on Cr is +0.4, and thus the σ-donating and π-accepting abilities of CO in $M(CO)_6$ appear to differ rather little.

The results obtained here yield physically reasonable bond order–bond length relationships[2] in these complexes. The plot of Mo–C bond order against bond length using ~1.2 and ~1.7 as the bond orders in $Mo(CO)_6$ and $Mo(CO)_3$(dien), respectively, is comparable in its essential features to other such curves. A CO bond order of ~2.3 in $Mo(CO)_3$(dien) also is consistent with the CO bond lengths reported (1.153 ± 0.016 Å.).[2] Cox and Jeffrey[18] have compiled a list of eleven C=O bond lengths, which vary from 1.14 to 1.22 Å. The mean was 1.19 Å. Vaughan and Donohue[19] give a value of 1.20 Å. for the length of a pure C=O double bond from the fit obtained with Pauling's bond order–bond length relationship.[20] Thus it is entirely reasonable that a bond length of 1.15 Å. should correspond to a bond order of ~2.3 rather than 2.0, especially since C–O bond lengths should vary little for bond orders between 2 and 3.[2]

Acknowledgments.—The author thanks Mr. Larry W. Houk for valuable assistance, and Drs. L. H. Jones and Heinz Haas for rewarding discussions.

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[20] L. Pauling, "The Nature of the Chemical Bond," 2nd Ed., Cornell University Press, Ithaca, N. Y., 1948, p. 175.

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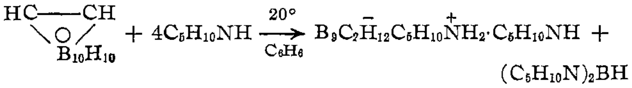
RECEIVED APRIL 19, 1965

Comments on the Reaction of Amines with 1,2-Dicarbaclovododecaborane(12)

Sir:

Zakharin and Kalnin[1] recently described the facile degradation of 1,2-dicarbaclovododecaborane(12) with piperidine to produce a piperidinium salt of the corresponding dodecahydrodicarbaundecaborate(1−) which contains an additional molecule of piperidine. When



heated under vacuum, this product eliminated one mole of piperidine and produced the simple piperidinium salt. The Russian workers consequently suggested that the loosely bound piperidine molecule is attached to the dodecahydrodicarbaundecaborate(1−) anion by a weak dative B–N bond. The resulting complex would be isoelectronic with a hypothetical $B_{11}H_{13}^{-4}$ ion.

In view of our recent investigations of the chemistry of dicarbaundecaborane(13),[2–4] we became intrigued by the possibility that the weakly-bound piperidine molecule was actually present in the crystalline phase as a hydrogen-bonded complex with piperidinium ion and not directly attached to the dodecahydrodicarbaundecaborate(1−) ion. We have examined the ^{11}B n.m.r. spectrum of authentic piperidinium dodecahydrodicarbaundecaborate(1−) in piperidine solution and in 95% ethanol solution. Comparison of the resulting spectra with the ^{11}B n.m.r. spectrum of the trimethylammonium salt of dodecahydrodicarbaundecaborate(1−) in 95% ethanol solution proved the three spectra to be identical in all respects with the characteristic resonances shown in Table I. In view of these results, we conclude that the ubiquitous piperidine molecule is not bonded to the dodecahydrodicarbaundecaborate(1−) anion, but is held in the crystal lattice by hydrogen bonds (or less specific interactions). Only the rarest of coincidences would allow the ^{11}B n.m.r. spectrum of a $B_9C_2H_{12}(\text{amine})^-$ complex to be identical with that of the uncomplexed $B_9C_2H_{12}^-$ ion.

TABLE I

^{11}B N.M.R. CHEMICAL SHIFTS RELATIVE TO TRIMETHYL BORATE

$B_9C_2H_{12}^-C_5H_{10}\overset{+}{N}H_2\cdot C_5H_{10}NH$		$(CH_3)_3\overset{+}{N}HB_9C_2H_{12}^-$
Piperidine	95% ethanol	95% ethanol
26.0	26.5	26.3
32.1	32.4	32.5
37.0	37.5	37.7
42.4	43.4	43.2
50.2	51.2	51.8
55.6	57.3	57.3

We have recently extended the utility of the piperidine degradation of icosahedral carboranes by quantitatively converting 1-phenyl-1,7-dicarbaclovododecaborane(12) to the corresponding dodecahydrodicarbaundecaborate(1−) ion[3] with this reagent in benzene at the reflux temperature.

Acknowledgment.—This work was generously supported by the Army Research Office (Durham).

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RECEIVED JUNE 17, 1965