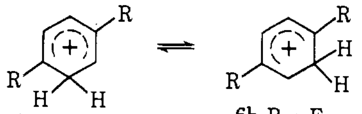
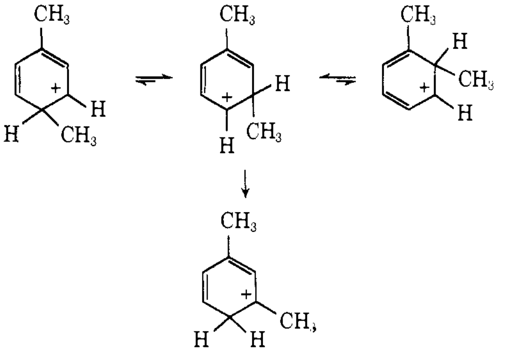


6a, R = F
7a, R = CH_3

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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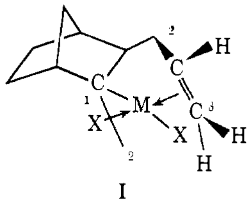
Received December 18, 1971

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

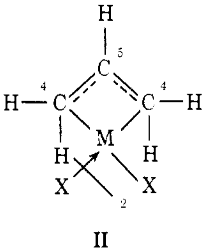
Sir:

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]

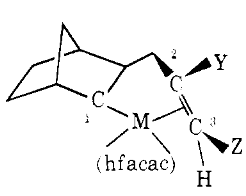
We have obtained $\delta^{13}C$ data for the σ-bonded carbon C^1 and the olefinic carbons C^2 and C^3 for the series of complexes I[3] [M = Pd, Pt, X_2 = hexafluoroacetylacetonate (hfacac); X = Cl, Br, I (dimers)]. $\delta^{13}C$ data have also been obtained or previously reported[4] for the π-allyl 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.



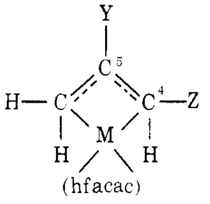
I



II



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).

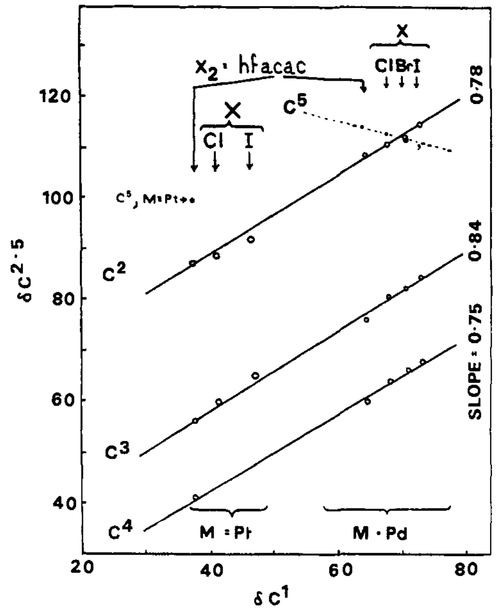

Figure 1. Plots of δC^2(I), δC^3(I), δC^4(II), and δC^5(II) *vs.* δC^1(I) as a function of M and X. δC values are given as downfield shifts relative to TMS.

2.04 Å, Pd–C^2 = 2.17 Å, and Pd–C^3 = 2.16 Å.[9] In complex II [M = Pd; X = OAc (dimer)] Pd–C^4 = 2.16 Å.[10] If nonbonding paramagnetic shielding effects (σ_p) alone account for the changes in δC, then the slope of the plots of C^2, C^3, and C^4 *vs.* C^1 should be *ca.* $(r_{Pd-C^1})^3/(r_{Pd-C^2})^3 = (2.04)^3/(2.17)^3 = 0.81$. This is in reasonable agreement with the observed slopes of 0.75–0.84.[11]

The magnitude of $\Delta\delta C$ and hence nonbonding metal d-orbital shielding parameters for olefinic and terminal π-allylic carbons are approximately the same as evidenced by the similar slopes in Figure 1. The shielding effects of the "coordinated hydrocarbon substituents" Y and Z in the series of complexes III and IV are also similar for π-olefinic and π-allylic carbons as is evidenced by the linear correlations obtained from plots of δC^3(III) *vs.* δC^4(IV) (see Figure 2) and δC^2(III) *vs.* δC^5(IV) (see Figure 3). (Figures 2 and 3 are plots of δC of the π-allylic carbons in III *vs.* δC of the *same* C atom in the "enyl" complexes IV derived from norbornene "insertion" into the appropriate complex (III)[3].) Again a correlation is obtained regardless of whether M = Pd or Pt.

The increase in shielding of C^5 in II (M = Pd) as the trans effect of X increases is not as marked as the decrease in shielding of C^4(II). This observation suggests that the nonbonding shielding effect of the metal d orbitals in four-coordinate planar d^8 complexes is anisotropic in agreement with the calculations of Buckingham and Stephens.[2,12]

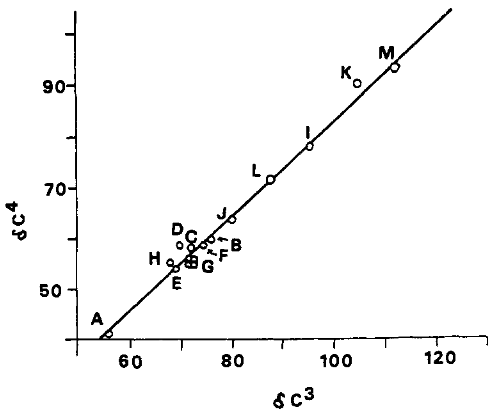

Figure 2. Plot of δC^3(III) *vs.* δC^4(IV) as a function of the hydrocarbon substituents, Y and Z. The substituents (Y,Z) are as follows: A and B (H,H); C (Me,H); D (Cl,H); E (*t*-Bu,H); F (*t*-BuCH$_2$,H); G (MeEtCH,H); H (Ph,H); I (H,CH$_3$); J (H,COOMe); K (CH$_3$,*t*-Bu); L (CH$_3$,CH$_2$OMe); M (*t*-BuCH$_2$,*t*-Bu); A (M = Pt); B–M (M = Pd). In complexes III and IV where Y = MeEtCH (point G) the Y substituent is chiral. Diastereotopic pairs are thus possible and a doubling of the ^{13}C nmr resonances is observed for C^2, C^3, and C^4.

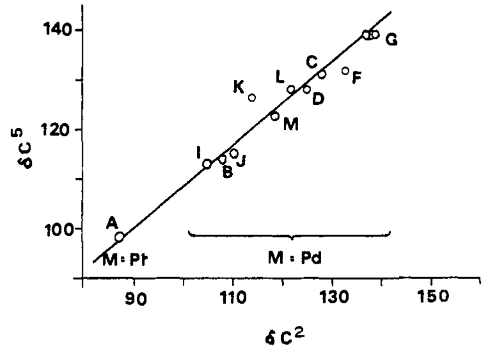

Figure 3. Plot of δC^2(III) *vs.* δC^5(IV) as a function of hydrocarbon substituents, Y and Z. Points A–M for same complexes as given in Figure 2.

It would be surprising if the observed changes in δC, as X and M are varied, were completely independent of the mode of metal–carbon bonding. The linear correlations in Figure 1 between δC of σ-bonded C's, olefinic C's, and terminal π-allylic C's would be understandable if the major parameter in all these metal–carbon bonds was a σ-bonding component. If metal-d to olefin-π^* back bonding in metal–olefinic hydrocarbon and metal–allylic hydrocarbon bonding were other than a secondary effect of minor importance, linear correlations between δC of olefinic or allylic C's and σ–C's of the type shown in Figure 1 would be unlikely.[13] Further studies on a variety of π-olefinic and enyl complexes of transition metals are currently in progress in order to assess further the validity of these conclusions.

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(9) M. Zocchi, G. Tieghi, and A. Albinati, *J. Organometal. Chem.*, **33**, C47 (1971).

(10) M. R. Churchill and R. Mason, *Nature* (*London*), **204**, 777 (1964).

(11) (a) The absence of a σ_p term to shielding in Ag(I)–olefin complexes owing to silver's full d^{10} electron configuration accounts for the small, *ca.* 4 ppm, upfield shift of $\delta^{13}C$ on coordination of an olefin to Ag(I).[11b] (b) R. G. Parker and J. D. Roberts, *J. Amer. Chem. Soc.*, **92**, 743 (1970).

(12) (a) It may be that shielding of C^5 (II) (which, in contrast to C^1–C^4, is located between coordination sites) is only slightly affected (or perhaps even deshielded[2b]) by nonbonding metal d orbitals. The metal could possibly be regarded as an α' substituent with respect to C^5.[12b] In olefinic hydrocarbons the change in δC associated with an α' substituent is in the opposite sense to that associated with the same substituent in an α position.[12b] (b) The definition of α and α' is that given by Roberts, *et al.*[12c] (c) D. E. Dorman, M. Jautelat, and J. D. Roberts, *J. Org. Chem.*, **36**, 2757 (1971).

(13) SCCMO calculations by Brown and Owens[14] on a series of π-allyl complexes of Ni, Pd, and Pt suggest that the π-allyl ligand is primarily an electron-donating ligand and in complexes of the type described here operates almost exclusively in this mode.

(14) D. A. Brown and A. Owens, *Inorg. Chim. Acta*, **5**, 675 (1971).

Acknowledgment. This work was supported by the National Research Council of Canada.

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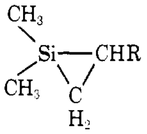
Received September 27, 1972

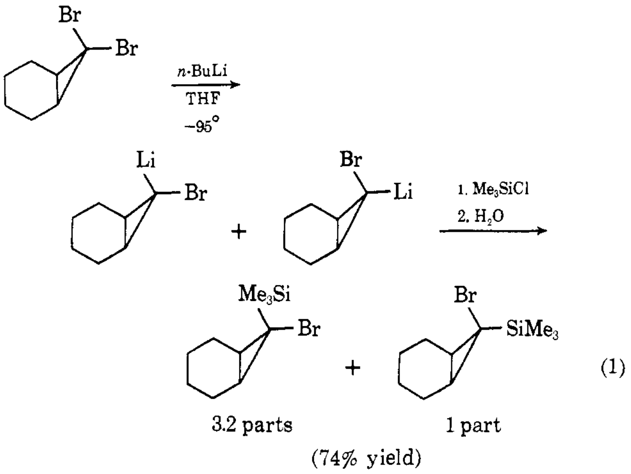
Substituted 7-Siladispiro[2.0.2.1]heptanes. The First Stable Silacyclopropanes

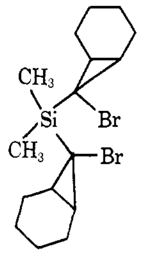
Sir:

Various attempts have been made to prepare silacyclopropanes, but all reactions designed to produce this ring system have been reported to give acyclic or larger (>3) cyclic organosilicon compounds.[1] No evidence is available which could distinguish between thermodynamic and kinetic instability as the explanation for the apparent nonexistence of any compounds containing an SiC_2 ring.[2] Most of such published attempts were directed toward relatively lightly substituted silacyclopropanes of type I. If kinetic factors dominate, then a stabilization of such a ring system might be achieved by significantly increasing the degree of substitution of the ring carbon atoms, preferably with rather bulky groups.[3] We have tested this approach and have found that it does indeed permit the preparation of stable compounds containing the silacyclopropane system.



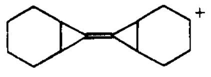
I, R = H or alkyl





II

Our synthesis of such silacyclopropanes is based on our studies of the chemistry of *gem*-lithiobromocyclopropanes.[4] These have been found to alkylate trimethylchlorosilane and trimethyltin chloride. For instance, the reaction sequence shown in eq 1 could be carried out. When this lithium reagent was treated with dimethyldichlorosilane in place of Me_3SiCl, silane II, mp 114–116°, could be isolated by crystallization from methanol. Treatment of a THF solution of II with an excess of magnesium at room temperature during 1.5 hr resulted in consumption of about 1 g-atom of Mg/mol of II. The organic layer was decanted under nitrogen and the solid remaining extracted with pentane. Distillation of the combined organic solutions gave a white, crystalline solid, III, bp 95–97° (0.01 mm), mp 72–74°, in 75–80% yield. This product was air sensitive and had to be handled under an inert atmosphere.[5] Combustion analysis (Alfred Bernhardt Mikroanalytisches Laboratorium) established the empirical formula $C_{16}H_{26}Si$ (*Anal.* Calcd: C, 77.97; H, 10.63; Si, 11.40. Found: C, 77.91; H, 10.59; Si, 11.17). A high-resolution mass spectrum of III (modified CEC-21-110B at 70 eV) showed *inter alia* the molecular ion $C_{16}H_{26}Si^+$ (*m/e* found, 246.1807; calcd, 246.1804), a $[C_{16}H_{26}Si-CH_3]^+$ ion (*m/e* found, 231.1570; calcd, 231.1569), and a fragment ion $C_{14}H_{20}^+$ *m/e* found, 188.1564; calcd, 188.1565). The latter very likely is IV. No ions corresponding to a dimeric species, $C_{32}H_{52}Si_2$, or its fragments resulting from CH_3 fission, were observed.[6] The product III reacted exothermally with CCl_4 at room temperature when solutions were prepared for spectroscopic studies. Solution of III in anhydrous methanol also resulted in an exothermic reaction which gave a product, bp 94–96° (0.01 mm), whose combustion analysis indicated the formula $C_{17}H_{30}OSi$. Nmr and ir data showed it to be a methoxysilane. The volatility of III, its mass spectrum, and its anomalously high reactivity (for a tetraorganosilane) suggested that it was a highly strained silacyclopropane derivative, dispiro[bicyclo[4.1.0]heptane-7-2′-silacyclopropane-3′,7′′-bicyclo[4.1.0]heptane. Its methanolysis product then would be IIIa.



IV

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[1] *Inter alia:* (a) J. D. Roberts and S. Dev, *J. Amer. Chem. Soc.*, **73**, 1879 (1951); (b) P. S. Skell and E. J. Goldstein, *ibid.*, **86**, 1442 (1964); (c) O. M. Nefedov and M. N. Manakov, *Angew. Chem.*, **78**, 1039 (1966); (d) W. H. Atwell and D. R. Weyenberg, *J. Amer. Chem. Soc.*, **90**, 3438 (1968); (e) J. W. Connolly, *J. Organometal. Chem.*, **11**, 429 (1968); (f) Y.-N. Tang, G. P. Gennaro, and Y. Y. Su, *J. Amer. Chem. Soc.*, **94**, 4357 (1972).

[2] Skell and Goldstein[1b] have suggested that the SiC_2 ring is thermally unstable due to excessive ring strain introduced by the presence of the silicon atom, and this explanation has again been cited by others[1f] more recently.

[3] This approach has served well in the stabilization of small organic ring systems, the least substituted of which were not very stable toward ring opening or other reactions; *cf.* F. D. Greene and S. S. Hecht, *J. Org. Chem.*, **35**, 2482 (1970), and references therein.

[4] (a) R. L. Lambert, Jr., Ph.D. Thesis, Massachusetts Institute of Technology, 1972; (b) D. Seyferth and R. L. Lambert, Jr., report in preparation.

[5] The melting point, in fact, was dependent on the care which was taken to exclude air during the isolation and purification of the product. The highest melting point observed was that cited.

[6] Species corresponding to $C_{16}H_{26}SiO^+$ and $C_{15}H_{23}SiO^+$ were observed in all mass spectra of III in variable intensity. In low-resolution mass spectra, the intensity of these ions was observed to depend on the care with which air had been excluded from the samples, being lowest for the samples with the highest melting points. These peaks are believed to be due to the presence of an oxidation product, either present initially or formed during introduction of the samples into the mass spectrometer.