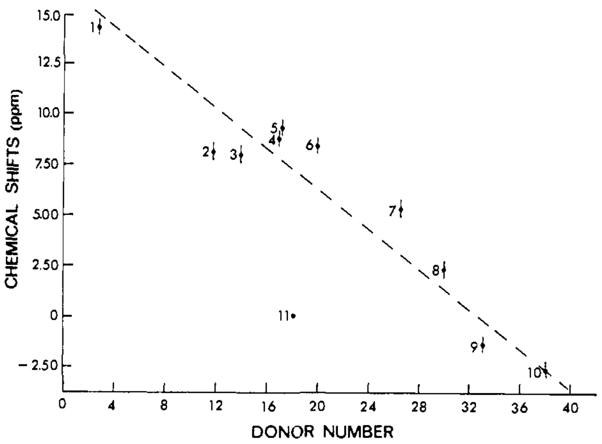

Figure 1. Plot of ^{23}Na chemical shifts *vs.* donor number of the solvents (1) nitromethane, (2) benzonitrile, (3) acetonitrile, (4) acetone, (5) ethyl acetate, (6) tetrahydrofuran, (7) dimethylformamide, (8) dimethyl sulfoxide, (9) pyridine, (10) hexamethylphosphoramide, (11) water.

about by the formation of the inner solvation shell. In such cases it would be expected that the chemical shifts would be related to the solvating abilities of the respective solvents. An empirical approach to the evaluation of the complexing (or donor) ability of the solvents is provided by Gutmann's "donor numbers."[2] The latter are simply the enthalpies (in kcal/mol) of complex formation between the given solvent and antimony pentachloride in 1,2-dichloroethane solutions. As shown by Gutmann, the donor numbers can be quite useful in predicting the behavior of nonaqueous systems. It was reasonable to expect, therefore, that there might be a relationship between the donor numbers and the relative chemical shifts for the solvated sodium ions. A plot of chemical shift *vs.* donor numbers (Figure 1) shows that this is indeed the case. The only discrepancy appears to be water, which, according to our data, should have a donor number of $\sim$33 instead of 18 as given by Gutmann. The linearity of the plot shows that the relative chemical shifts of ^{23}Na yield useful information on the solvating abilities of the solvents at least *vis à vis* the sodium ion.

Table I. Chemical Shifts of Sodium-23 Resonance in Different Solvents[a]

Solvent	$NaPh_4B$, Hz	NaI, Hz
Hexamethylphosphoramide	−41	−40.6
Pyridine	−20	−60.0
Water	0	0
Dimethyl sulfoxide	+37	
Methanol	+72	
Dimethylformamide	+83	+67
Acetonitrile	+127	+76
Tetrahydrofuran	+124	−100
Acetone	+136	+55
Ethylacetate	+147	
Nitromethane	+256	

[a] 0.5 *M* solutions.

A preliminary experiment was performed on the complexation of the sodium ion with the crown compound dicyclohexyl-18-crown-6,[3] which is known to form strong complexes with the alkali metal ions.[4] Equimolar amounts of the crown compound and of sodium tetraphenylborate were dissolved in nitromethane, and the search was made for the ^{23}Na resonance. However, no evidence for this resonance was obtained. Increasing amounts of sodium tetraphenylborate were added to the solution and a *very broad* peak appeared with a chemical shift equal to that of the tetraphenylborate in pure nitromethane. It is evident that the strong interaction between the crown compound and Na$^+$ ion broadens the resonance to such an extent that it is no longer visible under our experimental conditions.

Preliminary results were also obtained with ^{7}Li nuclear magnetic resonance. Only lithium perchlorate was used thus far. The results, however, do not indicate the same correlation with the donor number as for ^{23}Na chemical shifts. A possible explanation for this difference in behavior may be the fact that in the case of ^{23}Na the paramagnetic shielding term σ_p is $\sim$30 times larger than the diamagnetic term σ_d, and thus the former dominates the chemical shifts.[1] In the case of ^{7}Li, the values of the two terms are much closer, which may account for the variation in the chemical shifts. In general, our results agree with those of Akitt and Downs.[5]

It is seen from the above results that the use of nmr spectroscopy of the alkali nuclei makes a very important contribution to the elucidation of the structure of electrolyte solutions. This work is being continued.

Acknowledgment. The authors gratefully acknowledge the support of this work by the National Science Foundation. They are also indebted to Mr. A. W. Burkhardt of this laboratory for help with the instrumentation and to Dr. H. K. Frensdorff of Du Pont for the gift of dicyclohexyl-18-crown-6.

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(2) V. Gutmann, "Coordination Chemistry in Nonaqueous Solutions," Springer-Verlag, Vienna, 1968, and references therein.

(3) C. J. Pedersen, *J. Amer. Chem. Soc.*, **89**, 7017 (1967).

(4) C. J. Pedersen, *ibid.*, **92**, 386 (1970).

(5) J. W. Akitt and A. J. Downs, "Alkali Metals Symposium," The Chemical Society, London, 1967, p 199.

(6) NIH Predoctoral Fellow.

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Received May 22, 1970

The Dynamic Stereochemistry of Some π-Allylpalladium Compounds

Sir:

Isomerization reactions of π-allylpalladium complexes have been the subject of several recent mechanistic investigations.[1,2] We wish to present evidence which confirms the most recent mechanistic proposals and comment on the effect of substituents on the magnitude of the energy barriers.

The ambient temperature spectrum of di-μ-chloro-bis(*trihapto*(*syn*-1-isopropylallyl))dipalladium(II)[3] **(1)** is summarized in Table I. The diastereotopic methyl

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(1) J. W. Faller and M. E. Thomsen, *J. Amer. Chem. Soc.*, **91**, 6871 (1969).

(2) P. W. N. M. van Leeuwen and A. P. Praat, *Chem. Commun.*, 365 (1970).

(3) Using the nomenclature suggested by F. A. Cotton, *J. Amer. Chem. Soc.*, **90**, 6230 (1968). An alternative name is di-μ-chloro-bis-(*syn*-4-methylpent-1(3)-enyl)dipalladium(II).

Table I. Spectral Data for **1**[a]

τ values							J values, Hz				
H_2	H_{3s}	H_{1a}	H_{3a}	H_4	CH_{3a}	CH_{3b}	H_2H_{1a}	H_2H_{3a}	H_2H_{3s}	H_1H_4	H_4,CH_3
4.99 (sex)	6.32 (d)	6.42 (q)	7.48 (d)	8.12 (m)	8.938 (d)	8.962 (d)	11.5	11.5	6.5	5.0	6.5

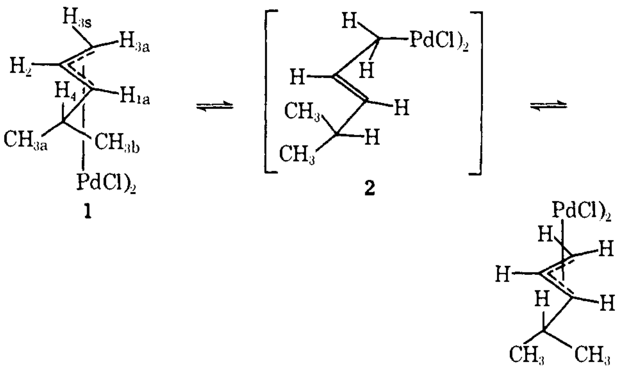
[a] Spectra were recorded for solutions in o-$C_6H_4Cl_2$ with 10% p-$C_6H_4Cl_2$ added as lock signal, at 100 MHz. Spectra at higher temperatures were recorded for samples sealed under N_2. Spectra in $CDCl_3$ and C_6D_6 gave similar J values but different τ values.

Table II. Spectral Data for **4**[a]

τ values							J values, Hz	
H_{3s}	H_{1a}	H_{3a}	H_4	$2\text{-}CH_3$	CH_{3a}	CH_{3b}	$H_{1a}H_4$	$H_4CH_{3a\text{ or }b}$
6.51 (s)	6.85 (d)	7.65 (s)	8.1 (m)	8.17 (s)	8.77 (d)	9.13 (d)	9.10	6.5

[a] Similar comments to those made in Table I are applicable.

groups in the prochiral isopropyl group are anisochronous[4] appearing as doublets at τ 8.938 and 8.962; $\Delta\nu = 2.4$ Hz for a spectrum in o-$C_6H_4Cl_2$. Assignment of syn stereochemistry comes from the two large (11.5 Hz) and one small (6.5 Hz) coupling constants of H_2. When spectra were recorded at higher temperatures the isopropyl doublets began to broaden above 50° and coalesced at 77°. Exchange rates for the collapse of the two isopropyl doublets to one doublet were calculated for spectra near coalescence using an adapted Saunders multi-site exchange program.[5] At 80° the exchange rate was 7.5 sec^{-1} giving $\Delta F^{\ddagger}_{80} = 19.4 \pm 0.3$ kcal/mol from the Eyring equation. In the same temperature region the signals due to the H_{3a} and H_{3s} protons began to broaden. The rate of the exchange process responsible for this broadening was calculated to be 6.3 sec^{-1} at 80° using the slow-exchange approximation for line broadening[6] giving $\Delta F^{\ddagger}_{80} = 19.5$ kcal/mol. On further heating the H_{3a} and H_{3s} signals continued to broaden and finally coalesced at 142 ± 2°. At this temperature the rate of exchange is 258 sec^{-1} as calculated by the usual coalescence method[7] (using $\Delta\nu = 116$ Hz) and $\Delta F^{\ddagger}_{142} = 19.7 \pm 0.3$ kcal/mol. At 142° the H_2 proton absorbed as a doublet of triplets with $J_{H_{1a}H_2} = 5.0$ Hz and $J_{H_2H_{3s}} = J_{H_2H_{3a}} = 9.0$ Hz. This latter value is the average of the two ambient temperature coupling constants. In contrast to the above changes the signal due to H_{1a} remained unchanged in the temperature range 25–148°.



In order to rationalize the above observations it is necessary to describe a process which allows the diastereotopic isopropyl methyl groups and the diastereotopic allylic protons H_{3a} and H_{3s} to become enantiotropic *at the same rate* and in which the bonding geometry of the allylic proton H_{1a} remains essentially unchanged. A process which meets these requirements must involve torsion around the C_2–C_3 bond, face exchange of the palladium atom, and essentially constant geometry of H_{1a} relative to H_2 and H_4. These requirements are clearly met by the intervention of a σ-bonded palladium system **2**, previously suggested by Vrieze, *et al.*,[8] either as an intermediate or transition state. Such a system possesses a symmetry plane bisecting both the angle between H_{3a} and H_{3s} and the angle between the diastereotopic methyl groups. Time-averaged over the equilibrium **1** ⇌ **3**, both pairs of protons become enantiotropic, and the signals coalesce. This work thus unambiguously confirms the most recent investigations in this field.[1,2]

Spectra of di-μ-chloro-bis(1,2,3-*trihapto*(*syn*-1-isopropyl-2-methylallyl))dipalladium(II) (**4**) (see Table II) have been reported previously.[9] This compound is the 2-methyl homolog of **1**, yet the anisochronous signals for the diastereotopic isopropyl methyl groups remained unchanged for spectra over the range +30 to +100°. However, when spectra were recorded for solutions in o-$C_6H_4Cl_2$ above 100° the two methyl doublets and the allylic protons H_{3a} and H_{3s} began to broaden. The isopropyl doublets had almost coalesced at 155° when extensive decomposition set in. The rate for the exchange process at 155° was calculated as 15 sec^{-1} from the methyl groups' spectra using the Saunders program and as 22 sec^{-1} from the allylic protons' signals using the slow exchange approximation. The Eyring equation gives $\Delta F^{\ddagger}_{155} = 22.9$ kcal/mol using the average value of the two rates. This dramatic increase in free energy of activation for the exchange processes in **4** over those in **1** can be attributed either to ground-state stabilization or transition-state destabilization effects of the methyl group. Further experiments are in progress which are designed to elucidate the origin of this large substituent effect.

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(4) See K. Mislow and M. Raban, *Top. Stereochem.*, **1**, 1 (1967), for terminology.

(5) M. Saunders, *Tetrahedron Lett.*, 1699 (1963). The program iterates the exchange rate to obtain the best least-squares fit with the experimental spectrum. Calculations were performed using the Queen's University ICL 1907 digital computer.

(6) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 1, Pergamon Press, Oxford, 1964, p 481; F. A. L. Anet, *J. Amer. Chem. Soc.*, **86**, 458 (1964).

(7) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, p 224.

(8) P. W. M. N. Van Leeuwen, K. Vrieze, and A. P. Praat, *J. Organometal. Chem.*, **20**, 219 (1968), and references therein.

(9) R. Huttel, H. Christ, and K. Hertzog, *Chem. Ber.*, **97**, 2710 (1964).

Acknowledgments. We thank the Ministry of Education, Northern Ireland, for a research grant (to C. W. A.) and Dr. W. B. Jennings for his helpful comments and assistance.

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Received April 24, 1970

Planar Tetracoordinate Carbon

Sir:

The tetracoordinate tetrahedral carbon has magnificently served biological systems for millions of years and our imaginations for but a century.[1] We here open the problem of stabilizing tetracoordinate planar carbon. It would seem too much to hope for a simple carbon compound to prefer a planar to a tetrahedral structure. Our more modest goal is to consider how to stabilize a planar geometry so that it could serve as a thermally accessible transition state for a classical racemization experiment.

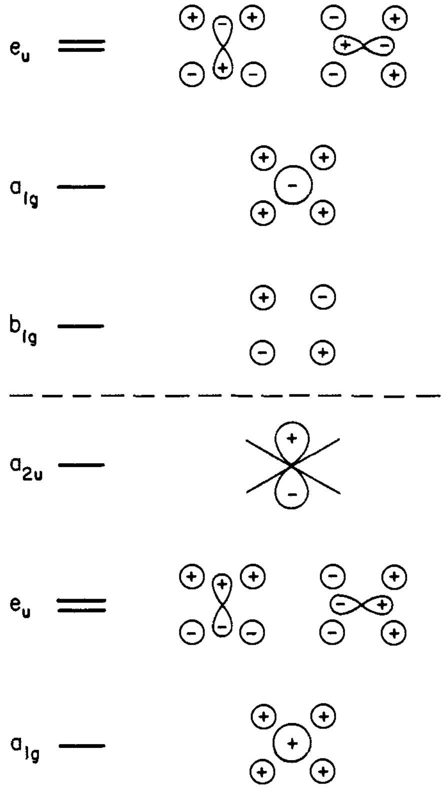


Figure 1. The molecular orbitals of planar methane. Levels below the dashed line are occupied. The representation of the e_u levels is of course not unique.

A rational procedure begins with an analysis of the electronic structure of planar methane. We form a normal set of sp^2 hybrids at the carbon. Two hybrids engage in normal two-electron two-center bonds with two hydrogens, using up two of the four carbon valence electrons. The third hybrid participates in a two-electron three-center bond[2] with the remaining two hydrogens. *This three-center bond utilizes only the hydrogen* electrons. The remaining two valence electrons of carbon are placed in the 2p orbital perpendicular to the molecular plane (**1**). Resonance among equivalent structures with different relative placement of three-center and two-center C–H bonds achieves equivalence of all hydrogens. Alternatively the molecular orbitals of planar CH_4 are shown in Figure 1.

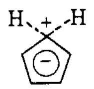
1

The following characteristics of a planar methane emerge from either picture. (1) All C–H bonds are weaker than in tetrahedral methane. (2) Since the three-center bonding uses only H electrons there is considerable electron transfer from H to C. (3) The planar carbon atom possesses a pure 2p lone pair perpendicular to the molecular plane. (4) The transformation of tetrahedral to planar methane is a symmetry-allowed process for either a twisting ($T_d \rightarrow D_2 \rightarrow D_{4h}$) or a squashing ($T_d \rightarrow D_{2d} \rightarrow D_{4h}$) pathway.

An extended Hückel (EH) calculation[3] makes tetrahedral CH_4 more stable than a square-planar geometry with identical bond lengths of 1.10 Å by 5.5 eV. A CNDO[4] computation yields 8.1 eV for the same quantity. An approximate *ab initio* calculation[5] produces a barrier of 10.8 eV. To reduce lifetimes for racemization from eons to the experimentally accessible scale the planar geometry must be stabilized or the tetrahedral destabilized. The electronic structure of planar CH_4 suggests the ways in which stabilization may be achieved.

Delocalization of the lone pair may be accomplished by attaching substituents to carbon which are good electron acceptors, as in $C(CN)_4$. The planar–tetrahedral energy difference, ΔE, is reduced to 3.4 eV.[6] Alternatively we may incorporate the lone pair as part of a $4n + 2\pi$ electron system, as in the planar geometry of cyclopentadiene, **2**. ΔE for **2** is 4.2 eV[7] and the planar geometry is best described as a σ cation of an aromatic anion, **3**. In a model benzenonium ion **4**, ΔE is reduced to 2.9 eV. Substitution of H by less electronegative groups lowers ΔE still further—in $C(BH_2)_4$ to 1.8 eV, in $C(SiH_3)_4$ to 2.9 eV. In the latter case 3d orbitals on Si were included; Si then acts as a σ donor and π ac-

2



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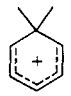

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[1] J. H. van't Hoff, "Voorstel tot uitbreiding der tegenwoordig in de scheikunde gebruikte strukuurformules in de ruimte," Utrecht, 1874; J. A. LeBel, *Bull. Soc. Chim. Fr.*, **22**, 337 (1874).

(2) W. N. Lipscomb "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963, p 27.

(3) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); **40**, 2474, 2480, 2745 (1963); *Tetrahedron*, **22**, 521, 539 (1966). A Slater exponent of 1.3 for hydrogen was used in the present work.

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(5) H. J. Monkhorst, *Chem. Commun.*, 1111 (1968). This calculation predicts approximately equal bond lengths in T_d and D_{4h} methane.

(6) This and all subsequent values of ΔE quoted are from extended Hückel calculations.

(7) The actual value could be lower. We did not optimize the position of the sterically hindered hydrogens in the planar geometry.