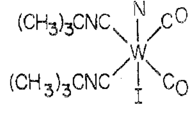
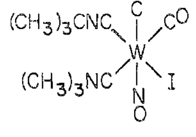
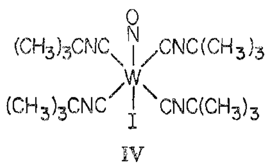
has the necessary nitrosyl group to form *trans*-$W(CO)_4(NO)Cl$, whereas nitrosyl chloride must also function as a nitrosylating agent in its reaction with $W(CO)_6$. This dichotomy in the action of nitrosyl chloride on transition metal systems can account for the very different pathways in its reactions with $W(CO)_6$ and $HW_2(CO)_9NO$.

The tendency for $HW_2(CO)_9NO$ to form halides of the type *trans*-$W(CO)_4(NO)X$ with halogenating agents is also demonstrated by the reaction of $HW_2(CO)_9NO$ with elemental iodine to give *trans*-$W(CO)_4(NO)I$ in yields up to 70% based on available nitrosyl groups. Since only one of the two tungsten atoms in $HW_2(CO)_9NO$ has a nitrosyl group, halogenation of $HW_2(CO)_9NO$ must also lead to other tungsten complexes from the tungsten atom without the nitrosyl group. These tungsten by-products can complicate the separation of pure *trans*-$W(CO)_4(NO)X$ derivatives from the halogenation of $HW_2(CO)_9NO$. In the preparation of *trans*-$W(CO)_4(NO)I$ from $HW_2(CO)_9NO$ and iodine, separation of a pure product is facilitated if excess iodine is used. The remaining tungsten products from this preparation can appear as brown solids insoluble in dichloromethane or as a brown, very strongly adsorbed band on the chromatography column after removal of the *trans*-$W(CO)_4(NO)I$. The iodination of $HW_2(CO)_9NO$ in benzene, furthermore, can give erratic yields of a blue volatile solid of stoichiometry $[W(CO)_4I]_n$; the nature of this product is uncertain. Reaction of $HW_2(CO)_9NO$ with bromine has been shown spectroscopically to produce *trans*-$W(CO)_4(NO)Br$, but a reliable procedure has not been found for separating pure *trans*-$W(CO)_4(NO)Br$ from the $W(CO)_6$ concurrently produced in this reaction.

Colton and Commons have reported some reactions of *trans*-$W(CO)_4(NO)X$ ($X = Cl, Br, I$) with simple tertiary phosphines and arsines[6] to give either monosubstituted *mer*-$W(CO)_3L(NO)X$ or disubstituted *cis*-$W(CO)_2L_2(NO)X$ ($L = (C_6H_5)_3P, (C_6H_5)_3As$; $X = Cl, Br, I$) depending upon the severity of the reaction conditions. We have found conditions for the reaction of *trans*-$W(CO)_4(NO)I$ with *tert*-butyl isocyanide where the dicarbonyl *cis*-$(Me_3CNC)_2W(CO)_2(NO)I$, the monocarbonyl $(Me_3CNC)_3W(CO)(NO)I$, or even the carbonyl-free *trans*-$(Me_3CNC)_4W(NO)I$ can be obtained simply by varying the reaction temperature from room temperature to 110°. Stereochemistries of *cis*-$(Me_3CNC)_2W(CO)_2(NO)I$ with the pairs of both the carbonyl and *tert*-butyl isocyanide ligands in relative cis positions (*i.e.*, IIIa or IIIb) and of *trans*-$(Me_3CNC)_4W(NO)I$ with the nitrosyl and iodide ligands in trans positions (*i.e.*, IV with local C_{4v} symmetry) are supported by the observed numbers and positions of $\nu(CN)$ and $\nu(CO)$ frequencies, but the available infrared data do not allow either a decision between IIIa and IIIb for the disubstituted derivative or an unequivocal elucidation of the stereochemistry of the trisubstituted derivative $(Me_3CNC)_3W(CO)(NO)I$. However, structure IIIa seems more probable than IIIb for the disubstituted *cis*-$(Me_3CNC)_2W(CO)_2(NO)I$ in view of its single, sharp *tert*-butyl proton nmr resonance and its formation from *trans*-$W(CO)_4(NO)I$. In *cis*-$(Me_3CNC)_2W(CO)_2(NO)I$ the two $\nu(CO)$ frequencies are separated by 64 cm^{-1} whereas the two $\nu(CN)$ frequencies are separated by only 19 cm^{-1} indicating that the stretch–stretch interaction constants are appreciably smaller for the *tert*-butyl isocyanide ligands than for the carbonyl ligands in accord with previous observations[13] on octahedral *tert*-butyl isocyanide metal carbonyl complexes, particularly those of the type *fac*-$(Me_3CNC)_3M(CO)_3$ ($M = Cr, Mo, W$). In the series $(Me_3CNC)_nW(CO)_{4-n}(NO)I$ ($n = 2$–4) the position of the $\nu(NO)$ frequency decreases by ~40 cm^{-1} upon each successive substitution of a carbonyl group with a *tert*-butyl isocyanide ligand in accord with expectations based on the weaker π-acceptor ability of *tert*-butyl isocyanide relative to carbon monoxide.[14]


IIIa


IIIb


IV

Colton and Commons[7] have also reported some *cis*-(bidentate)$W(CO)_2(NO)X$ complexes from the ligands $(C_6H_5)_2ECH_2E(C_6H_5)_2$ ($E = P$ or As) with methano bridges. We have prepared the closely related complex *cis*-$[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]W(CO)_2(NO)I$; the analogous chloride was previously prepared by a different method.[15]

Reactions of *trans*-$W(CO)_4(NO)I$ with appropriate reactive organometallics could provide a route to novel organotungsten carbonyl nitrosyls. Thus *trans*-$W(CO)_4(NO)I$ reacts with thallium cyclopentadienide or, less efficiently, sodium cyclopentadienide to give the known[11] $C_5H_5W(CO)_2NO$, but this preparation of $C_5H_5W(CO)_2NO$ is less convenient than those currently in use. Unfortunately, attempts to make more interesting organotungsten carbonyl nitrosyls by variations of this method as described in the Experimental Section led to uniformly negative results.

Acknowledgment. We are indebted to the National Cancer Institute for partial support of this work under Grant CA-12938-02.

Registry No. *cis*-$(Me_3CNC)_2W(CO)_2(NO)I$, 52699-24-8; $(Me_3CNC)_3W(CO)(NO)I$, 52699-25-9; *trans*-$(Me_3CNC)_4W(NO)I$, 52699-26-0; $[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]W(CO)_2(NO)I$, 51132-29-7; *trans*-$W(CO)_4(NO)I$, 39899-82-6; $HW_2(CO)_9NO$, 52699-27-1.

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(14) F. A. Cotton, *Inorg. Chem.*, 3, 702 (1964).
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Studies of Boranes. XLI.[1] A New Boron Hydride, Tridecaborane(19)

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In this paper the synthesis and properties of $B_{13}H_{19}$ and attempts to identify intermediates in its formation are reported. A brief report of X-ray crystal structure of this compound has already appeared.[2]

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(1) For the preceding paper see J. Rathke and R. Schaeffer, *Inorg. Chem.*, 13, 760 (1974).
(2) J. C. Huffman, D. C. Moody, J. W. Rathke, and R. Schaeffer, *J. Chem. Soc., Chem. Commun.*, 308 (1973).

Experimental Section

Apparatus and Materials. Standard high-vacuum techniques as described elsewhere[3] were used throughout this investigation. Mass spectra were measured on an AEI Model MS-9 mass spectrometer at 70 eV. The ^{11}B magnetic resonance spectra were recorded on a Varian Associates HR-220 spectrometer at 70.6 MHz. Uv spectra were measured on a Cary 14 spectrometer. Diborane(6), hexaborane(10), and octaborane(12) were prepared by literature methods.[4-6] Dimethyl ether and boron trifluoride were obtained from the Matheson Co.

Pyrolysis of Hexaborane(10) with Diborane(6). A total of 13.5 mmol of B_2H_6 and 7.17 mmol of B_6H_{10} was heated in a sealed tube to 80–90° for 2 hr. All but 0.4 mmol of the starting B_2H_6 was recovered even though only a very small amount of B_6H_{10} was left undecomposed. The following boranes were identified by their mass spectra: $B_{16}H_{20}$, $B_{13}H_{19}$, $B_{10}H_{14}$, n-B_9H_{15}, B_8H_{12}, B_5H_9. Nonvolative residue and H_2 were also obtained.

Pyrolysis of Hexaborane(10). A sample of B_6H_{10} (367 mg) was sealed in a 30-ml Pyrex break-seal tube and heated to 80–90° for 2 hr to form a red-brown oil. The tube was cooled to −196° and hydrogen (3.08 mmol) was removed. Decaborane(14) (30.6 mg), B_6H_{10} (119 mg), and much smaller amounts of B_8H_{12} and B_5H_9 were pumped from the tube at room temperature and identified by their mass spectra. The tube was then heated to 80° and 19.5 mg of a mixture containing nearly equal amounts of $B_{16}H_{20}$ and $B_{13}H_{19}$ distilled out of the heat zone as a yellow liquid which collected above the heated portion of the tube. The red-brown residue remaining in the tube (192 mg) was very soluble in methylene chloride but insoluble in pentane. An ^{11}B nmr spectrum of the methylene chloride solution showed broad peaks characteristic of a polymeric material. Tridecaborane(19) was removed from most of the $B_{16}H_{20}$ by slow distillation at room temperature. The $B_{16}H_{20}$, identified by its ^{11}B nmr and mass spectra, formed colorless crystals which did not sublime rapidly at this temperature whereas $B_{13}H_{19}$ distilled as an oil which slowly crystallized. Pure samples were obtained by allowing the mixture to stand for several days in an evacuated tube at room temperature. Yellow crystals of $B_{13}H_{19}$ (mp 43.5–44°) were then manually separated. A sample purified this way showed a molecular ion in the mass spectrum at m/e 162 (calcd for $^{11}B_{13}H_{19}$, 162) and when dissolved in n-hexane showed intense peaks at 2190 and 3325 Å in the uv spectrum. A 70.6-MHz ^{11}B nmr spectrum of such a sample is shown in Figure 1.

Decomposition of Octaborane(12) in Hexaborane(10) Solution. A mixture of B_8H_{12} (1.62 mmol) and B_6H_{10} (3.57 mmol) was allowed to stand at room temperature for 1 hr in a break-seal tube. Vigorous bubbling occurred and the solution turned yellow-brown. Fractionation of the products gave H_2 (0.91 mmol), $B_{16}H_{20}$ (35.8 mg), and nonvolatile material (54.1 mg). The only other products isolated were unreacted B_6H_{10} and B_8H_{12}.

Tridecaborane(19) from the Acid-Base Reaction of B_7H_{12} and B_6H_{10}. A Me_2O solution containing 1.43 mmol of KB_6H_9 was prepared as previously described.[7] Into this solution was condensed 0.80 mmol of B_2H_6, and KB_7H_{12} was formed by stirring overnight (approximately 10 hr) at −78° (similar to the procedure of Shore and coworkers[8] for the formation of $Bu_4NB_7H_{12}$ in CH_2Cl_2). The Me_2O and unreacted B_2H_6 (0.06 mmol)[9] were pumped from the vessel at −78°. Two milliliters each of Me_2O and liquid HCl were condensed on top of the solid KB_7H_{12} at −196° and warmed to −78° with stirring. The reaction was quenched after 30 min, and the H_2 was measured (1.40 mmol). The excess Me_2O and HCl were removed at −78°. Hexaborane(10) (2.1 mmol) and BF_3 (3.0 mmol) were condensed on top of the $B_7H_{11}\cdot OMe_2$[10] and allowed to warm to −45°. After 1 hr the white pasty solution was warmed to room temperature, and stirring was continued for 2 hr. Only 0.30 mmol of H_2 was evolved during this period.

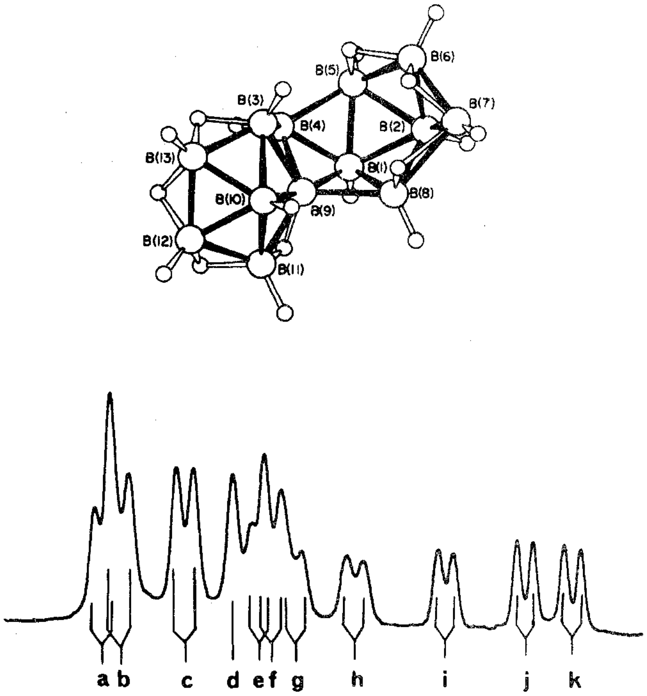

Figure 1. The structure and 70.6-MHz ^{11}B nmr spectrum of $B_{13}H_{19}$ measured in CH_2Cl_2. Chemical shifts (ppm referenced to external $BF_3\cdot Et_2O$) and coupling (±10 Hz) are as follows: a (−13.9, 150), b (−11.3, 156), c (−2.5, 162), d (+4.0), e (+7.2, 130), f (+9.3, 160), g (+12.2, 140), h (+20.4, 160), i (+32.4, 140), j (+43.2, 150), k (+49.6, 160).

The volatiles were slowly distilled from the reaction vessel at room temperature and condensed into a −196° trap. After 1.5 hr a trace of yellow solid ($B_{13}H_{19}$) could be detected pumping from the vessel, so a 0° trap was placed between the vessel and the 196° trap. After several hours of pumping at room temperature, the residual $B_{13}H_{19}$ was driven from the vessel by heating to 80–90°. The $B_{13}H_{19}$ obtained was contaminated with a trace of colorless liquid which appeared to decompose on standing at room temperature overnight. The yellow crystalline $B_{13}H_{19}$ (0.07 mmol), which was subsequently pumped away from the trace impurities, was shown to be pure by its ^{11}B nmr and mass spectra.[11]

The more volatile reaction products which initially condensed in the −196° trap were fractionated through a series of traps: −46, −112, and −196°. The −196° trap contained 1.5 mmol of a mixture of B_2H_6 and BF_3, while 3.4 mmol of B_6H_{10} stopped in the −112° trap. The −46° trap contained only a small amount of the expected $BF_3\cdot OMe_2$ along with a larger amount of clear viscous liquid, which we have not been able to characterize, but it is probably a mixture.

Results and Discussion

The structure and ^{11}B nmr of $B_{13}H_{19}$ is shown in Figure 1. The singlet due to B(9) is the only resonance in the spectrum which can be assigned with any confidence. Unlike other hydrides containing more boron atoms than $B_{10}H_{14}$ (*e.g.*, n-$B_{18}H_{22}$, i-$B_{18}H_{22}$, $B_{16}H_{20}$, and the proposed structure of $B_{14}H_{18}$), the structure of $B_{13}H_{19}$ is not that of a known boron hydride sharing two boron atoms with a decaborane framework. The molecule can be described as a hexaborane cage sharing two boron atoms with an n-nonaborane framework suggesting that stable hydrides containing multiple icosahedral fragments will be more numerous than previously expected.

Hexaborane(10), known to be a Lewis base,[12,13] has al-

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[6] J. Dobson, P. C. Keller, and R. Schaeffer, *Inorg. Chem.*, 7, 399 (1968).

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[8] H. D. Johnson, II, and S. G. Shore, *J. Amer. Chem. Soc.*, 93, 3798 (1971).

[9] The B_2H_6 was separated from the Me_2O by reaction with Me_2S. The $Me_2S\cdot BH_3$ was then fractionated and weighed.

[10] The identity of the $B_7H_{11}\cdot OMe_2$ was established by the stoichiometry of the reaction of KB_7H_{12} with Me_2O and HCl and also by a ligand replacement reaction using Me_2S. Further studies of the $B_7H_{11}\cdot L$ (L = OMe_2, Me_2S, NMe_3) are currently under way.

[11] The difficulty experienced in obtaining the $B_{13}H_{19}$ pure of this liquid contaminant varied for different preparations.

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ready been shown to react with several acidic borane intermediates.[14,15] One might have expected, then, that it might also react with the acid BH_3. It was our expectation that since no B_7 hydrides have been isolated, $B_6H_{10}\cdot BH_3$ might lose H_2 with formation of an acid[16] which would react with more B_6H_{10} to form a B_{13} hydride. This prediction appeared to be borne out when $B_{13}H_{19}$ was isolated by pyrolysis of B_6H_{10} in the presence of B_2H_6. However, the yield of $B_{13}H_{19}$ did not appear to be greatly affected when B_2H_6 was not added to the B_6H_{10}. Because of the low yields, no quantitative data were obtained to compare the two reactions accurately. Isolation of B_8H_{12}, its decomposition product $(B_{16}H_{20})$,[15] and its reaction products with B_2H_6 (n-B_9H_{15} and $B_{10}H_{14}$)[17] suggested the possibility that B_8H_{12} might be an intermediate in the formation of $B_{13}H_{19}$. There is also a structural similarity between B_8H_{12} and the larger of the two boron frameworks in $B_{13}H_{19}$. Loss of BH_3 from the known adduct of B_6H_{10} and B_8H_{12} $(B_{14}H_{22})$[15] might appear to be a suitable pathway for the formation of $B_{13}H_{19}$. Although no $B_{13}H_{19}$ was isolated when B_8H_{12} was allowed to decompose in the presence of B_6H_{10} at room temperature, the data do not exclude the possibility that an intermediate generated from B_6H_{10} at higher temperatures reacts with B_8H_{12} to form this hydride.

In an attempt to determine the importance of the B_7 hydride intermediate in the formation of $B_{13}H_{19}$ and to establish a more systematic synthesis, the reaction scheme of eq 1 and 2 was devised. The thermally unstable $B_7H_{11}\cdot$

$$KB_7H_{12} + HCl(l) \xrightarrow{Me_2O} B_7H_{11}\cdot OMe_2 + H_2 \tag{1}$$

$$B_7H_{11}\cdot OMe_2 + BF_3 \xrightarrow{B_6H_{10}} BF_3\cdot OMe_2 + B_{13}H_{19} + H_2 \tag{2}$$

OMe_2 was obtained in essentially quantitative yield, but $B_{13}H_{19}$ could only be isolated in low yield from subsequent reaction with BF_3 and B_6H_{10}. The low yield suggests that most of the B_7H_{11} decomposes before it can be successfully trapped by the B_6H_{10}.

Acknowledgment. The authors gratefully acknowledge support from the National Science Foundation (Grants GP-24266X and GP40499X).

Registry No. $B_{13}H_{19}$, 43093-20-5; B_6H_{10}, 23777-80-2; B_7H_{11}, 12430-08-9.

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[15] J. Rathke and R. Schaeffer, *Inorg. Chem.*, 13, 3008 (1974).

[16] Loss of hydrogen might occur by attack of a terminal hydrogen atom, with its pair of electrons, on a bridge proton which would result in initial formation of a single B–B bond and an empty boron orbital. If the electron deficiency of the empty orbital could not be alleviated internally by formation of a three-center bond, the resulting hydride would be a Lewis acid.

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Correspondence

Chemical Shifts of Carbon Atoms Bound to Transition Metals

AIC400985

Sir:

A large number of papers have recently appeared in which detailed rationalizations were supplied for the carbon-13 chemical shifts of carbon atoms bound to transition metals. We wish to point out that those rationalizations have been contradictory and misleading and also to suggest that in the coordination sphere of a transition metal simple explanations are unlikely to be valid.

Although traditional equations for calculation of carbon chemical shifts contain two terms, denoted "diamagnetic" and "paramagnetic"

$$\sigma = \sigma_d + \sigma_p \tag{1}$$

where σ_d reflects the screening due to electrons in the electronic ground state and σ_p screening due to the mixing of ground and excited states under the influence of the magnetic field, this is an artificial distinction which has meaning only in the context of the computational technique used.[1] In fact, as recently emphasized,[2] the relative magnitudes of the two terms depend upon the gauge chosen for the magnetic field vector potential A. Furthermore, calculations which do not involve gauge-invariant atomic orbitals (GIAO's) even produce values for the total screening constant, σ, which depend upon the choice of origin for the coordinate system.[3] (The use of GIAO's has lately begun to show excellent results for very simple molecules.[3-5])

So treatments of *total* screening constants in complex transition metal systems must be regarded with some suspicion and any which considers only that term traditionally called "paramagnetic" is almost certainly incomplete. The frequent assumption that variations in the "diamagnetic" term are negligible is doubtful. Flygare and Goodisman[6] have suggested a simple formula (later endorsed for homopolar molecules by Sadlej[7]) for estimating such effects, *i.e.*

$$\sigma_d = \sigma_d(\text{free atom}) + \frac{e^2}{3mc^2}\sum_\alpha \frac{Z_\alpha}{r_\alpha} \tag{2}$$

Application of a heuristically justified "local" version of this equation greatly improved the agreement between observed and calculated carbon-13 shifts in hydrocarbons.[8] A transition metal, particularly one of the third row, in light of this equation should produce enormous effects on the "diamagnetic" term of a directly bound carbon. For example, estimates of the second term in eq 2 of *ca.* 120, 190, and 340 ppm are appropriate to iron, ruthenium, and osmium, respectively. These will clearly vary between complexes. It is not surprising, then, that literature explanations of carbon-13 shifts in transition metal complexes on the basis of the "paramagnetic" term alone have frequently been contradictory.

An example of the difficutly in attributing principal causes

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