ratio were carried out at an attenuation of 4 for the *cis* peak, 8 for the *trans* peak.

As mentioned earlier, at each temperature a *cis*-rich and a *trans*-rich sample was equilibrated; in a few cases more than one. Each equilibrated sample was analyzed at least three times. The equilibrium constants tabulated in Table II are therefore averages of at least six analytical determinations in each instance. In no case was a systematic difference noted between equilibrium mixtures obtained from the *cis* side and from the *trans* side. Standard deviations, $\Delta K'_X$, were computed for each raw analysis and similarly, deviations Δr were computed for each determination of response ratio (r). The deviations shown in Table II are $\Delta K_X = K_X(\Delta K'_X/K'_X + \Delta r/r)$ where K'_X is the raw area ratio uncorrected for response ratio.

The data for K_X shown in Table II were fed to a Univac 1107 computer with instructions to plot a least-squares plot of ln K_X *vs.* $1/(273.16 + t)$. The computer was then instructed to put out, in addition to the plot, $\Delta H^\circ_X = Rm/1000$ where $R = 1.9872$ cal/deg mol and m is the slope of the least-squares plot. The computer was also instructed to compute the statistical slope error,[36] Δm, to put out $\Delta\Delta H^\circ = R\Delta m/1000$, and to compute the standard entropy difference $\Delta S^\circ = Rb$, where b is the intercept of the plot and the corresponding statistical error $\Delta\Delta S^\circ = R\Delta b$, where Δb is the statistical intercept error. The resulting computer output for ΔH° and ΔS° is tabulated in Table I. ΔG°_{25} was calculated as $\Delta G^\circ_{25} = \Delta H^\circ - 298.16\Delta S^\circ$ (ΔG° and ΔH° in cal/mol). The corresponding error was computed as $\Delta\Delta G^\circ = \Delta\Delta H^\circ + T\Delta\Delta S^\circ + \Delta S^\circ\Delta T$, the last term actually being negligible.

Acknowledgment. We are grateful to Professor Oliver G. Ludwig for his helpful advice with the computer program and error treatment and to Dr. R. J. L. Martin for his help and encouragement in the eary stages of this investigation. Acknowledgment is made to the Air Force Office of Scientific Research (Grant AF-AFOSR-772) and to the donors of the Petroleum Research Fund (Grant 266-A), administered by the American Chemical Society, for support of this research.

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Nuclear Magnetic Resonance Spectroscopy. Carbon-13 Coupling Constants in Organometallic Compounds[1a]

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Received October 4, 1967

Abstract: High-resolution, natural-abundance ^{13}C nuclear magnetic resonance spectra have been obtained for the tetramethyl derivatives of group IV and the dimethyl derivatives of group IIb. The one-bond coupling constants between carbon and the spin $^1/_2$ metal atoms as well as the "through-metal" vicinal carbon–proton coupling constants are discussed in terms of the Fermi contact coupling mechanism.

Because of their simplicity and high symmetry, the tetramethyl derivatives of the group IV elements have been extensively studied by nuclear magnetic resonance spectroscopy. These studies have included determination of the proton chemical shifts,[2] ^{13}C chemical shifts,[2] one-bond, carbon–proton coupling constants,[2,3] and two-bond, metal–proton coupling constants.[3] Recently some carbon–metal coupling constants in compounds of this type have been determined by heteronuclear tickling experiments,[4] and a rather complete nmr investigation of dimethylmercury has been carried out.[5]

The ^{13}C spectra previously reported were obtained with rapid passage in the dispersion mode. Under these conditions line widths are such that, while the large, one-bond, carbon–proton coupling constants can be resolved, the noise level is normally too high to allow the observation of carbon–metal coupling, partly because the percentage of total metal with spin $^1/_2$ is low. Heteronuclear tickling experiments, while monitoring proton resonances, have made the observation of carbon–metal coupling possible, but difficulties in the interpretation of tickling experiments can lead to erroneous conclusions. The heteronuclear tickling technique not only failed to resolve the vicinal, carbon–proton coupling constants, but the stated error limits fail to include the actual values of these coupling constants.[4,5] In the present work, high-resolution, natural-abundance ^{13}C spectra were obtained in the absorption mode with slow passage conditions and time averaging and permitted the direct observation and measurement of carbon–metal couplings as well as of ^{13}C–X–C–H couplings which have not heretofore been reported.

Experimental Section

The compounds used in this study were obtained from commercial sources and used without further purification. The samples were placed in 10-mm precision-ground sample tubes with approximately 10% benzene for an internal proton lock signal. The samples were degassed and sealed under vacuum. High-resolution ^{13}C spectra were obtained using the Varian DFS-60 spectrometer.[6]

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Proton decoupling was accomplished using a Hewlett-Packard 5100 frequency synthesizer and a Boonton 230A power amplifier.

Results

The one-bond, carbon–metal coupling constants and vicinal, carbon–proton coupling constants of the tetramethyl derivatives of group IV are given in Table I. The coupling constants and ^{13}C chemical shifts of the dimethyl derivatives of group IIb are given in Table II.

Table I. Carbon-13 Nmr Parameters for the Tetramethyl Derivatives of Group IV

	J_{CX}[a]	J_{CXCH}[a]	J_{CH}[a]	δ_C[b]
C	36.2 ± 1	4.8	124.3	161.4 (164.9)[c]
Si	51	2.1	118.2	193.0
Ge	. . .	1.9	124.4	193.6
Sn	330 ± 5	1.3	127.7	202.1
Pb	250	1.05	134.2	196.2

[a] In hertz. [b] In parts per million upfield from carbon disulfide. [c] Central carbon.

Table II. Carbon-13 Nmr Parameters for the Dimethyl Derivatives of Group IIb

	J_{CX}[a]	J_{CXCH}[a]	J_{CH}[a]	δ_C[d]
Zn	. . .	. . .	121.6	197.0
Cd	512[b] 537.5[c]	. . .	126.6	191.8
Hg	690	1.74	129.6	169.3

[a] In hertz. [b] ^{111}Cd. [c] ^{113}Cd. [d] In parts per million upfield from carbon disulfide.

The carbon–carbon coupling in neopentane was determined for natural abundance ^{13}C with complete proton decoupling. Under these conditions, the 0.04% of the molecules with adjacent ^{13}C give an AB spectrum having $J/\delta = 0.67$. Because of the low signal-to-noise ratio from molecules of this type, it was not possible to observe the weak, outer lines of the AB quartet. The coupling constant was obtained from the positions of the lines arising from molecules containing only one ^{13}C and the two inner lines of the AB pattern by neglecting the isotope effect of ^{13}C on the chemical shift of an adjacent ^{13}C. Isotope effects are present and can be observed in other compounds, but the effect is small. The coupling constant is the average of four separate determinations involving 1000 scans each. The error is believed to be ±1 Hz.

The metal–carbon coupling constants were measured with complete proton decoupling except for dimethylcadmium and tetramethyltin. The only isotope of germanium with a nonzero spin has a spin of $^9/_2$ and a natural abundance of 7%. No carbon–germanium coupling was observed. For dimethylcadmium, the individual satellites due to the isotopes ^{111}Cd and ^{113}Cd could be resolved, but this was not the case for the various tin isotopes in tetramethyltin for which only a single composite band was seen. Vicinal, carbon–proton coupling was not seen in the case of dimethylcadmium and dimethylzinc because of rapid intermolecular methyl exchange.[7] At our normal probe temperatures, the exchange process is too rapid to allow the observation of the small, vicinal, carbon–proton coupling constants, but does not greatly affect the large, one-bond coupling between carbon and cadmium.

The relative signs of the coupling constants have not been determined in this study, but on the basis of the molecular orbital theory of spin–spin coupling proposed by Pople and Santry[8] the signs of both the one-bond, carbon–metal and vicinal carbon–proton reduced coupling constants are expected to be positive. This prediction agrees with the signs of the one-bond coupling constants which have been studied by the heteronuclear tickling technique.[4,5]

Discussion

Karabatsos[9] has extended the valence-bond calculations for the contact contribution of the geminal, proton–proton coupling constant[10] to the case of geminal, carbon–proton coupling. The major assumption was that the contributions of the various canonical structures to the valence-bond formulation of the three-atom geminal fragments do not change on substitution of a carbon atom for a proton. The carbon–proton, geminal coupling should further depend only on the choice of a specific form for the carbon 2s orbital and the hybridization of the carbon orbital forming the carbon–proton valence bond. The hybridization of an orbital used in forming a "long bond" is not necessarily the same as that forming the valence bonds in the perfect pairing structure.

Smith,[3] following Karabatsos, related the X–C–H geminal coupling in the tetramethyl derivatives of group IV to the H–C–H coupling in methane. The problem of choosing a form for the central atom s orbitals is more difficult for the heavier elements. Smith adopted an empirical approach and calculated effective nuclear charges (Z^*) for s-like orbitals which gave the best fit with the observed spin–spin coupling constants.

The equations which Smith and Karabatsos formally derived for geminal coupling are valid for any Fermi contact interaction between atoms whose s and p orbitals have similar energies. The most general form of such an expression must allow for the variation of both the form and the hybridization of the orbitals used by both atoms in forming the valence bonds. Equation 1 relates the Fermi contact contribution to the one-bond, carbon–metal coupling constant in the tetramethyl derivatives of group IV to the carbon–carbon coupling in neopentane

$$J_{CX} = \left(\frac{\alpha_x^2}{\alpha_c^2}\right)\left(\frac{\Delta E_c}{\Delta E_x}\right)\left(\frac{Z_x^*}{Z_c^*}\right)^3\left(\frac{n_x}{n_c}\right)^3\left(\frac{g_x}{g_c}\right)J_{CC} \qquad (1)$$

where α^2 is the fractional s character of the carbon orbital forming the carbon–metal bond, ΔE is the average energy approximation term, n is the principal quantum number of the period to which the central atom belongs, Z^* is the effective nuclear charge of the orbital used by the central atom in forming the carbon–metal bond, and g is the magnetic moment of the central atom. For one-bond couplings, eq 1 is attractive theoretically, because the valence-bond structure which contributes

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Table III. Comparison of the Calculation of the One-Bond, Carbon–Metal Coupling by the Method of Karabatsos and Smith with the Observed Values

	J_{CH}	α_H^2	α_X^2	Z_X^*	μ	n_X	J_{CX} Calcd	J_{CX} Obsd
C	124.3	0.248	0.256	3.29	0.70	2	(36.2)[a]	36.2
Si	118.2	0.236	0.291	6.02	−0.55	3	58.6	51
Ge	124.4	0.249	0.256	10.9	−0.88	4	204	. . .
Sn	127.7	0.255	0.137	16.3	∼−1.0	5	369	330
Pb	134.2	0.268	0.196	22.6	0.58	6	276	251

[a] Assumed value.

the most to the coupling constant is the perfect pairing structure, and the coefficient of this structure in the valence-bond wave function changes insignificantly from unity for the purposes of calculating the coupling constant in covalent molecules for which ionic structures are unimportant.

For the case of one-bond, carbon–metal coupling in the tetramethyl derivatives of group IV the hybridization of each orbital of the central atom forming a bond to carbon contains 25% s character by symmetry. The hybridization of the carbon orbital forming the bond to the metal is not exactly sp^3 since the four substituents on the carbon are not identical. The degree of hybridization of this orbital may be assigned by the method of Juan and Gutowsky.[11]

Assuming that a carbon atom uses a single 2s orbital to form its four bonds, the variation of the one-bond, carbon–proton coupling constant was attributed to changes in the hybridization of the carbon orbital forming the carbon–proton bond. This approach has been criticized[12] and in the cases where electronegative substituents are present, the parameter which most strongly influences the carbon–proton coupling constant is the effective nuclear charge of the carbon 2s orbital rather than its hybridization. When no electronegative substituents are present, the correlation of s character with the carbon–proton coupling constants seems valid. When the fraction of s character in the C–H bond is fixed, the remaining s character, if any, must reside in the carbon–metal bond. The s characters of the carbon hybrid orbitals calculated in this way for the tetramethyl derivatives of group IV have been tabulated by Smith.[3]

In this work, the Z^* values, which Smith found gave the best agreement for the geminal X–C–H coupling constants, were used. A further assumption was made that the average energy approximation term is constant throughout this series. There is no justification for this assumption, but at present assignment of a series of numerical values to this term seems dubious. Smith related the sum of the X–C and C–H bond energies to the average excitation energy for the geminal X–C–H fragment and commented that this ratio was, in fact, also near unity.

The parameters used and the results of the calculations are given in Table III and show the rather good agreement between the coupling constants calculated in this rather naive way and the experimental values. The agreement, if not fortuitous, tends to justify the belief that the Fermi contact interaction is the dominant coupling mechanism and that, for elements of similar electronegativity, simple correlations with bond order and electron density at the nucleus are valid.

In a more restrictive sense, Karabatsos' results suggest that the carbon–carbon coupling in neopentane should be related to the one-bond, carbon–proton coupling in isobutane by the relationship $J_{CC} = 0.3 \cdot J_{CH}$. The calculated value of 37.5 Hz agrees well with the experimental value of 36.2 Hz. Similarly, the one-bond, carbon–metal coupling constant should be 0.3 times the one-bond, metal–proton coupling constants in the trimethylmeta hydrides. The results of this calculation are given in Table IV. The relationship does not hold for the heavier members of group IV. The most plausible explanation for the failure of the Karabatsos equation in these cases is that one or more of the assumptions on which the derivation is based are not valid. In particular, the wave functions of the two series of compounds may not be comparable. Chemically, this is reasonable because, although the carbon–proton bond closely resembles the carbon–carbon bond, the metal–proton and metal–carbon bonds are not at all similar in their properties.

Table IV. A Comparison of Coupling Constants Involving Carbon with Those Involving Protons

	J_{XH}, in $HX(CH_3)_3$[a]	J_{XC},[a] calcd	J_{HXCH}, in $HX(CH_3)_3$[a]	J_{HXCH},[a] calcd
C	125	36.5	6.8[d]	2.0
Si	202[b]	61	. . .	. . .
Ge	. . .	. . .	3.8[e]	1.1
Sn	1700[c]	510	2.4[c]	0.72
Pb	2397[c]	720	1.5[c]	0.45

[a] In hertz. [b] E. A. V. Ebsworth and J. J. Turner, *J. Chem. Phys.*, **36**, 2628 (1962). [c] H. D. Kaesz and N. Flitcroft, *J. Amer. Chem. Soc.*, **85**, 1377 (1963). [d] J. S. Waugh and F. W. Dobbs, *J. Chem. Phys.*, **31**, 1238 (1959). [e] T. Birchall and W. L. Jolly, *Inorg. Chem.*, **5**, 2177 (1966).

A second possibility is that one or both of these coupling constants has a significant contribution from either the orbital or the dipole interactions. Both these contributions are negligible if one of the coupled nuclei is a proton, and the results presented above on the one-bond, carbon–metal couplings tend to show that these too are dominated by the Fermi contact term.

Reeves and Wells[13] proposed a correlation of the reduced coupling constants with atomic number according to eq 2, where Z_x is the atomic number of

$$\left(\frac{J_{xy}}{\gamma_x\gamma_y}\right)^{1/2} = AZ_x + B \tag{2}$$

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nucleus x, γ is the magnetic moment, and A and B are constants for a single series of atoms y.

The results of applying this correlation to the case of one-bond, carbon–metal coupling constants in the tetramethyl derivatives of group IV are given in Figure 1. Although the equation correlates geminal, metal–proton coupling constants quite well, the fit for one-bond, carbon–metal coupling constants is less satisfactory.

The main difference between eq 1 and 2 is in the choice of a form for the s orbital of the central atom. Both equations have arbitrary constants to absorb this unknown factor. Neither equation can predict the negative sign of the reduced carbon–fluorine coupling constant. For this, a more sophisticated treatment such as the molecular orbital theory of Pople and Santry is needed.[8]

The vicinal C–X–C–H coupling constants should be related to the H–X–C–H couplings in the trimethylmetal hydrides by the relationship $J_{\text{CXCH}} = 0.3J_{\text{HXCH}}$.[9] The results of this calculation are given in Table IV. As was the case for most of the carbon–proton vicinal coupling constants studied by Karabatsos, the observed values are more positive than those predicted. Though the magnitudes of the coupling constants are not predicted precisely, the trend toward smaller values with the heavier members of group IV is reproduced.

No discussion will be made of the variations in the ^{13}C spectra of the dimethyl derivatives of group IIb because of the limited amount of available data.

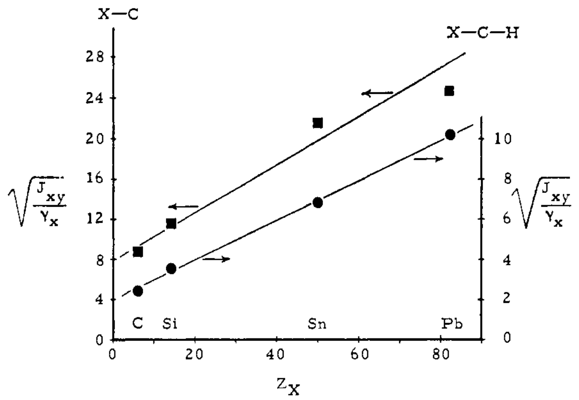

Figure 1. Reeves and Wells correlations of the C–X and X–C–H coupling constants in the tetramethyl derivatives of group IV: ●, X–C–H; ■, X–C.

Since the completion of this work, several papers have appeared presenting the same or related data.[14] Thus, Dreeskamp and Stegmeir[15] have obtained carbon–metal and vicinal carbon–proton couplings in some of the same compounds by heteronuclear tickling techniques using ^{13}C-enriched samples. Litchman and Grant[16] have observed the carbon–carbon coupling in neopentane while McFarlane[17] has measured the tin–carbon coupling in tetramethyltin. Also, Dean and McFarlane[18] have reexamined the spectrum of dimethylmercury and determined the vicinal carbon–proton coupling by tickling techniques.

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Equilibration Studies. The Energy Differences for Some Six-Membered Heterocyclic Methyl Amide–Imidate Isomer Pairs

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Abstract: The isomer pairs O-methylvalerolactim (**5**)–N-methylvalerolactam (**6**), 2-methoxypyridine (**7**)–N-methyl-2-pyridone (**8**), 4-methoxypyridine (**9**)–N-methyl-4-pyridone (**10**), and 2,6-diphenyl-4-methoxypyridine (**11**)–2,6-diphenyl-N-methyl-4-pyridone (**12**) have been equilibrated in the liquid phase by using the common alkylated derivatives as catalysts. Calorimetric determinations of the heats of isomerization at 130° for the first three cases, in conjunction with estimated differences in heats of vaporization, kinetic energies, and zero-point vibrational energies, allow estimates of the chemical binding energy differences for each isomer pair. In this sense, the amide is considerably more stable than the imidate for the pairs **5**–**6** and **7**–**8**; in contrast, the isomers **9**–**10** are of comparable stability. The present results indicate that environmental effects can contribute several kcalories/mole to the relative isomer stabilities in the condensed phase. The π-stabilization energy of **7** is estimated to be 6 ± 7 kcal/mol greater than that of **8**. A mechanism involving alkyl transfer from the catalyst to the imidate is suggested for the equilibration reaction and is supported by isotopic scrambling data.

Chemical, physical, and spectral investigations have established that an amide is generally more stable than its isomeric imidate.[2–6] Quantitative estimates of protomeric equilibria **1**–**2** are available for a large number of heteroaromatics[6] although contributions to

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