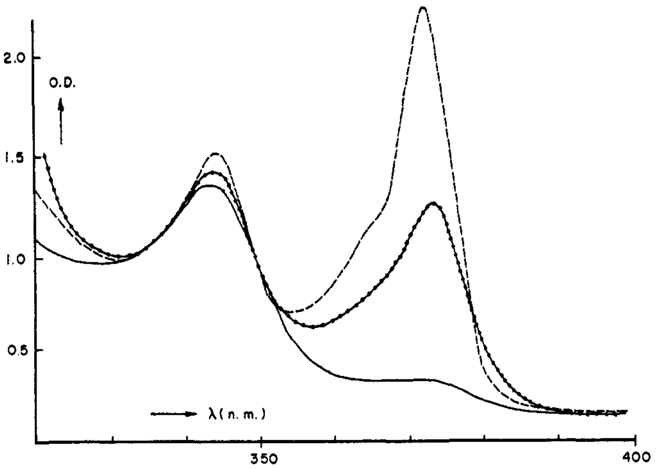

Figure 1. Temperature dependence of the near-uv spectrum of fluorenylstrontium ($Sr^{2+}Fl_2^-$) in THF: (——) 24.5°; (–·–·–·–) −15.4°; (– – –) −76.1°.

As the temperature decreases, K_1 increases rapidly ($\Delta H = -12.3 \pm 2$ kcal mol^{-1}), and K_2 increases much more slowly. One expects, therefore, the apparent enthalpy to decrease sharply due to the factor $2/(2 + K_1)$. The second term, $(2K_2/(1 + 2K_2))\Delta H_2$, however, is expected to increase slowly. If the second term is small in the temperature region where the first term vanishes, the apparent enthalpy is expected to approach zero before it rises again to its low-temperature limit, where $\Delta H = \Delta H_2$. Inspection of Figure 2 indicates that the system qualitatively conforms to the predicted behavior.

A more quantitative correlation can be obtained by reasonable estimates of K_1 and K_2 at any one temperature. One can then calculate K_1 and K_2 at all temperatures provided that ΔH_1 and ΔH_2 are known. ΔH_1 is known (see above) and K_1 can be calculated under the reasonable assumption that at high temperatures the 372-nm absorption band is due to $Fl^-||Sr^{2+}Fl^-$.[8] K_2 can now be calculated in the region where $K_1 \gg 1$ (−70 to −100°, Table I), since there $R = 1 + 2K_2$ and ΔH_2 can then easily be evaluated in the usual manner. Table I lists the extrapolated K_1 and K_2 values for a number of temperatures. R can now be calculated at all temperatures and the calculated log R *vs.* $1/T$ plot is shown in Figure 2. It can be seen that the experimental plot is well simulated by a two-step process. Enthalpy and entropy values for the two processes are calculated to be: $\Delta H_1 = -12.3 \pm 2$ kcal mol^{-1}, $\Delta S_1 = -47 \pm 7$ cal deg^{-1} mol^{-1}; $\Delta H_2 = -2.8 \pm 1$ kcal mol^{-1}, $\Delta S_2 = -17 \pm 5$ cal mol^{-1}.

Table I. Values of R, K_1, and K_2 at a Number of Temperatures[a]

$1/T \times 10^3$	T, °C	R	K_1	$K_2 \times 10^2$
3.44	+18.0	0.103	0.18	2.1
3.77	−8.4	0.489	1.26	3.3
3.99	−22.1	0.950	5.50	4.6
4.45	−48.0	1.37	87.4	8.7
4.92	−70.0	1.49	1,700	17
5.85	−102.0	2.66	526,000	74

[a] Total carbanion concentration = 6.5×10^{-4} M.

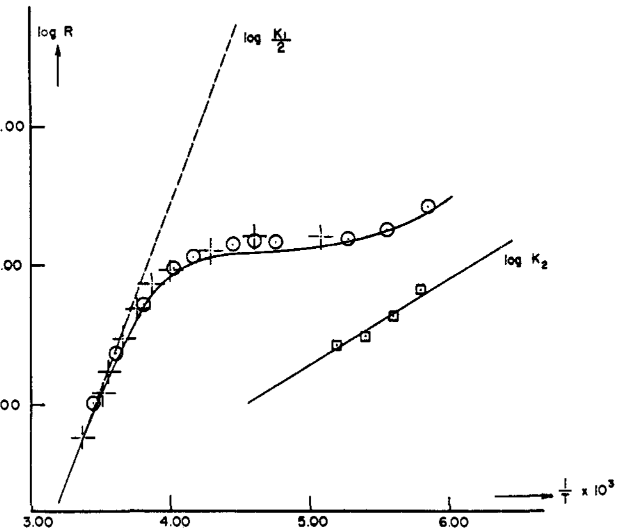

Figure 2. The ratio of [separated ion pairs] to [contact ion pairs] as a function of temperature: R = [separated ion pairs]/[contact ion pairs]; (⊙–¦–) refer to runs on different samples; (——) calculated log R *vs.* $1/T$ curve; (– – –) calculated values of the log of the equilibrium constant of the first solvation step K_1 *vs.* $1/T$; (⊡) calculated values of the log of the equilibrium constant of the second solvation step K_2 at the four lowest temperatures.

Results on other systems such as fluorenylbarium–trimethylene oxide suggest that this surprisingly specific two-stage solvation process may be quite general in solutions of this type.

Acknowledgment. Support by the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (GP-26350), and an equipment grant to one of us (T. E. H.) by the University of Florida Graduate School are gratefully acknowledged. The authors wish to thank Mr. U. Takaki and Dr. K. H. Wong for carrying out some of the spectral measurements.

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[8] Since at high temperatures K_1 and $K_2 \ll 1$, it follows from (1) that $R = K_1/2$.

Stable Carbocations. CXXXVI.[1] Intramolecular 1,2-Hydrogen Shifts in Difluoro- and Dimethylbenzenium Ions

Sir:

Protonation of isomeric difluorobenzenes and xylenes in superacids has been studied.[2,3] However, there was no report on the temperature-dependent behavior of these ions. Furthermore, *o*-difluorobenzene was not protonated in FSO_3H-SbF_5 solution at low temperature.[2] Using the improved $HF-SbF_5-SO_2ClF$ superacid system we presently wish to report the results of temperature-dependent nmr (^1H and ^{19}F) studies of

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[1] Part CXXXV: G. A. Olah and Y. K. Mo, *J. Amer. Chem. Soc.*, **94**, 5341 (1972).

[2] G. A. Olah and T. E. Kiovsky, *ibid.*, **89**, 5692 (1967).

[3] G. A. Olah, *ibid.*, 87, 1103 (1965).

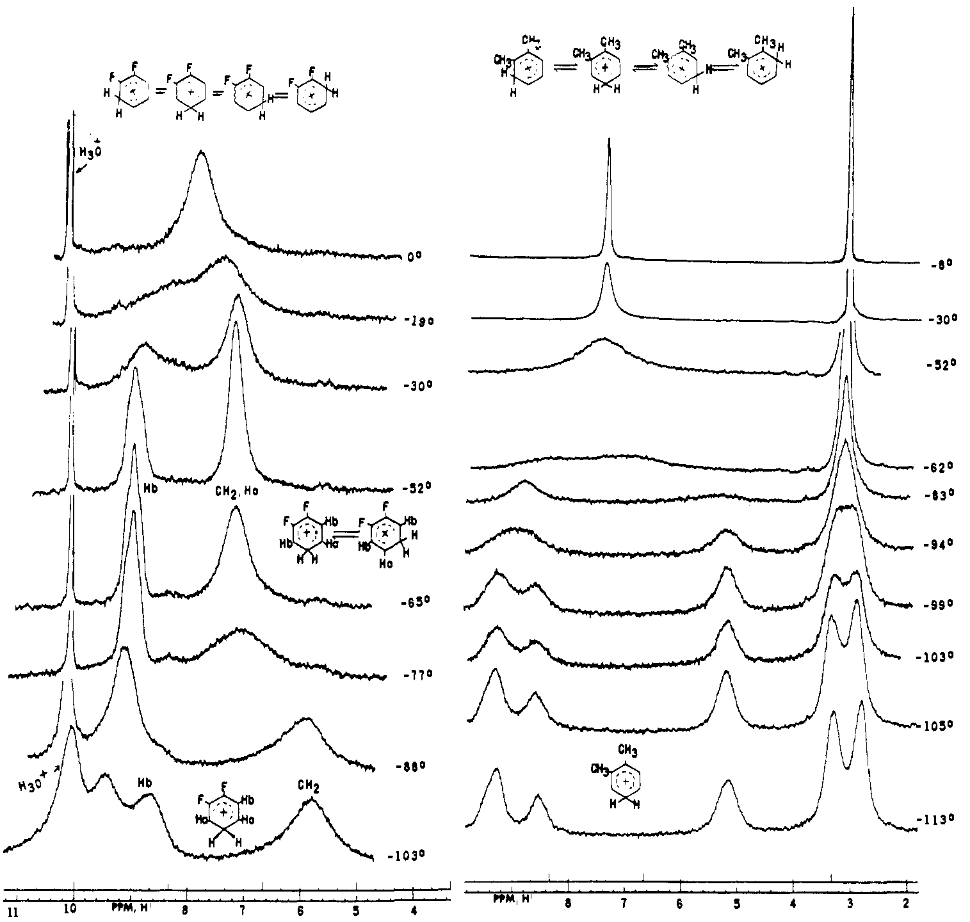
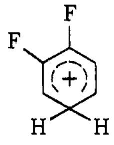


Figure 1. Temperature-dependent pmr spectra (60 MHz) of 3,4-difluoro- (left) and 3,4-dimethylbenzenium ions (right).

difluoro- and dimethylbenzenium ions. We feel that this study is of particular interest with regard to intramolecular 1,2-hydrogen shifts in aromatic systems.

The temperature-dependent pmr spectra (60 MHz) of *o*-difluorobenzene in HF–SbF$_5$–SO$_2$ClF solution are shown in Figure 1 (left side). At −103°, a broadened absorption is observed at δ 5.8, corresponding to the methylene protons of the benzenium ion.[2-6] In the vinyl proton region, two broadened absorption lines at δ 8.7 and 9.5 are observed (the resonance line at δ 10.5 being due to the oxonium ion, H$_3$O$^+$, caused by impurity moisture in the solvent). The integration of peak areas tells the number of protons corresponding to each signal, the more deshielded vinylic proton absorption having twice the intensity of the more shielded one. In the ^{19}F nmr spectrum, two very broad absorptions were found at ϕ 32.4 and 124.4 corresponding to the fluorine shifts of para and meta fluorine atoms of fluorobenzenium ions.[2] These data clearly suggest observation of the static (or "frozen out") 3,4-difluorobenzenium ion, **1**.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As the temperature of the solution was raised (*e.g.* to −88°), the two vinylic proton absorption lines collapsed to a broadened peak at δ 9.2 and the methylene proton absorption line also broadened and became slightly deshielded. Further warming of the solution caused the methylene proton resonance to become more deshielded and also broadened. Meanwhile, the deshielded vinylic proton absorption became less broadened as the temperature was increased. At −52°, only two resolved absorption lines were observed at δ 7.1 and 9.1 with a peak area ratio of 3:2. In the ^{19}F nmr spectrum, the two absorptions became broadened as the temperature increased and at −77° merged into the base line. These observations indicate a rapid degenerate equilibration of 3,4-difluorobenzenium ions (**1a** and **1b**). 2,4-Difluorobenzenium ions **1a** and **1b** are equivalent, *i.e.*, degenerate. The interconversion of **1a** and **1b** takes place by a 1,2-hydrogen shift *via* a transition state of the benzonium ion **2** nature.[7] There is no indication in the low-temperature nmr spectra of a benzonium ion intermediate (**2**, π complex with a two-electron, three-center bond hydrogen-bridged structure). It is increasingly apparent from this study that benzonium ion complexes of aromatic hydrocarbons represent only transition states and not stable intermediates. This observation is in accord with similar behavior of alkenes and has substantial importance re-

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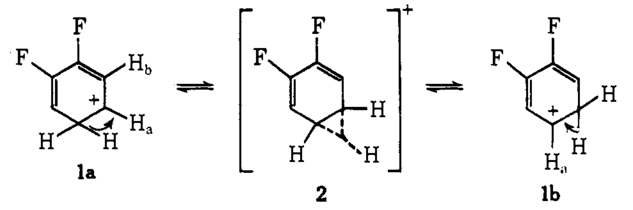
(4) G. A. Olah, R. H. Schlosberg, D. P. Kelly, and Gh. D. Mateescu, *J. Amer. Chem. Soc.*, **92**, 2548 (1970).

(5) G. A. Olah, R. H. Schlosberg, R. D. Porter, Y. K. Mo, D. P. Kelly, and Gh. D. Mateescu, *ibid.*, **94**, 2034 (1972).

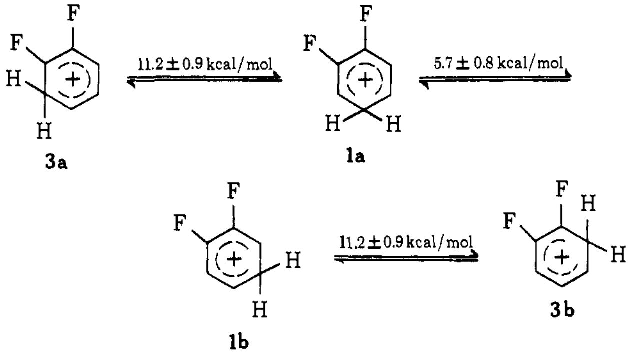
(6) D. M. Brouwer, E. L. Mackor, and C. MacLean in "Carbonium Ions," Vol. 2, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1970.

(7) G. A. Olah, *Accounts Chem. Res.*, **4**, 240 (1971).



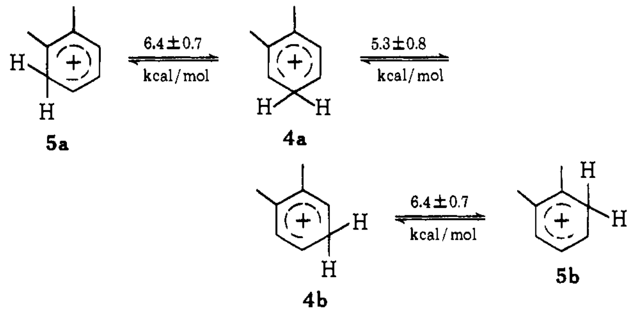
lating to the mechanistic details of electrophilic aromatic substitutions.

As the temperature is raised further, the two absorption lines became again broadened and finally collapse to a single absorption at δ 7.9 (from −52 to 0°). In the ^{19}F nmr spectrum, no new absorption lines were observed (except those of solvent).[8] Thus, there is a second temperature-dependent dynamic process in the 3,4-difluorobenzenium ion (**3a** ⇌ **1a** ⇌ **1b** ⇌ **3b**). When the exchange rate becomes more rapid than the nmr time scale (at 0°), then all the protons become equivalent. This process also takes place through 1,2-hydrogen shifts. Since the two processes can be separately observed by pmr, calculation of activation parameters can be treated independently. The activation energies, E_a, of the two processes were calculated by a multiple-site exchange program[9] and were found to be 5.7 ± 0.8 kcal/mol with a preexponential factor A of $10^{8.9\pm0.7}$ and 11.2 ± 0.9 kcal/mol with a preexponential factor A of $10^{12.4\pm0.9}$, respectively.



In the benzenium ion and alkylbenzenium ions,[6,10] both intra- and intermolecular exchanges are possible and were reported. In the case of difluorobenzenium ions, intermolecular exchange is unlikely, even at 0°, when considering the experimental evidence of the pmr spectra. The calculated average proton shift of CH_2 and H_a in ion **1a** or **1b** is (5.8 × 2 + 9.5)/3 = δ 7.03, in good agreement with the experimentally observed value δ 7.1. A similar calculated average shift of one of the ortho and meta protons is δ 9.1, which is identical with the experimentally observed value. This is also the case when all protons become equivalent (at 0°). The calculated average shift is (8.7 + 9.5 × 2 + 5.8 × 2)/5 = δ 7.9 (slightly broadened).[5] Besides the excellent agreement of pmr parameters with those calculated for intramolecular exchange processes, further evidence for the purely intramolecular nature of exchange was obtained when *o*-difluorobenzene was deuterated in DF–SbF_5–SO_2ClF solution at −78°. Deuteration was found to take place only at C-4 and C-5, as shown by the equal intensity of the two proton absorptions in the pmr spectrum of 3,4-difluorobenzenium ion in the temperature range from −103 to −61°. When the temperature of the solution was raised above −52°, the intensity of the two resonances changed. The intensity of the more deshielded absorption decreased and that of the shielded absorption increased reaching the ratio of 2:3. At the same time, the intensity of the acid peak (present due to a small amount of protic acid impurity in the DF–SbF_5–SO_2ClF solution) was not affected.

As it was known from our previous work that a methyl group and a fluorine atom can stabilize a benzenium ion to about the same extent,[2–6] we also undertook the study of protonated *o*-xylene **4** in the same superacid medium. The 3,4-dimethylbenzenium ion **4** has been prepared previously by Olah[3] in HF–SbF_5–SO_2 solution at −65° and by Brouwer, *et al.*,[6] in HF–BF_3 solution at −120°. However, no temperature-dependent study of **4** was reported. *o*-Xylene was protonated in HF–SbF_5–SO_2ClF solution at −112°. The pmr spectrum of ion **4** showed temperature dependence (Figure 1 right) similar to that of ion **1**. But the two different processes (**4a** ⇌ **4b** and **4a** ⇌ **5a** or **4b** ⇌ **5b**) are not completely separable as shown by the temperature-dependent pmr spectra. Thus, the energy barrier difference between the two processes must be smaller than that of ion **1**. Consequently, the first process (lower energy barrier, **4a** ⇌ **4b**) can be recognized by the collapsing of the two methyl absorptions (from −113 to −94°). The activation energy, E_a, for this process was calculated to be 5.3 ± 0.8 kcal/mol with a preexponential factor A of $10^{8.8\pm0.6}$. The activation energy, E_a, for the second process (**4a** ⇌ **5a** or **4b** ⇌ **5b**) was calculated from the temperature-dependent nature of the vinyl and methylene proton absorptions and was found to be 6.4 ± 0.7 kcal/mol with a preexponential factor A of $10^{10.3\pm0.7}$.



Protonation of *p*- and *m*-difluorobenzene as well as *p*- and *m*-xylene was studied previously in our laboratories.[2,3] No temperature-dependent behavior of these ions **6** and **7** has been reported. In HF–SbF_5–SO_2ClF solution we now find the nmr spectra of protonated *p*-difluorobenzene **6** and *p*-xylene **7** to be temperature dependent.

Results indicate that intramolecular hydrogen exchange (**6a** ⇌ **6b** and **7a** ⇌ **7b**) occurs below −74°.

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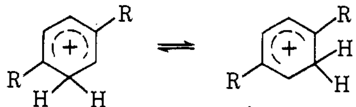
(8) No ^{19}F nmr resonance was detectable for the rapidly equilibrating ions **1a** and **1b**. This is because the ortho and meta F shifts are separated by 92 ppm and the rate constant for observing the coalescence of the two signals is calculated to be 11,526 sec^{-1}. Thus, at the temperatures used in this work, the rate constant is expected to be much smaller than this value. Consequently, the two resonances became too broad to be observed even at 0°.

(9) The theoretical spectra were calculated by means of a multiple-site exchange program based on an equation of H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956). The program was obtained originally from Dr. T. Gerig and was adapted to the Univac 1180 by Dr. W. E. Heyd of this department.

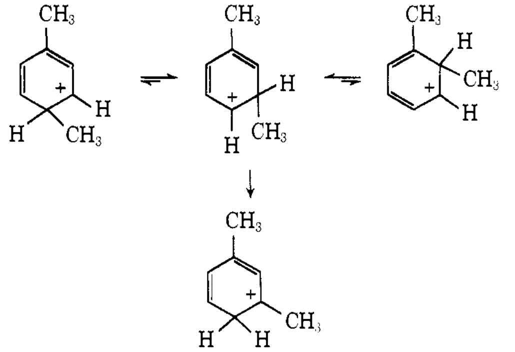
(10) D. M. Brouwer, *Recl. Trav. Chim. Pays-Bas*, **87**, 611 (1968).



6a, R = F
7a, R = CH_3

6b, R = F
7b, R = CH_3

However, above −74° intermolecular hydrogen exchange with the solvent becomes predominant. Recently, Brouwer studied the isomerization of *o*- and *p*-xylenes in HF-SbF_5 at 25° to give the more stable *m*-xylene.[10] The activation energies for the isomerization were found to be 21.4 and 20.4 kcal/mol, respectively. In our work we did not observe isomerization of *o*- and *p*-xylene to occur (observed by nmr) in HF–SbF_5–SO_2ClF solution below 0°, in accordance with the higher activation energy of the methyl migration process.



Protonation of *m*-difluorobenzene and *m*-xylene gives the 2,4-difluoro and dimethylbenzenium ions in HF–SbF_5–SO_2ClF solution, with no indication of temperature dependence of the nmr (^1H and ^{19}F) spectra between −90 and −10°.

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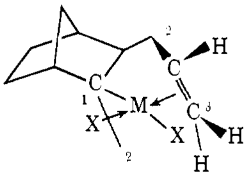
Studies of Carbon-13 Shielding Effects in Metal-Alkyl, Metal-Olefin, and Metal-Allyl Bonds

Sir:

In a recent ^{13}C nmr study it has been suggested that the magnitude of the upfield shift experienced by olefinic C atoms on coordination to a metal is closely correlated with the extent of metal-d to olefin-π^* back bonding.[1] We here report evidence that this is not the case and that in fact a major contributor to δC is a *nonbonding* shielding parameter, associated with partially filled metal d orbitals, similar to the concept proposed to account for δH in transition metal hydrido complexes.[2]

We have obtained $\delta^{13}C$ data for the σ-bonded carbon C^1 and the olefinic carbons C^2 and C^3 for the series of complexes I[3] [M = Pd, Pt, X_2 = hexafluoroacetylacetonate (hfacac); X = Cl, Br, I (dimers)]. $\delta^{13}C$ data have also been obtained or previously reported[4] for the π-allyl complexes II [M = Pd, Pt,[5] X_2 = hfacac; M = Pd, X = Cl, Br, I (dimers)].[6] Plots of $\delta^{13}C$ of C^2(I), C^3(I), and C^4(II) *vs.* $\delta^{13}C^1$(I) as a function of M and X give the linear correlations shown in Figure 1 (δC values are given as downfield shifts from TMS). Increasing the trans effect of X in the order hfacac < Cl < Br < I results in a deshielding of the σ-bonded carbon C^1, the olefinic carbons C^2 and C^3, and the π-allyl terminal carbons C^4. Also, these carbon atoms are more shielded for M = Pt than for M = Pd.



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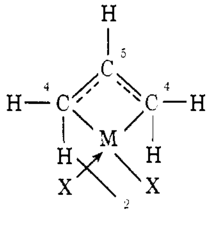

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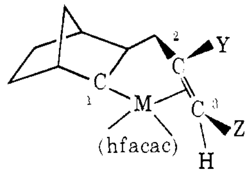
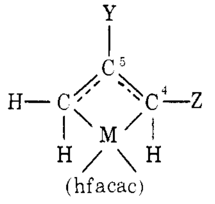


III



IV

These observations parallel those observed for δH in the complexes *trans*-[$MHX(PEt_3)_2$] (M = Pt, Pd; X = Cl, Br, I, etc.).[2,7,8] The linear correlations shown in Figure 1 suggest that the change in chemical shift on going from palladium–carbon to analogous platinum–carbon bonds is primarily due to a change in a nonbonding shielding term rather than to changes in the mode or degree of metal–carbon bonding. Nonbonding shielding effects of partially filled d orbitals will be extremely sensitive to the metal–carbon separation. In particular, the paramagnetic shielding term, σ_p, will be a function of $(r_{M-C})^{-3}$.[2] As such, the greater magnitude of $\Delta\delta C$ for C^1 on changing M or X relative to $\Delta\delta C$ for C^2, C^3, and C^4 (as evidenced by the slopes of the appropriate plots in Figure 1) may well be due to the shorter metal-carbon bond length for C^1 relative to those observed for C^2, C^3, and C^4. In complex I [M = Pd; X = OAc (dimer)] Pd-C^1 =

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[1] M. H. Chisholm, H. C. Clark, L. E. Manzer, and J. B. Stothers, *J. Amer. Chem. Soc.*, **94**, 5087 (1972).

[2] A. D. Buckingham and P. J. Stephens, *J. Chem. Soc.*, 2747 (1964); (b) *ibid.*, 4583 (1964), and references cited therein.

[3] (a) R. P. Hughes and J. Powell, *J. Organometal. Chem.*, **30**, C45 (1971); (b) M. C. Gallazzi, T. L. Hanlon, G. Vitulli, and L. Porri, *ibid.*, **33**, C45 (1971).

[4] B. E. Mann, R. Pietropaolo, and B. L. Shaw, *Chem. Commun.*, 790 (1971).

[5] In $CDCl_3$ solution allyl(hexafluoroacetylacetonato)platinum(II) consists of a mixture of a π-allylic monomer of structure II and a μ-allyl dimer: R. P. Hughes and J. Powell, unpublished results.

[6] $\delta^{13}C$ nmr spectra were recorded at 25.16 MHz using a Varian XL100-15 spectrometer operating in the fourier transform mode. New data reported here are for $CDCl_3$ solutions. Previously reported data of π-allylic palladium(II) complexes are for CH_2Cl_2 solutions. Changing the solvent from $CDCl_3$ to CH_2Cl_2 has very little effect on the δC values of the complexes I–IV. Assignment of resonances of complexes I–IV (M = Pd) is based on an analysis of proton-coupled ^{13}C nmr spectra together with known ^{13}C data of organic norbornanes. Assignment of spectra in complexes I and II (M = Pt) is further facilitated by observation of $J_{^{195}Pt-^{13}C}$ (*ca.* 760 Hz, C^1; 280 Hz, C^2; and 305 Hz, C^3).

[7] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 5075 (1962).

[8] J. Powell and B. L. Shaw, *ibid.*, 3879 (1965).