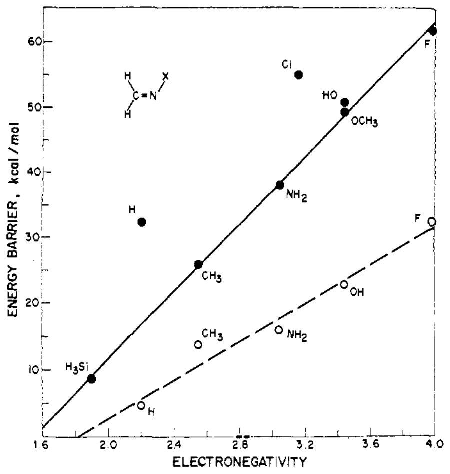

Figure 1. Calculated barriers of planar nitrogen inversion in $H_2C{=}NX$ *vs.* Allred electronegativity of the atom in group X bonded to the imino nitrogen: solid line and solid circles, values from CNDO/2 scheme (present work); dashed line and open circles, values from EHMO calculations.[16]

germyl imine should have a barrier to inversion of *ca.* 12 kcal/mol, based on an electronegativity of 2.01 for germanium,[15] in reasonable agreement with the barrier observed for **1**.

Previously reported[16] EHMO calculations on $H_2C{=}NX$ have indicated a similar trend of planar nitrogen inversion barriers *vs.* electronegativity of first-row elements (dashed line, Figure 1). However, barriers obtained by this method appear to be considerably lower than expected for comparable imine systems.[3a,13]

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Received August 14, 1971

Boron–Carbon Coupling Constants. I. 1-Methylpentaborane(9)

Sir:

Since the first direct determination of a $^{11}B-^{11}B$ coupling constant from our laboratories,[1] we have been interested in obtaining qualitative and semiquantitative information concerning the factors which influence boron–boron coupling constants. In connection with this study, it became of interest to examine the ^{13}C chemical shifts and possible carbon coupling constants to boron in some of the organoboron compounds used in this research. We wish to report here some preliminary data on the ^{13}C spectrum of 1-methylpentaborane(9). A more detailed presentation of $^{11}B-^{11}B$ and $^{11}B-^{13}C$ coupling constants will be the subject of future publications.[2]

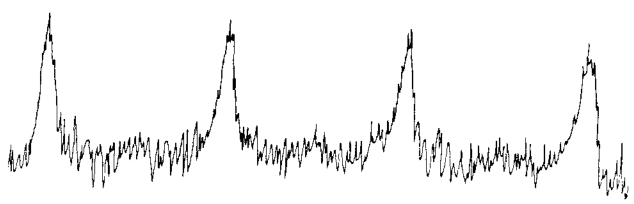

Figure 1. ^{13}C nmr spectrum (25.2 MHz) of neat 1-$CH_3B_5H_8$ after 12,000 pulses, with an acquisition time of 4 sec per pulse, showing a J_{BC} of 72.6 Hz. The methyl carbon is shielded with respect to CS_2 by 205.0 ppm. A capillary of C_6F_6 furnished the ^{19}F lock signal.

The ^{13}C spectra were obtained on a Varian XL-100-15 nmr spectrometer operating in the Fourier transform mode at 25.2 MHz. The ^{13}C spectrum is shown in Figure 1. The chemical shift of the methyl carbon is 205 ppm more shielded than that of CS_2. The value of the boron–carbon coupling constant is 72.6 ± 0.5 Hz. Experimental work is currently in progress to determine the sign of J_{BC}.

Since this is the first reported $^{11}B-^{13}C$ coupling constant for a boron nucleus in a nonsymmetrical environment,[3] it is of interest to examine this coupling constant in terms of the nature of the carbon–boron bonding in this molecule. It can easily be shown from approximate molecular orbital and valence-bond theories of spin-coupling constants[4-6] that *if* the coupling constant is dominated by the Fermi contact mechanism, the coupling constant, J_{AB}, can be "related" to the fractional "s character" in the bond between atoms A and B; hence the hybridization of the atoms. Thus, if the Fermi contact mechanism dominates J_{BC} we can deduce a *crude* value for the hybridization of the apex boron in 1-$CH_3B_5H_8$.

To accomplish this, one can compare boron–carbon couplings to carbon–carbon coupling constants by multiplying the value of J_{BC} by the ratio of the magnetogyric ratios, γ_C/γ_B. The calculated value of 57 Hz is reminiscent of J_{CC} values observed in $CH_3C({=}O)X$ compounds when X is an electronegative substituent,[7] *i.e.*, J_{CC} values between 54 and 59 Hz. From this comparison, one can conclude that the value obtained for J_{BC} in 1-$CH_3B_5H_8$ is not unlike the values for J_{CC} found for sp^3-hybridized carbons bound to sp^2-hybridized carbons.

Recently, Blizzard and Santry have confirmed that the Fermi contact contribution to J_{CC} is the dominant mechanism.[8] Pople and Santry[9] and, more recently, Jameson and Gutowsky[10] have shown that the orbital-dipole contribution to the coupling constant (the second largest contributing mechanism[7]) would increase as one goes from lithium to fluorine in the periodic table. It would be expected that the orbital-dipole mechanism contributes even less to J_{BC} values than to J_{CC} values and, therefore, an approximate hybridization for the apex boron in 1-$CH_3B_5H_8$ is sp^2. This hybridization

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agrees well with that predicted by Lipscomb's equations of balance for the 4120 styx structure of B_5H_9.[11] This value can be contrasted to a recent localized molecular orbital calculation in which sp$^{1.3}$ is obtained for the hybridization of the apex boron in B_5H_9.[12]

At present we are examining the ^{11}B and ^{13}C nmr of other organoboranes and carboranes to better characterize this important nmr parameter.

Acknowledgment. The XL-100-15 nmr spectrometer was purchased with funds from a National Science Foundation Department Development Grant. J. D. O. is grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and P. D. E. to the University of South Carolina Committee on Research and Productive Scholarship for support of this research.

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Univalent Palladium Complexes

Sir:

In industrial olefin catalysis by palladium(II) complexes it is known[1-3] that reduction of Pd(II) species takes place through decomposition of organopalladium(II) intermediates and that reoxidation of Pd(0) species can be effected with the aid of one-electron oxidant, cupric salt. Implication of Pd(I) species has been suggested[4,5] for these processes. However, no report has been made on univalent palladium complexes except the peculiar arene-sandwiched dimeric compound $[Pd\text{-}Al_2Cl_7(C_6H_6)]_2$[6,7] and the elusive complex of unknown molecular weight $[Pd(C_6H_6)(H_2O)ClO_4]_n$.[4] We wish to report here preparations and properties of novel diamagnetic, dimeric palladium(I) complexes.

These complexes are accessible through two routes from "$Pd(RNC)_2$."[8,9] One successful preparation uses $PdX_2(RNC)_2$ obtained by treating either palladium(II) halides (PdI_2 or $PdBr_2$) or the Kharash complex $PdCl_2(PhCN)_2$ with an excess of *tert*-BuNC in benzene. The palladium(II) complexes PdX_2(*tert*-BuNC)$_2$ (**1**, X = Cl; **2**, X = Br; **3**, X = I) are monomeric, thermally and air stable compounds[10] with spectroscopic features listed in Table I.

Table I. *tert*-Butyl Isocyanide–Palladium(II) and –Palladium(I) Complexes

Compound	^{1}H nmr, ppm	Ir,[a] cm^{-1} N≡C	Ir,[a] cm^{-1} Pd—X	λ_{max},[b] nm (ϵ)
cis-$PdCl_2$(*tert*-BuNC)$_2$[c]	8.43 (s)[d]	2251 2236	338 318	
trans-$PdBr_2$(*tert*-BuNC)$_2$[e]	8.47 (s)[d]	2224	269	
trans-PdI_2(*tert*-BuNC)$_2$[e]	8.46 (s)[d]	2216	231	
[PdCl(*tert*-BuNC)$_2$]$_2$-(C_6H_5Cl)	8.43 (s)[f] 2.65[g]	2166	259	307 (8000)
[PdBr(*tert*-BuNC)$_2$]$_2$	8.46 (s)[f]	2170	185	317 (6700)
[PdI(*tert*-BuNC)$_2$]$_2$	8.45 (s)[f]	2178	164	345 (8500)

[a] Nujol mull. [b] Measured in CH_2Cl_2: the extinction coefficients suggest that these absorption arise from charge transfer. [c] The cis configuration is deduced on the basis of the two ir NC and Pd–X stretching bands. [d] *tert*-Butyl proton resonances measured in chloroform at room temperature using TMS as a reference. [e] The ir data dictate the trans configuration. [f] Measured in acetone-d_6 using TMS as a reference. [g] Aromatic protons complex multiplets.

To a freshly prepared, cold (−30°) chlorobenzene solution of "Pd(*tert*-BuNC)$_2$" was added under nitrogen an equimolar amount of analytically pure **1**. The mixture was stirred for 4 hr maintaining the temperature around −30°. After 4 hr, the temperature was allowed to reach 0° within ~1 hr. Upon chilling at −20°, the palladium(I) complex [PdCl(*tert*-BuNC)$_2$]$_2$(C_6H_5Cl) (**4**) precipitates as yellow needles[11] (70%). This is fairly air and thermally stable; the decomposition (under nitrogen) starts slowly around 150° and was rapid above 200°. An equimolar mixture of Pd(*tert*-BuNC)$_2$ and **2**, dissolved in cold (−30°) ether, was stirred for 5 hr, allowing the temperature to rise in a similar fashion as above. The solvent being removed *in vacuo*, the residue was recrystallized from a *n*-hexane–tetrahydrofuran mixture to give [PdBr(*tert*-BuNC)$_2$]$_2$ (**5**) as orange prisms[10] (88%), dec 138–152°. Similarly, [PdI(*tert*-BuNC)$_2$]$_2$ (**6**) was obtained as orange needles[10] (90%), dec 125°, slightly soluble in benzene.

The oxidative addition of organic halides, *e.g.*, $PhCH_2I$ or XCH_2COOCH_3 (X = Cl, Br), to Pd(*tert*-BuNC)$_2$ led to **6** *via* the σ-alkyl isocyanide complex **7** (*cf.* Scheme I). Attempted preparations of phosphine-palladium(I) complexes from $Pd(PPh_3)_4$ and $PdI_2(PPh_3)_2$ have been unsuccessful. The capability of alkyl isocyanide ligands for stabilization of the odd valence state is noteworthy.

The three complexes **4**–**6** have bridging halogen atoms, as inferred from their ir spectra, which lack absorptions in the 1600–1800-cm^{-1} region, suggesting the absence of a bridging isocyanide group (>C=NR), but show low-frequency Pd-X stretching bands (Table I) assigned to bridging halogen–metal stretching vibrations.[12] The structure predicts two NC stretching

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(10) The elemental analysis as well as the vapor pressure osmometric molecular weight measurement in benzene conformed to the calculated values.

(11) It gave a good elemental analysis. The molecular weight in benzene was found as 603, 620 (calcd 729), indicating its slight dissociation of chlorobenzene. A question raised by a referee concerns the dissociation asking if some special mode of bonding to the aromatic ring is involved. The oxidative addition (cleavage of the C–Cl bond) can be excluded from the absence of terminal Cl–Pd stretching vibration. Solvated aromatics are found in some rhodium(I) complexes [R. Ugo, F. Bonati, and S. Cenini, *Inorg. Chim. Acta*, **3**, 220 (1969)]. When the chloropalladium(I) complex was prepared by the alternative route using alkyl halide in benzene (see Scheme I), it was obtained as a benzene adduct, [PdCl(*tert*-BuNC)$_2$]$_2$(C_6H_6), dec 155°, which also gave a good elemental analysis.

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