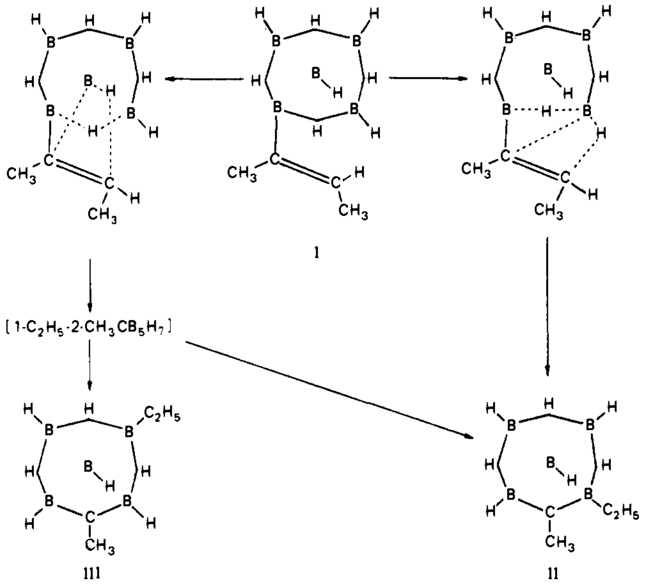
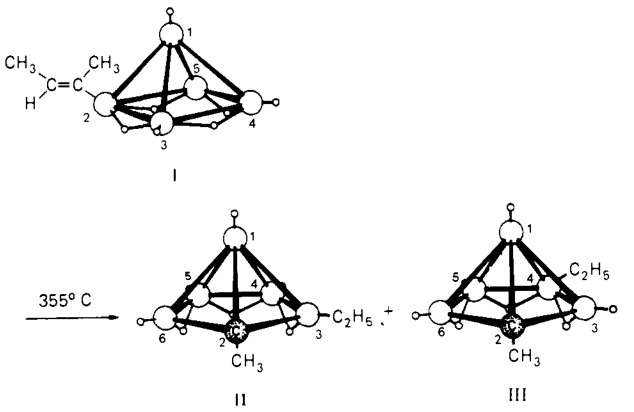
Scheme I. Proposed Mechanism for the Conversion of 2-(*cis*-2-Butenyl)pentaborane(9) (I) into $2\text{-}CH_3\text{-}3\text{-}C_2H_5CB_5H_7$ (II), and $2\text{-}CH_3\text{-}4\text{-}C_2H_5CB_5H_7$ (III).



($B_{3,5}$-H, 2 H), 2.32 (B_4-H, 1 H), 1.03 (B_1-H, 1 H), −1.33 (H_{Br}, 2 H), and −2.52 ppm (H_{Br}, 2 H), as well as the resonances expected from the butenyl group at 5.76 (q, J = 6.9 Hz, CH), 1.71 (s, CH_3), and 1.61 ppm (d, J = 6.9 Hz, CH_3). Cis addition at the alkyne was confirmed by the reaction of I with excess glacial acetic acid. Analysis of the resulting 2-butene by GLC[7] indicates a cis/trans ratio of 97.2:2.8.

Since compounds such as I have been proposed as the first step intermediates in thermally induced carborane syntheses, it was expected that I could be converted into carboranes easily. The thermolysis reactions of I were therefore investigated, and it was found that the quick passage of I through a heated tube (355 °C) in vacuo indeed results in an 86% conversion of I into carborane products. The two major products are $2\text{-}CH_3\text{-}3\text{-}C_2H_5CB_5H_7$ (II, 37%) and $2\text{-}CH_3\text{-}4\text{-}C_2H_5CB_5H_7$ (III, 39%) as shown.



Compound II was previously known[8] and was identified by comparison of its ^{11}B and ^1H NMR spectra with literature values. Compound III is a previously unreported isomer, the structure of which was deduced from the spectroscopic data.[9]

Previously, CB_5H_9 and its alkyl derivatives were synthesized in only low yields from the thermal reactions of pentaborane(9) and acetylene,[2a] or in moderate yields from the reaction of $2,5\text{-}C_2B_6H_8$ with tetramethylammonium borohydride.[8] Thus, the combined discovery of a metal assisted synthesis of alkenylpentaborane(9) derivatives and their subsequent conversion into the corresponding alkyl derivatives of CB_5H_9 provides an attractive new route to this unusual monocarbon carborane.

The formation of II and III as major products in this reaction is consistent with the reaction sequence originally proposed by Williams[2b] for the corresponding thermal reaction. This mechanism is shown in Scheme I and involves an internal hydroboration of the butenyl group by an adjacent B–H group (boron positions 1 or 3) followed by an ethyl group migration to generate II and $1\text{-}C_2H_5\text{-}2\text{-}CH_3CB_5H_7$. The latter compound may then readily rearrange under the reaction conditions in a manner similar to the thermal rearrangement of 1-alkylpentaboranes to 2-alkylpentaboranes[10] to yield both II and III.

The results presented above are important not only because they provide further insight into the mechanism of the reactions of boron hydrides and alkynes, but, in addition, they illustrate a new direction of potentially great importance in boron cage chemistry, that is, the use of transition metal complexes as catalytic reagents to induce reactions which previously could be carried out only under severe conditions.[11] Indeed, we have now obtained results similar to those described above with a variety of catalysts and boron cage systems and this will be discussed in a future publication.

Acknowledgment. We thank the Karcher and Busch Foundations for fellowships (R.W.) and the Army Office of Research for support of this work.

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(2) (a) T. P. Onak, G. B. Dunks, J. R. Spielman, F. J. Gerhart, and R. E. Williams, *J. Am. Chem. Soc.*, **88,** 2061 (1966). (b) R. E. Williams in "Progress In Boron Chemistry", Vol. 2, R. J. Brotherton and H. Steinberg, Eds., Pergamon Press, New York, 1970, Chapter 2.

(3) Recently, higher percent conversions and turnover rates have been observed for this reaction using other transition metal catalysts: R. Wilczynski and L. G. Sneddon, unpublished work.

(4) Tricresyl phosphate (TCP), 6% on 60–80 mesh Chromosorb W; 80 °C; $R_V(B_5H_9)$ = 1.0, R_V(I) = 15.0.

(5) Relative to $BF_3\cdot O(C_2H_5)_2$ with positive sign indicating shift to lower field.

(6) Relative to Me_4Si with positive sign indicating shift to lower field.

(7) Durapak phenyl isocyanate/Proacil C; 80–100 mesh; 35 °C.

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(11) In this regard, Fehlner has reported the stoichiometric reaction of a transition metal complex, $B_4H_8Fe(CO)_3$, with 2-butyne under photolytic conditions to form a four carbon carborane; see T. P. Fehlner, *J. Am. Chem. Soc.*, **99,** 8355 (1977).

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Preparation of a "Stabilized Formyl" Complex from Carbon Monoxide and Hydrogen and the Crystal Structure of a Derivative in Which the C–O Bond Has Been Cleaved

Sir:

There is now good evidence that a formyl complex is unstable with respect to a hydrido carbonyl complex when a coordination site is vacant.[1] Therefore to form one from a hydrido carbonyl complex would seem possible only if the formyl complex were somehow "stabilized". One means of doing so is to bind the formyl ligand to another metal (or a main group Lewis acid).[2] We have now shown that this principle is valid by isolating a dimeric tantalum hydrido formyl complex from the reaction of a dimeric tantalum hydride complex with carbon monoxide.

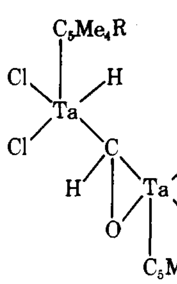
$Ta(\eta^5\text{-}C_5Me_5)(propylene)Cl_2$ reacts readily and cleanly at 25 °C with hydrogen at 40 psi in pentane to give a sparingly soluble diamagnetic green crystalline product, **1a**. The same product is obtained on reacting $Ta(\eta^5\text{-}C_5Me_5)(CH_2CMe_3)_2Cl_2$[4] with hydrogen under similar conditions. The analogous $\eta^5\text{-}C_5Me_4Et$ product (**1b**) is more soluble in benzene and more easily characterized. **1b** is dimeric in benzene and its ^1H NMR spectrum shows a peak of area 1 (relative to one $\eta^5\text{-}C_5Me_4Et$) at δ 10.45. We ascribe this peak to a hydride ligand since its IR spectrum shows a moderately intense broad peak at 1585 cm^{-1} which shifts to 1150 cm^{-1} if deuterium is substituted for hydrogen. The IR and NMR spectra of **1a** are analogous. Therefore we believe both are dimeric hydride complexes with the formula $Ta_2(\eta^5\text{-}C_5Me_4R)_2Cl_4H_2$:[5]

$$Ta(\eta^5\text{-}C_5Me_4R)(propylene)Cl_2 + H_2 \xrightarrow[1\ h]{pentane} \underset{\mathbf{1}}{Ta_2(\eta^5\text{-}C_5Me_4R)_2Cl_4H_2} \quad (1)$$

Their structure is most likely one in which the two hydrides bridge the two metals and there is formally a metal-metal single bond. A sparingly soluble red complex with the formula $Ta_2(\eta^5\text{-}C_5Me_4R)_2Cl_5H$[7] is a byproduct (~5%) in the reaction of $Ta(\eta^5\text{-}C_5Me_4R)(CH_2CMe_3)_2Cl_2$ with hydrogen;[8] it, too, must contain a bridging hydride since only one type of $\eta^5\text{-}C_5Me_4R$ group is present.

$Ta_2(\eta^5\text{-}C_5Me_4Et)_2Cl_4H_2$ reacts with 1 equiv of CO at 0 °C to give orange microcrystalline $Ta_2(\eta^5\text{-}C_5Me_4Et)_2Cl_4H_2(CO)$.[9] Its ^1H NMR spectrum shows two singlets (each of area 1) at δ 7.52 and 6.08 and two different $\eta^5\text{-}C_5Me_4R$ groups. In the product prepared with ^{13}CO, the δ 7.52 peak is split by 20 Hz while the 6.08 peak is split by 168 Hz. Therefore we believe the proton which gives rise to the second peak is bound to the carbonyl carbon atom. In the ^{13}C NMR spectrum the signal for this carbon atom is found at 168 ppm (a doublet with J_{CH} = 168 Hz). We postulate that this dimer is an η^2-formyl complex because we have recently prepared a related η^2-acetone or "metallaoxirane" complex, $(\eta^5\text{-}C_5Me_5)Me_2\overline{Ta\text{-}O\text{-}C}Me_2$,[10a] and because the C-H coupling constant in oxirane itself is 176 Hz.[10b] A plausible structure is shown:

$Ta_2(\eta^5\text{-}C_5Me_4R)_2Cl_4H_2 + CO \longrightarrow$



(2)

We can confidently discount the alternative "oxycarbene" structure $[(\eta^5\text{-}C_5Me_4R)Cl_2Ta{=}C(H)\text{-}O\text{-}Ta(H)Cl_2(\eta^5\text{-}C_5Me_4R)]$ based on the fact that the chemical shift of the carbon atom is close to that of the metallaoxirane ring carbon atom in $(\eta^5\text{-}C_5Me_5)Me_2\overline{Ta\text{-}O\text{-}C}Me_2$ and the fact that the signal for the carbon atom in a known oxycarbene complex, $(\eta^5\text{-}C_5H_5)_2(H)Nb{=}CHOZr(H)(\eta^5\text{-}C_5Me_5)_2$,[11] is found at 265 ppm, as one would expect.

The complex with the formula $Ta_2(\eta^5\text{-}C_5Me_4R)_2Cl_5H$ reacts with 1 mol of CO to give an analogous "stabilized formyl" complex which has a chloride ligand in place of the terminal hydride ligand. It has not been characterized as well owing to its poor solubility properties, but a signal for the erstwhile carbonyl carbon atom in the ^{13}CO product is found at 169 ppm.

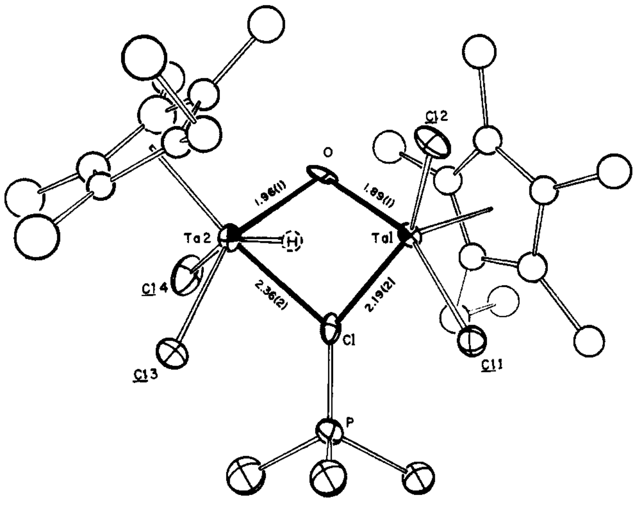


Figure 1. The molecular geometry of $[(\eta^5\text{-}C_5Me_4Et)TaCl_2H](\mu\text{-}CHPMe_3)(\mu\text{-}O)[(\eta^5\text{-}C_5Me_4Et)TaCl_2]$ showing the distances within the $Ta(\mu\text{-}C)(\mu\text{-}O)Ta$ bridge. The terminal hydride ligand on Ta(2) is shown in its deduced position (see text). ORTEP-II diagram, 30% probability ellipsoids.

So far all attempts to cause the remaining hydride in **2** to transfer to the "formyl" carbon atom [to give $(\eta^5\text{-}C_5Me_4R)Cl_2\overline{Ta\text{-}O\text{-}C}H_2$] in the presence of potential ligands such as ethylene (which could capture the "$Ta(\eta^5\text{-}C_5Me_4R)Cl_2$" fragment as a tantallacyclopentane complex[12]) have failed. We found that **2** also did not react readily with either excess H_2 or CO under mild conditions (50 psi, 25 °C, 1 day). Since we had not been able to grow any suitable crystals for X-ray examination, we attempted to form a derivative by adding PMe_3 to one or both tantalums in **2**. The product is a nicely crystalline yellow dimer with the formula $Ta_2(\eta^5\text{-}C_5Me_4R)_2Cl_4(H)(CHO)(PMe_3)$.[13] The hydride is now found at δ 10.0 and the "formyl" proton at δ 1.8 in the ^1H NMR spectrum. The major change is that the "formyl" carbon atom now gives a signal at 94 ppm in the ^{13}C NMR spectrum and is coupled strongly to phosphorus (J_{CP} = 44 Hz); the latter suggests that PMe_3 is now directly bonded to that carbon atom.

Suitable crystals of this compound were subjected to an X-ray structural determination. The complex crystallizes in the noncentrosymmetric orthorhombic space group $P2_12_12_1$ ($D_2{}^4$; No. 19) with a = 17.937 (8), b = 12.452 (4), c = 14.022 (5) Å; V = 3132 (2) Å^3; ρ(calcd) = 1.93 g cm^{-3} for mol wt 908.320 and Z = 4. Diffraction data were collected with a Syntex P2$_1$ automated four-circle diffractometer using a coupled θ(crystal)2θ(counter) scan technique[14] and graphite-monochromatized Mo Kα radiation. Data were corrected for absorption (μ = 77.7 cm^{-1}) and the structure was solved by a combination of Patterson, difference-Fourier, and full-matrix least-squares refinement techniques. All nonhydrogen atoms were accurately located, the final discrepancy indices being R_F = 5.2 and R_{wF} = 4.0% for all 2338 independent reflections with $4.5° < 2\theta < 45.0°$; no data were rejected.

The molecular geometry of what is actually $(\eta^5\text{-}C_5Me_4Et)Cl_2HTa(\mu\text{-}CHPMe_3)(\mu\text{-}O)TaCl_2(\eta^5\text{-}C_5Me_4Et)$ is shown in Figure 1. Ta(1) is linked to a $\eta^5\text{-}C_5Me_4Et$ ligand, to two chloride ligands, and to the bridging atoms C(1) and O; the coordination environment about Ta(1) is of the "four-legged piano stool" or "3,4" type, characterized by essentially equivalent Cp-Ta(1)-L angles;[15] Cp-Ta(1)-Cl(1), 106.2; Cp-Ta(1)-Cl(2), 106.9; Cp-Ta(1)-C(1), 112.1; Cp-Ta(1)-O, 102.0°. In contrast to this, Ta(2) is linked to a η^5-C_5Me_4Et ligand, to two chloride ligands, to a *terminal hydride ligand*, and to the bridging atoms C(1) and O; the coordination environment of Ta(2) is thus best described as a "3,4,1" type. We emphasize that we did not locate directly the terminal hydride ligand on Ta(2). However, there is clearly a hole in the pseudooctahedral arrangement around Ta(2) where it should be; i.e., Cl(3)-Ta(2)-Cl(4), 96.5 (2); Cl(4)-Ta(2)-O, 98.0 (3); but O-Ta(2)-Cl(3), 150.1 (3)°. The observable Cp-Ta(2)-L angles are Cp-Ta(2)-Cl(3), 101.1; Cp-Ta(2)-Cl(4), 104.7; Cp-Ta(2)-O, 100.3; Cp-Ta(2)-C(1), 172.5°.

We propose that the C-O bond in the "η^2-formyl" ligand is disrupted when PMe_3 attacks the carbon. Angles within this system [C(1)-Ta(1)-O, 78.0 (6); Ta(1)-O-Ta(2), 102.1 (5); O-Ta(2)-C(1), 72.7 (5); Ta(1)-C(1)-Ta(2), 82.2 (6)°] and the cross-bridge distances [Ta(1)···Ta(2) = 2.992 (1) and C(1)···O, 2.579 (2) Å] do not allow an unambiguous assessment as to the importance of any direct tantalum-tantalum bonding. The Me_3PCH moiety is best regarded as a phosphonium ylide, the P-C(1) distance being 1.750 (18) Å, compared with P-Me distances of 1.834 (20), 1.840 (21), and 1.847 (25) Å. Similar distances were found in the related species $Fe_2(CO)_6[(CHO)P(Ph_2C_6H_4)]$.[16]

Evidently, the "formyl" ligand in **2** is grossly "overstabilized" as a metallaoxirane complex of d^0 Ta(V). Nevertheless, we feel that there must be some circumstances where such stabilization is great enough to yield a fair concentration of metallaoxirane but not great enough to prevent its reacting further with CO or H_2. We think that these results further provoke the question as to whether intermolecular addition of M-H to M-CO may be more favorable than intramolecular addition of M-H to M-CO (with or without any stabilization in either case)[17] and also raise some intriguing questions concerning nucleophilic attack at an "η^2-formyl" carbon atom.

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(9) Calcd for $Ta_2(\eta^5\text{-}C_5Me_4Et)_2Cl_4H_2(CO)$: C, 33.19; H, 4.36. Found: C, 33.62; H, 4.40. Mol wt calcd: 832. Found: 800 ± 50 (benzene).

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EPR Detection of $(CF_3)_3CI^-$. A Test Case Regarding the Stability of RX^- Radical Anions

Sir:

Recent EPR studies have shown that electron attachment to certain halides of saturated carbon, including the perfluorocycloalkanes and trifluoromethyl halides, leads to the formation of stable σ^* radical anions.[1-3] The stability of the CF_3X^- (X = Cl, Br, I) series of radical anions contrasts with the fact that the methyl halides invariably undergo a dissociative reaction immediately after electron capture, only the weakly bound $CH_3\cdot\text{---}X^-$ species being produced even in a rigid crystalline matrix.[4,5] This difference has led Symons to postulate[6] that the tendency for the dissociation of RX^- is determined by the change which occurs in orbital hybridization and configuration at the α-carbon atom in the formation of the potential radical R·, a large change as exemplified by[4,5]

$$CH_3X^- \rightarrow CH_3\cdot\text{---}X^- \tag{1}$$

bringing about the immediate dissociation of the virtual RX^- species. We report here a test case which invalidates this general proposition.

Although the CF_3 radical is pyramidal,[7] the $C(CF_3)_3$ radical is judged to be nearly planar on the basis of the ^{13}C hyperfine coupling of 44.3 G for the α carbon.[8] Thus, according to the above postulate, the $(CF_3)_3CX^-$ radical anions should be unstable and only the neutral $(CF_3)_3C$ radicals should be produced on electron attachment to the perfluoro-*tert*-butyl halides. We find, however, that the EPR spectrum of a γ-irradiated solution of $(CF_3)_3CI$ in a 2-methyltetrahydrofuran glass (Figure 1) provides clear evidence for the radical anion.

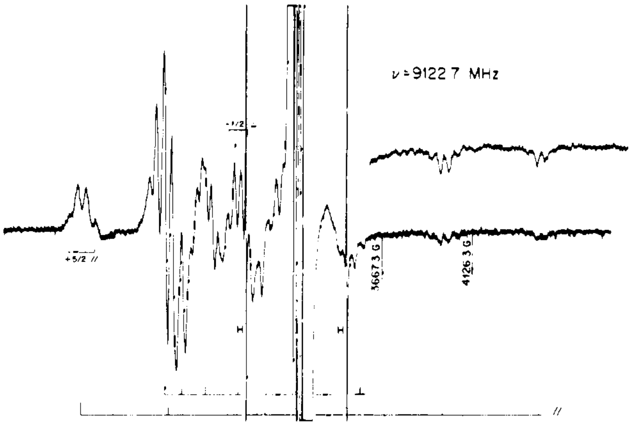

Figure 1. First-derivative EPR spectrum of a 2-methyltetrahydrofuran glass containing 4 mol % perfluoro-*tert*-butyl iodide recorded at 87 K after γ irradiation at 77 K for a dose of 1.5 Mrad. The stick diagrams show the features assigned to the $(CF_3)_3CI^-$ radical anion, and the upper trace at high field was obtained under conditions of larger amplification, modulation, and response time.

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