including triple-deckers.[1a,b,2] As shown in Scheme I (A), the removal of one or both B–H–B bridge protons to form the mono- or dianion (**1**$^-$ or **1**$^{2-}$) with subsequent coordination of a transition metal–ligand unit to the open face is a convenient route to homo- and heterobimetallic triple-decker species **2**. An apparently straightforward extension of this approach would be the reaction of 2 equiv of **1**$^-$ or **1**$^{2-}$ ions with a metal cation to generate tetradecker stacks (**3**) as in Scheme I (B). However, attempts at such reactions in our laboratory have been unsuccessful, and no species of type **3** have been characterized.[3] (A related class of tetradecker complexes, bridged by two C_3B_2 organoboron rings, is well established.[4])

Here we describe an unexpected discovery which has led directly to a solution of the "carborane tetradecker stacking problem" and has opened the way to the utilization of reactions of class B in preparing multidecker sandwiches. More generally, it reflects the sensitivity[1a,b] of the metal-binding capability of the metallacarborane C_2B_3 face to its electron population and charge distribution, a finding with potentially broad synthetic implications. The B(5)-acetyl complex $(C_5Me_5)Co[Et_2C_2B_3H_4\text{-}5\text{-}C(O)Me]$ (**4a**) (compound **3** in the preceding communication[5]), on deprotonation with *n*-butyllithium followed by addition of $NiBr_2$ in THF, afforded a dark brown crystalline air-stable complex, **5a**, in 41% isolated yield.[6] Spectroscopic[6] and crystallographic[7] charac-

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