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Methoxy Group Rotation in Alkylanisyl Carbenium Ions as a Probe of the Relative Charge Delocalization Abilities of Phenyl, Cyclopropyl, and Methyl Groups

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Contribution from the Laboratoire de Physicochimie des Hydrocarbures, Institut de Chimie, 67000 Strasbourg, France, and the Institute of Chemistry, University of Uppsala, S-751 21 Uppsala, Sweden. *Received April 14, 1980*

Abstract: The torsional barrier around the phenyl–methoxy C–O bond in a series of *p*-anisyl-R,R′C$^+$ carbenium ions, with R and/or R′ = H, Me, c-Pr, Ph, has been studied by means of low-temperature carbon-13 NMR spectroscopy, using either line-shape analysis or ^{13}C spin saturation transfer techniques. The free energy of activation of the barriers has been used to estimate the relative electron-releasing ability of the methyl, phenyl, and cyclopropyl groups. The order of charge delocalization ability was found to be c-Pr > Ph > Me both in secondary and tertiary cations.

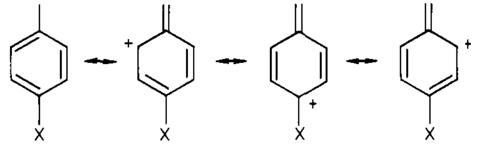
Since the early spectroscopic work by Deno[2] underlining the intense conjugation in cyclopropylcarbenium ions, many solvolytic studies have been devoted to estimate the relative electron-releasing power of the methyl, phenyl, and cyclopropyl groups toward an adjacent electron-deficient center. Since the solvolytic studies are only based upon energy differences between the covalent precursor and the carbenium like transition state or intermediate, great hope was raised when Olah[3] and his group developed a method which allows the direct spectroscopic observation of the carbocations under stable ion conditions.

Since then, several authors have extensively used mainly chemical shifts obtained by NMR spectroscopy as a tool for investigating the charge delocalization in methyl, phenyl and cyclopropyl substituted stable carbenium ions. Olah and coworkers[4] assumed early that the ^{13}C chemical shift of the carbenium center itself was the best probe and on the basis of their results concluded that no simple uniform sequence of charge-delocalizing ability by neighboring groups such as phenyl and cyclopropyl could be predicted in structurally widely different ions. On the other hand, it was shown by several groups[5,6] that when the chemical shifts of nuclei (like ^{1}H, ^{13}C, and ^{19}F) not directly bearing the positive charge were used as probes, the results showed good agreement with the data obtained from solvolytic studies[7] and equilibrium rate measurements.[8] These results indicate that the relative magnitude of charge delocalization ability increases from alkyl to phenyl to cyclopropyl. However a theoretical study based on combination of ab initio calculation and ion cyclotron studies[9] pointed out that the phenyl group is superior to cyclopropyl in delocalizing the charge in secondary cations but that the reverse was true for tertiary ions.

On the basis of our previous work on measurements of barriers in aromatic carbonyl compounds[10] and related superacid acidity measurements,[11] we here suggest an alternative method for the estimation of the relative electron-releasing properties of methyl, phenyl, and cyclopropyl groups adjacent to a carbocationic center. This method uses the torsional barrier around the phenyl–oxygen bond in a series of *p*-anisyl carbenium ions.

Results and Discussion

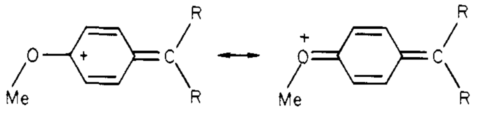
The existence of the barrier to rotation around the phenyl carbenium carbon bond has been recognized very early from magnetic nonequivalence of the ortho and meta nuclei at low temperature in ^{1}H NMR spectra.[12] The origin of this torsional barrier is the π-bond formation between the aromatic π system and the vacant orbital of the adjacent carbon (formulas Ia–d).



Ia Ib Ic Id

The height of this barrier in the cyclopropylmethylphenyl carbenium ion ($\Delta G^{\ddagger}_{171\mathrm{K}}$ = 36.0 kJ/mol) has recently been measured by Sorensen.[13]

In the *p*-anisyldialkyl carbenium ions (X = OCH$_3$), the methoxy group helps to delocalize the positive charge (II) with an accompanying increase of the barrier to rotation around the phenyl-C$^+$ carbon bond. This also results in partial double-bond character



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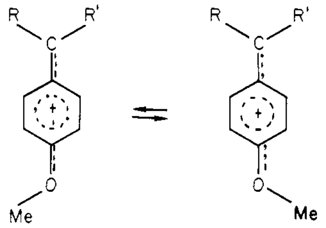

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Table I. Activation Parameters[a] for the Barriers to Rotation around the C-O Bond in Ions 1-9

ion	1	2	3	4	5	6	7	8	9
R	H	H	H	H	Me	Me	Me	c-Pr	
R'	H	Me	Ph	c-Pr	Me	Ph	c-Pr	c-Pr	anisole/H$^+$
temp, °C	−63.5 ± 1	−83.6 ± 1	−109.0 ± 1	−122.5 ± 1	−103.1 ± 0.4	−121.7 ± 1	−132.7 ± 1	−141.4 ± 1	−50.0 ± 1
pop.[b]	0.5	0.61	0.63	0.67	0.5	0.63	0.65	0.5	0.5
T_1, s	0.66 ± 0.2	0.47 ± 0.1	0.11 ± 0.01	0.006 ± 0.01	0.16 ± 0.01				1.54 ± 0.12
$\Delta G_{AB}^{\ddagger}$ [c]	50.4 ± 2.3	44.4 ± 1.5	37.2 ± 2.3	33.7 ± 2.6	38.2 ± 0.9	29.8 ± 0.8[d]	25.5 ± 1.2[e]	<24[f]	54.4 ± 1.7[c]
$\Delta G_{BA}^{\ddagger}$ [c]	50.4 ± 2.3	43.7 ± 1.5	36.4 ± 2.3	32.8 ± 2.6	38.2 ± 0.9	28.9 ± 0.8[d]	24.7 ± 1.2[e]	<24	54.4 ± 1.7[c]
$\Delta H_{AB}^{\ddagger}$ [g]			34.4 ± 0.8		29.0 ± 6.9	25.3 ± 8.8			
$\Delta S_{AB}^{\ddagger}$ [g]			−13.9 ± 4.6		−22.1 ± 9.2	−30.1 ± 5.7			
$\Delta H_{AB}^{\ddagger}$ [h]			35.9 ± 1.0		31.4 ± 1.7				
$\Delta S_{AB}^{\ddagger}$ [h]			−6.1 ± 5.4		−9.4 ± 9.6				

[a] $\Delta H^{\ddagger}$ and $\Delta G^{\ddagger}$ in kJ/mol, $\Delta S^{\ddagger}$ in J/(mol K). The errors on $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are statistical errors from the least-squares treatment. [b] Most populated conformer. [c] Obtained from spin-transfer saturation except for ions 6-8. [d] From complete line-shape analysis. [e] Line-shape analysis of the meta carbons only. [f] From coalescence. [g] Line-shape analysis only. [h] Both methods.

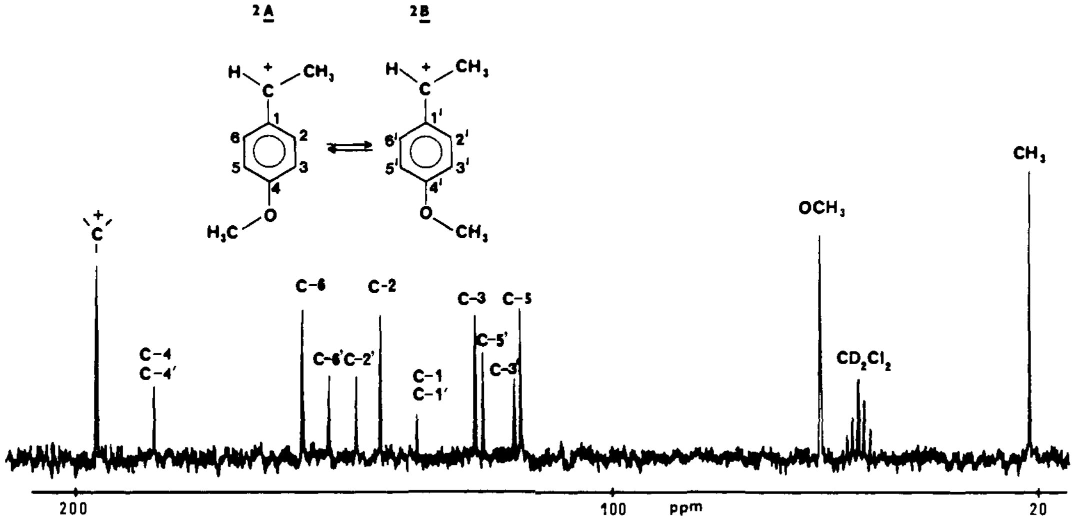

Figure 1. ^{13}C NMR spectrum of cation **2** at −83.6 °C.

of the phenyl oxygen bond which is noticeable by the coexistence at sufficiently low temperature of two the planar conformers IIIA and IIIB in the ^{13}C NMR spectra.

When R and R' are not identical, four distinct resonance lines originating from the ortho and meta carbons may be observed. It is interesting to note that the molar A/B ratio generally is different from unity despite the long distance between the methoxy group and the carbenium carbon substituents (Figure 1). The exchange rate of the two conformers IIIA $\rightleftharpoons$ IIIB by the rotational process around the phenyl–oxygen bond has been measured by transfer of ^{13}C spin saturation for ions **1–5**, by complete line-shape analysis for ions **6** and **7**, and by both methods for ions **3** and **4** (Figure 2). Only an upper limit of the barrier in ion **8** could be estimated. Additionally we have also measured the torsional barrier in C-protonated anisole **9** by transfer of ^{13}C spin saturation and the $\Delta G^{\ddagger}$ value agrees well with the early estimation of Brouwer[16] (on the basis of coalescence temperature). The enthalpy and entropy of the exchange processes have been estimated for ions **3**, **4**, and **6**. For ions **3** and **4** the temperature range used in the rate measurements was extended, allowing the application of the two complementary techniques. The entropy of activation was found to be close to zero as expected.[10] All data are gathered in Table I.

The Torsional Barrier around the Phenyl–Oxygen Bond. When the methoxy group is not involved in a formal charge delocalization, it has been shown in many molecules that the barrier around the C–O bond is extremely low.[21] But the participation of the oxygen lone pair in delocalizing a positive charge of an adjacent carbon results in a high barrier to rotation which has already been estimated for several cationic systems (Table II). The available data show that the barrier which is as high as 65 kJ/mol in dialkylmethoxy carbenium ions[20] is much lower when the positive charge can also be delocalized on other substituents of the carbenium ion center. In the *p*-anisyl cation series (Table I) the torsional barrier of the methoxy group is despite it's remoteness from the trivalent cationic center a very sensitive probe of the electron-releasing capability of the carbenium carbon substituents.

Starting from *p*-methoxybenzyl cation **1** (R = R' = H) in which the torsional barrier is 50 kJ/mol, the substitution of H by CH_3 (ion **2**) decreases the barrier to rotation by 6 kJ/mol. Substituting the methyl group by a phenyl ring (ion **3**) lowers the barrier by an additional 7 kJ/mol. Finally the substitution of the phenyl by a cyclopropyl group (ion **4**) further decreases the barrier by 4 kJ/mol. These results show clearly that in the secondary cations the electron-releasing ability increases upon going from methyl to phenyl to cyclopropyl.

Furthermore the results with the 1-(*p*-anisyl)ethyl cation series **2**, **5**, **6**, **7**, in which the hydrogen is replaced respectively by a methyl, phenyl, and cyclopropyl group, show that the barrier of **2** (44.4 kJ/mol) is lowered by 6, 14.6, and 19 kJ/mol respectively. This result again indicates that the electron-releasing ability is increasing from methyl to phenyl to cyclopropyl. Comparison of our results with cations **4** and **6** indicates that a cyclopropyl group has approximately as large electron-releasing power as phenyl and methyl taken together. This conclusion is also supported by our

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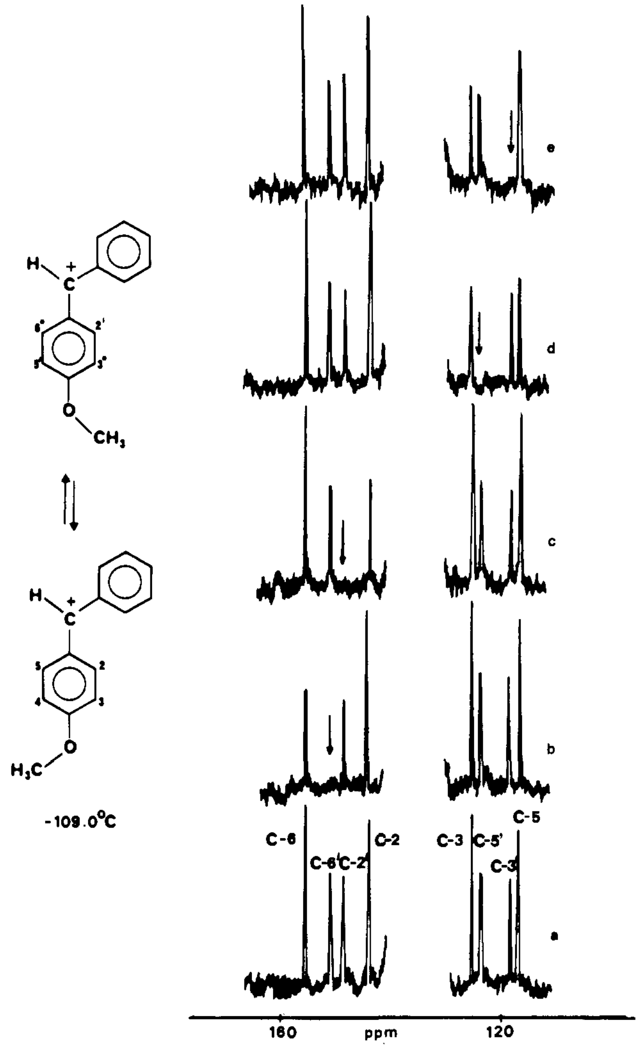
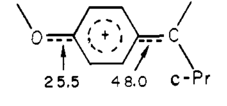


Figure 2. ^{13}C NMR spectra of cation 3 at −109 °C (only the ortho and meta carbon signals): (a) without saturation of any of the carbon atom; (b) with saturation of carbon C'$_6$; (c) with spectrum of carbon C'$_2$; (d) with saturation of carbon C'$_3$; (e) with saturation of carbon C'$_5$.

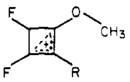
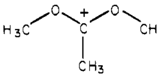
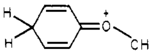
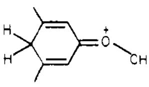
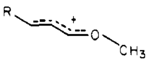
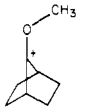
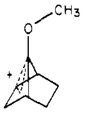
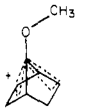
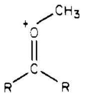
results with the dicyclopropyl-*p*-anisyl cation which is shown to have the lowest of our measured barriers, i.e., $\Delta G^{\ddagger} < 24$ kJ/mol.

An interesting point is the comparison of the barriers around the phenyl–oxygen bond with the barrier around the phenyl–carbenium carbon bond. In our experiments we notice from the unsymmetrical ions **2**–**4**, **6**, and **7** that the rotation around the phenyl–carbon bond is frozen-out which implies a much higher barrier for this process. Recently Sorensen measured such a barrier in the phenyl-methyl-cyclopropyl carbenium ion ($\Delta G^{\ddagger}$ = 36.0 kJ/mol).[13] Based on our work with aromatic hydroxy carbenium ions,[10] we estimate that a *p*-methoxy substituent will increase this barrier by at least 12 kJ/mol. This yields for ion **7** $\Delta G^{\ddagger}_{\text{C–C}^{+}(\text{rot.})} \simeq 48.0$ kJ mol^{-1} which may be compared with $\Delta G^{\ddagger}_{\text{C–O}(\text{rot.})} = 25.5$ kJ mol^{-1} from present work.



Correlating ^{13}C Chemical Shifts with Charge Densities. The temptation to estimate the charge density at the trivalent carbenium carbon directly from the ^{13}C chemical shift has been strong since Olah and co-workers showed that (i) in a large number of aromatic systems the calculated charge density could be linearly related to the ^{13}C chemical shifts[22,23] and (ii) in a given series of para-substituted phenyl carbenium cations the ^{13}C chemical shift of the carbenium carbon correlates well with Brown's σ_p^+ constants.[12] However the same authors have later shown that the carbenium carbon chemical shift cannot be used to estimate the charge delocalization when the substitution pattern on this carbon is not kept constant. This is easily understandable as ^{13}C chemical shifts of a given nucleus in neutral molecules are very dependent on the substituents (α effect). For this reason attempts using the ^{13}C chemical shift of the trivalent carbon itself end up with results difficult to rationalize in terms of charge density only.[4c] It seems however established that the para carbon chemical shift is a reliable indicator of the charge density at the carbenium carbon and the best probe to measure the electron demand from this carbon bond to a phenyl ring.

Table II. Activation Energy (kJ/mol) of the Methoxy Group Rotation in Various Cationic Systems

	R	$\Delta G^{\ddagger}$	$\Delta H^{\ddagger}$	ref
	F	68.6		14
	Cl	66.5		
	OCH$_3$	65.7		
		61.4^a		15
		52.9^a		16
		47.6^a		16
	H	85.6^a		17
	CH$_3$	78.0^a		
		77.0		18
		61.5		18
		49.0		18
	H		49.8 ± 5	19
	CH$_3$	>65		20

^{a} Calculated from data given in references.

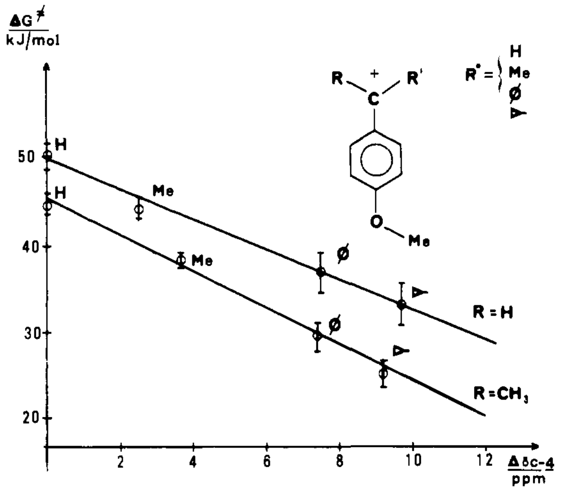


Figure 3. Correlation of the free energy of activation vs. $\Delta\delta C_4$ in both series of secondary and tertiary cations.

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Table III. ^{13}C Chemical Shifts[a] for Ions 1-9

ion	temp, °C	C-1	C-2	C-3	C-4	C-5	C-6	C$^+$	OMe	additional
9	−50	40.3	168.8	127.0	192.0	121.1	175.4		62.6	
1	−63.5	139.7	151.4	125.8	188.1	118.7	156.6	168.6	61.5	
2A	−83.6	136.2	143.1	125.4	185.6	116.9	157.7	196.2	60.9	22.2 (CH_3)
2B	−83.6	136.2	147.6	118.3	185.6	124.0	152.9	196.2	60.9	22.2 (CH_3)
3A	−109.3	134.7	143.6	125.1	180.6	116.1	155.4	182.7	59.3	132.1 (C'_1), 138.1 (C'_2)
3B	−109.3	134.7	148.0	117.4	180.6	123.4	150.8	182.7	59.3	131.0 (C'_3), 140.5 (C'_4)
4A	−122.5	139.5	139.9	123.0	178.4	113.9	151.5	208.6	58.5	31.1 (CH)
4B	−122.5	139.5	143.6	115.8	178.4	121.1	147.6	208.6	58.5	29.9 (CH_2)
5	−101.7	133.3	143.1	122.8	181.9	115.5	147.2	218.9	59.5	28.5 (CH_3)
6A	−132.7	133.4	142.0	122.4	178.2	114.3	151.3	207.7	58.7	27.2 (CH_3), 139.2 (C'_1), 135.2 (C'_2)
6B	−132.7	133.4	145.5	115.2	178.2	121.5	147.1	207.7	58.7	129.5 (C'_3), 138.4 (C'_4)
7A	−137.4	133.1	141.0[b]	121.0	176.4	113.8	139.9[b]	226.9	58.1	19.5 (CH_3), 33.2 (CH)
7B	−137.4	133.1	141.0[b]	113.8	176.4	121.0	139.9[b]	226.9	58.1	30.1 (CH_2)
8	−141.4	131.5	139.4	115.3	166.4	115.3	131.5	244.4	57.5	35.1 (CH), 30.9 (CH_2)

[a] In ppm from Me_4Si using CD_2Cl_2 as an internal standard (δ 53.8) for all ions except 1 (δ (OCH_3) 61.5 taken from ref 4a). [b] Not completely decoalesced.

The ^{13}C chemical shifts for all ions except **7** and **8** have been measured at temperatures well below the coalescence temperature, and the ortho and meta carbon signals could be observed decoalesced. Our values (Table III) are in fair agreement with the data obtained at higher temperatures by several authors.[24]

If we consider the series **1**–**4**, we notice an upfield shift of the C-4 carbon, indicating a decrease in electron demand when the substituent is changed from proton to methyl to phenyl to cyclopropyl (−2.5, −7.5, −9.7 ppm).

In the series **2**, **5**–**7** we notice again that successive replacement of H by a methyl, phenyl, and cyclopropyl group induces an ^{13}C upfield shift of −3.7, −7.4, and −9.2 ppm, respectively, for the C-4 carbon. These results have been plotted in Figure 3 and show that the above stated order is valid as well for secondary or for tertiary ions.

Conclusion

^{13}C NMR spectroscopic studies of a large series of *p*-anisyl carbenium ions show that the electron-releasing ability from a substituent toward the cationic center increases from methyl to phenyl to cyclopropyl in the way predicted by solvolytic data. The free energy of activation of the torsional barrier around the phenyl oxygen bond has been used as an effective probe for charge delocalization and shown to correlate closely with the ^{13}C chemical shifts of the methoxy group and the C(para) carbon. The ^{13}C chemical shift of the carbenium carbon should not be used to evaluate the charge delocalization as it is difficult to estimate the shift correcting factor due to the substituents on this carbon. We must keep in mind however in interpreting our data that the above sequence of electron releasing ability has been obtained with *p*-anisyl-substituted carbenium ions, in which the electron demand is inherently quite low. Nevertheless our results are in good agreement with those recently published by Arnett[25] which show on a very different basis (heat of formation measurements) that the relative stabilities of carbenium ions in superacid media agree with those obtained from solvolysis rate constants.

Experimental Section

Precursor Alcohols. Precursor alcohols either were commercially available (**1**, **2**, **6**) or were prepared by the standard Grignard reactions of the corresponding ketones. 1-(*p*-Anisyl)ethanol and α-cyclopropyl-*p*-methoxybenzyl alcohol were obtained by reduction of the corresponding ketones with aluminum propoxide.[26] In the case of α-methyl-α-phenyl-*p*-methoxybenzyl alcohol and α-cyclopropyl-α-methyl-*p*-methoxybenzyl alcohol we obtained, after the Grignard reactions, the dehydration product.

Preparation of Ions. The experimental technique for generation of the cations has been described earlier.[27] A 30–60-mg sample of precursor was dissolved in ca. 100 mg of CD_2Cl_2 and added at low temperature with efficient mixing to 0.4 mL of a solution of SbF_5 (ion **2**) of $HFSO_3$ in SO_2ClF, SO_2F_2, and $CFCl_2H$. Different acid mixtures were used: HSO_3F/SO_2ClF (1:1, v/v) for ion **9**, $SbF_5/SO_2ClF/SO_2F_2$ (1:1.3:1.3, v/v/v) for ion **1**, $HSO_3F/SO_2ClF/SO_2F_2$ (1:3:2, v/v/v) for **2** and **3**, HSO_3F/SO_2ClF (1:7, v/v) for ion **5**, and HSO_3F, SO_2ClF, SO_2F_2, and CF_2ClH (1:2:3:1, v/v/v/v) for ions **4**, **6**, **7**, and **8**. In all cases, except for the *p*-methoxybenzyl cation (**1**), the solutions obtained after vigorous stirring were clear and almost transparent, with a color ranging from pale yellow to dark red. For ion 1, the mixture obtained after mixing was darlky red-brown and not transparent and some precipitate got caught on the stirring rod. The spectrum accordingly showed poorer S/N than those of the other ion preparations. Because of this, only carbons 3 and 5 were used in the quantitative treatment of the spin-transfer experiments. Cation **2** showed after 6 or 7 h at −85 °C substantial degradation and the solutions became red-brown. The other cations are fairly stable at temperatures below −80 °C.

^{13}C NMR Spectra and Spin-Transfer Saturation Experiments. The ^{13}C NMR spectra were obtained with a JEOL FX 100 pulse spectrometer equipped with a 5-mm variable-temperature ^{1}H/^{13}C dual probe, external Li lock, quadrature phase detection, and a multiirradiation unit.

During the multiple irradiation experiments the multiirradiation unit supplied the noise modulated ^{1}H irradiation frequency, while the ^{13}C irradiation frequency was fed through the homonuclear gated decoupling unit of the instrument. In the transfer of spin saturation spectra a spectral width of 5–6 kHz, 8192 data points, was used with a pulse flip angle of 90° and pulse repetition time $>5T_1$.

The measurements of the spin–lattice relaxation times (T_1) have been made with the progressive saturation method using the pulse sequence (π, 90°) for ions **1** and **9**, while the inversion recovery method with the pulse sequence (180°, π, 90°) was applied to ions **2**–**5**. These methods could be applied since the spin–lattice relaxation times of the exchanging carbon are not significantly different. This conclusion is based on the fact that the intensity decrease of the bands from the exchanging carbon is independent of which carbon was saturated. The T_1 measurement sequences were analyzed off line though a nonlinear least-squares fitting procedure.[28]

The spin-transfer saturation method has been discussed earlier,[29] and the rate constant k_A was calculated by using eq 1 where T_{1A} is the

$$k_A = \frac{M_z^A(0) - M_z^A(\infty)}{M_z^A(\infty)} \frac{1}{T_{1A}} \tag{1}$$

spin-lattice relaxation time at site A, and $M_z^A(0)$ and $M_z^A(\infty)$ are the magnetizations (i.e., intensities) at site A in the absence and presence of irradiation at site B, respectively.

In the spin-transfer experiments of ions **2**–**5** and **9** measurements were made with saturation of each carbon 2, 3, 5, and 6 of the lowest populated conformer and carbon of the others. Only for ion **2** have carbons 2 and 6 of the most populated conformer been irradiated. As far as ion **1** is concerned only one measurement was performed: observation of carbon 5 while carbon 3 was saturated.

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Complete Line-Shape Analysis. Complete line-shape analysis was performed on ions **3**, **4**, and **6**–**8**.

The experimental spectra, obtained at (at least) ten different temperatures, were simulated with the program DNMR$_2$.[30] Ortho and meta carbon exchange were treated separately as a two spin exchange between two different populated sites. The population dependence on temperature was obtained from spectra below the coalescence and extrapolated for higher temperatures. The chemical shifts are found to be independent of the temperature. The transverse relaxation time T_2 was obtained in the coalescence region by monitoring the line width of a nonexchanging carbon. All calculations were performed on the Univac 1110 system of the Laboratoire de Calcul de Strasbourgh-Cronenbourg, France.

Temperature Measurements. The temperature was measured before and after each spin-transfer experiment by use of a chemical shift thermometer (CH_3OH in a mixture of $CHCl_2F$–$CHClF_2$, 1:1, v/v).[27a,b]

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Unusual M–C–H Angles, C–H Bond Activation, and α-Hydrogen Abstraction in Transition-Metal Carbene Complexes

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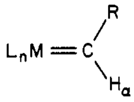
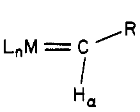
Abstract: Alkylidene complexes of electron-deficient transition metals display an interesting structural deformation in which the carbene appears to pivot in place while the C_α–H bond weakens. A molecular orbital analysis of these carbene complexes traces the deformation to an intramolecular electrophilic interaction of acceptor orbitals of the metal with the carbene lone pair. Bulky substituents on the metal and carbene protect the metal center from intermolecular reactions and control the extent of carbene pivoting. While a secondary interaction weakens the C–H_α bond and attracts the α-hydrogen to the metal, full transfer of hydride to the metal is a forbidden reaction, at least for a five-coordinate, 14-electron complex. The metal–hydrogen bonding interaction guides the hydride to a neighboring alkyl group, facilitating an α-elimination mode characteristic of the reactions of these compounds. The complexed carbene centers are unusually electron-rich, nucleophilic, by comparison with 18-electron d^6 stabilized carbene complexes. This is a consequence of an extremely effective Ta–C overlap.

It seems that nature has dealt us extremes in the interaction of transition-metal centers with organic ligands. Bonds may be dismantled completely, as in oxidative additions and kindred reactions. At the other end of the spectrum lies the uninteresting phenomenon of no interaction at all. The common consequence of chemical coordination is structural change, albeit in moderation. Thus CC bonds stretch and CR_2 or CR groups bend back, as in coordinated ethylenes and acetylenes. Bond alternation may be equalized, as in dienes. Substituents bend toward or away from the metal, as in cyclopolyenes. But there is no precedent for the remarkable structural change that occurs in the electron-deficient alkylidene complexes recently synthesized by Schrock and coworkers.[2,3] These have the general composition $L_nM(CHR)$. However, their geometry differs substantially from what might have been expected for a classical carbene complex, **1**. The carbene ligand appears to pivot in place (**2**) so that remarkably small M–C–H angles, down to 78°, and correspondingly large M–C–R angles, up to 170°, are seen. The analysis of this deformation is the subject of this paper.



1



2

The geometrical anomaly is only one of several unusual electronic and chemical properties of these alkylidene complexes of Ta, Nb, and W. They appear to be formed in α-elimination reactions of the type given by eq 1.

$$L_nM\begin{matrix}\diagup CH_2R\\ \diagdown R'\end{matrix} \longrightarrow L_nM-CHR + R'H \qquad (1)$$

The Schrock alkylidene complexes are nucleophilic rather than electrophilic.[2] The contrast with the heteroatom-substituted carbene complexes of the Fischer type[4] is sharp—it seems strange that a carbene coordinated to an electron-poor metal atom should be more electron-rich than one bound to an 18-electron d^6 center.

The Structural Background

Nine structures of the Schrock carbenes are at hand,[5] two of these neutron diffraction structures which are a necessity for

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