Singlet−Triplet Splittings and 1,2-Hydrogen Shift Barriers for Methylphenylborenide, Methylphenylcarbene, and Methylphenylnitrenium in the Gas Phase and Solution. What a Difference a Charge Makes

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Abstract: In the isoelectronic series methylphenylborenide, methylphenylcarbene, and methylphenylnitrenium, fundamental differences are predicted for singlet state geometries, singlet−triplet state splittings, barriers to singlet 1,2-hydrogen migration, and sensitivity of 1,2-hydrogen migration to solvent effects in *n*-heptane and acetonitrile. We conclude that isoelectronic analogies are dangerous for systems having different formal charges, and that the interaction of the divalent center with a conjugating substituent is very sensitive to the electron donating or withdrawing nature (and power) of the hypovalent atom. Solvent effects on the singlet−triplet splitting result from static polarity differences whereas the solvent effects on 1,2-hydrogen migration result primarily from polarizability differences. For the experimentally characterized carbene case, extensive comparison of calculated and measured results is provided.

Introduction

The wide occurrence of carbenes as reactive intermediates in many organic reactions[1−4] has made them the subject of extensive study, which has centered primarily on two aspects of their chemistry, namely multiplet energy splittings[5] (particularly the separation between the lowest energy singlet and triplet states) and reactivity. The parent carbene, CH_2, has a triplet ground state lying 9 kcal/mol below the lowest-energy singlet.[6,7] Experiment and well converged quantum mechanical studies indicate that alkyl and aromatic substitution preferentially stabilize the singlet state, with a stabilization of roughly 5 kcal/mol per methyl or phenyl substituent.[8−20] In the area of carbene reactivity, unimolecular rearrangements, particularly of singlet state carbenes, have been a focus of attention, in part because low-temperature matrix isolation techniques have permitted the chemistry of isolated carbenes to be followed in great detail.[4] One common mode of rearrangement available to carbenes having hydrogen atoms attached to their substituents is a 1,2-hydrogen migration (thereby creating a double bond between these two positions), which is very exothermic.[1−4,10,11,21−40] 1,2-Alkyl shifts are also well known, as are carbene insertions into more distantly located bonds, bimolecular carbene insertions, and carbene additions to double bonds.[1−4,28,40−43]

Nitrenium ions are isoelectronic with carbenes and are biologically implicated in carcinogenesis when substituted with

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aromatic groups.[44−47] In terms of physical characterization, they have received less study than their carbene cousins, at least in part because cations are more difficult to generate and cleanly characterize. The parent nitrenium, NH_2^+, has a triplet ground state lying 30 kcal/mol below the lowest-energy singlet.[48] Well-converged quantum mechanical studies indicate that alkyl and aromatic substitution strongly stabilize the singlet state compared to the triplet, with stabilizations of roughly 20 and 50 kcal/mol for a methyl and phenyl substituent, respectively.[13,49−52] The large differences in the magnitudes of substituent effects for carbenes vs nitrenium ions have been ascribed by two of us to the significantly different electronegativities of C and N^+ and the resulting differences in (hyper)conjugative interactions—indeed, the singlet phenylnitrenium may be more accurately described as an imino-substituted cyclohexadienyl cation.[13] The unimolecular reactivity of nitrenium ions has been described for a number of systems.[53−66] One difference between carbenes and nitrenium ions, however, is that it is experimentally difficult to characterize 1,2-hydrogen migration in alkyl-substituted nitrenium ions because the product iminium ion can also derive from a simple C-deprotonation/N-reprotonation. The exchangeable nature of the acidic iminium proton does not allow these alternative pathways to be readily distinguished.[67]

The isoelectronic analog of a carbene bearing a negative charge is a borenide anion, e.g., BH_2^-. The experimental observation of a borenide anion has not been established unequivocally.[68,69] Multireference configuration interaction calculations predict the parent system to be a bound anion for both the singlet and triplet states, with the two states being very nearly degenerate.[50]

The purpose of this article is to characterize how the charge

on the divalent atom affects reactivity by calculating barrier heights to 1,2-hydrogen migration (in the gas phase and in *n*-heptane and acetonitrile solutions) for the singlet states of methylphenylborenide (**1**−), methylphenylcarbene (**2**), and methylphenylnitrenium (**3**+). We also predict splittings between the singlet and triplet states of these molecules.

Computational Methods

Calculations were carried out with density functional theory (DFT). All geometries were optimized by using the gradient-corrected functionals of Becke[70] for exchange and of Perdew and Wang[71] for correlation with the cc-pVDZ basis set.[72] Results in analogous systems suggest that there is little quantitative sensitivity to the choice of correlation functional, although the use of gradient-corrected exchange is important.[13,51,73,74] Analytic frequency calculations were carried out to verify the nature of all stationary points and to calculate zero-point vibrational energies (for the singlet−triplet splittings) and thermal contributions to the enthalpy (for the hydrogen shift activation enthalpies and reaction exothermicities). For **1**−, single-point calculations were performed with use of the augmented aug-cc-pVDZ basis set.[72] Previous work[13,18−20,40,50,51,73−76] has demonstrated that such levels of theory predict state splittings and rearrangement barrier heights within about 2 kcal/mol as compared to either experiment or better-converged quantum mechanical calculations for systems analogous to those studied here.

Solvation effects in *n*-heptane and acetonitrile were accounted for by using the Austin Model 1[77,78] Solvation Model 5.4[79−81] (SM5.4/AM1). Polarization free energies for the gas-phase electronic structures (NOPOL energies) were calculated by employing atomic partial charges fitted[82] to the BPW91/cc-pVDZ (aug-cc-pVDZ for **1**−) electrostatic potentials (ESP charges). The SM5.4/AM1 model was extended to boron by assigning that atom a Coulomb radius of 1.98 Å and a total atomic surface tension of zero. For **2** and **3**+, the NOPOL energies calculated from BPW91/cc-pVDZ ESP charges agree very closely with those from the CM1A charge model[83] for which SM5.4/AM1 was parametrized; this confirms that it is reasonable to use these charges in general. The energetic consequences of solute relaxation (i.e., changes in the geometry and electronic structure) with respect to the surrounding solvent were evaluated as the differences between AM1 structures and wave functions for the gas phase and SM5.4/AM1 structures and wave functions in solution. Since CM1A is not parametrized for boron, such calculations were not undertaken for **1**−.

Density functional calculations were carried out with the Gaussian 94 program suite.[84] AM1 and SM5.4/AM1 calculations were carried out with a locally modified version of AMSOL version 6.1.1.[85]

Results and Discussion

Structures. Figure 1 illustrates the geometries of the singlet (**S**) and triplet (**T**) minima and the transition states (‡) for 1,2-hydrogen migration. The geometries of the triplets show a large bond angle at the divalent center and a plane of symmetry containing all of the heavy atoms, as expected by analogy to

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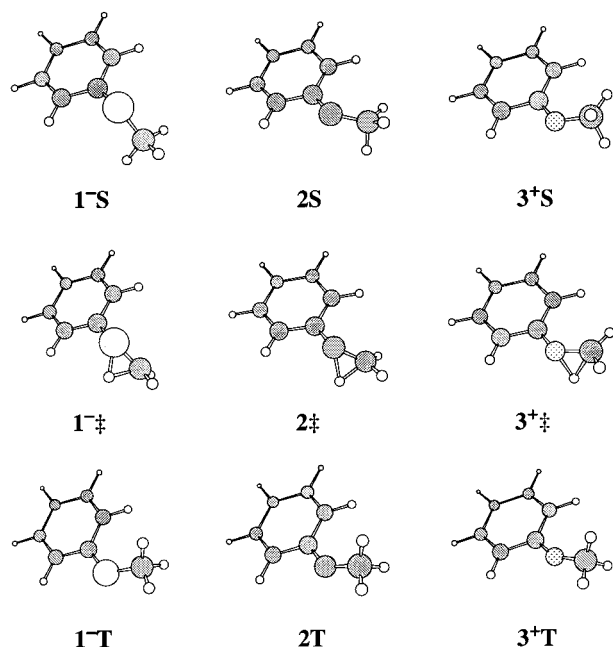
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Figure 1. BPW91/cc-pVDZ structures for relevant stationary points of 1^-, **2**, and 3^+.

Table 1. Calculated S−T Splittings and 1,2-Hydrogen Migration Barriers (kcal/mol) in the Gas Phase and Solution

	1^-	**2**	3^+
S−T gap $(\Delta H_0)^a$			
gas phase[b]	−4.1	1.8	−14.1
n-heptane[c]			
NOPOL[d]	−6.4	1.1	−14.4
relaxed[e]		1.0	−14.5
acetonitrile[c]			
NOPOL[d]	−8.7	0.3	−14.6
relaxed[e]		0.0	−14.5
1,2-shift barrier $(\Delta H_{298})^f$			
gas phase[b]	10.5	5.4	21.5
n-heptane[c]			
NOPOL[d,e]	10.4	5.5	20.4
relaxed[f]		5.1	19.4
acetonitrile[c]			
NOPOL[d,e]	9.1	5.5	18.8
relaxed[f]		4.4	13.0

[a] Includes zero-point contributions from DFT frequencies. A positive value implies the triplet is lower in energy than the singlet. [b] BPW91/aug-cc-pVDZ//BPW91/cc-pVDZ level for 1^-, BPW91/cc-pVDZ level for **2** and 3^+. [c] Gas-phase values modified by appropriate differential SM5.4/AM1 free energies of solvation. [d] Using DFT geometries and DFT ESP charges. [e] Using SM5.4/AM1 condensed-phase geometries and wave functions relative to AM1 gas-phase geometries and wave functions to gauge the relaxation effect, which is then added to the DFT-based NOPOL result. [f] Includes thermal contributions from DFT frequencies.

other carbenes and nitrenium ions.[13,18−20,40,50,51,73−76] The singlet geometries, on the other hand, reflect the significantly different electronegativities of the divalent centers. In 3^+**S**, the electropositive N^+ center is able to take maximum advantage of conjugation with the phenyl substituent acting as a π donor,[13,52,66,86] and hence it maintains the same plane of symmetry found in the triplets. Carbene **2**, on the other hand, rotates the methyl group out of plane (CCCC dihedral angle of 39.4°), sacrificing some conjugation to relieve steric interactions between the two substituents. In this regard, the importance of steric interactions in the singlets is further evident from the valence bond angles (deg) at the divalent center: PhCH, 105.9;[13] $PhNH^+$, 111.7;[13] Me_2C, 110.3;[16] Me_2N^+, 119.7;[51] **2S**, 116.7; and 3^+**S**, 123.7. The carbene and nitrenium angles are widest for **2S** and 3^+**S**, respectively, indicating (not unexpectedly) that the interaction between a phenyl group and a methyl group is more severe than that between phenyl and hydrogen or between two methyl groups.

In contrast to the above, boronide 1^-**S** has a torsion angle about the C_{ipso}−B bond of 90°. Such a rotation permits the boron atom to use maximal s character in the orbital containing its nonbonded pair of electrons while still maintaining significant overlap with the aromatic π system; the phenyl π system now serves as an electron *acceptor*, i.e., B^- acts as an electron *donating* center, not an electron attracting one.

State Splittings. The different modes of interaction, discussed above, between the divalent centers and the aromatic ring, are reflected in the singlet−triplet state splittings, which are listed in Table 1. For the unsubstituted parent systems CH_2 and NH_2^+ in the gas phase, the triplet states have been measured to be lower in energy than the singlet states by 9[6,7] and 30[48]

kcal/mol, respectively. The analogous two electronic states for BH_2^- are predicted to be almost degenerate;[50] BH_2^- has not been experimentally characterized.

Comparing these data to Table 1 shows that substitution of the divalent center with one methyl and one phenyl group stabilizes the carbene (**2**) singlet state relative to the triplet state by about 7 kcal/mol—apparently because the singlet enjoys larger conjugative and hyperconjugative interactions with its substituents than the triplet (note that methyl/phenyl substitution is about 3 kcal/mol *less* stabilizing than dimethyl substitution,[15,16,51] suggesting, as noted above, that unfavorable steric interaction between the methyl and phenyl groups offsets some of the electronic stabilization). Sugiyama et al. have measured the equilibria between singlet and triplet methylphenylcarbene in *n*-heptane and acetonitrile at 298 K and thereby determined the state splittings in these solvents to be 2.3 and 2.0 kcal/mol, respectively.[10] These values agree well with the gas-phase computation. The effects of *n*-heptane and acetonitrile solvation have been computed with use of the SM5.4/AM1 solvation models for these solvents (Table 1). Solvation is predicted to reduce the splitting to 1.0 and 0.0 kcal/mol, respectively. These values are still in quite reasonable agreement with experiment, although the additional stabilization of the singlet state by acetonitrile compared to *n*-heptane appears to be somewhat overestimated.

Similar decreases in S−T splittings with increasing solvent polarity are well known experimentally for both diaryl-[87−89] and arylalkylcarbenes.[90] This is of particular interest because the solvent effect on the relative spin populations may determine the solvent effect on relative product yields.[91−93] Eisenthal et al.[87−89] found that the gap for diphenylcarbene decreases from

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4.0 kcal/mol in isooctane to about 2.6 kcal/mol in acetonitrile, a 1.4 kcal/mol shift, which is more comparable to the *n*-heptane to acetonitrile shift of 1.0 kcal/mol we find for **2** (see Table 1).

The source of this singlet stabilization derives from the greater polarity of the singlet state compared to the triplet. The DFT ESP charges in the singlet indicate a charge transfer of 0.39 electrons across the C_{ipso}−$C_{carbene}$ linkage (measured as the total charge on either the aromatic ring or the ethylidene fragments). This separation is in the expected sense, i.e., charge transfer from the aromatic ring to the electrophilic carbene. In the triplet, however, this charge transfer is reduced to only 0.05 electron. The difference in the polarization free energies arising from these charge distributions accounts for essentially all of the differential solvation; differential short-range effects associated with cavitation, dispersion, solvent structure, etc., amount to only 0.1 kcal/mol. Increasing stabilization with increasing solvent dielectric constant is consistent with this analysis.

In the borenide, gas-phase substitution differentially stabilizes the singlet state by only 4 kcal/mol relative to BH_2^-, reflecting the limited ability of the methyl and phenyl substituents to act as efficient electron acceptors. In **1**$^-$, the singlet state is better solvated than the triplet because the CH_3B fragment bears more negative charge in the former state (by 0.22 electron unit). This derives from a combination of geometric and conjugative effects.

In the nitrenium cation, the singlet stabilization relative to NH_2^+ is 44 kcal/mol. This contrasts dramatically with the stabilizations observed for the carbene and the borenide because of the very electropositive character of the nitrenium center.[13,49,52,86,94] This differential singlet stabilization is reduced by 6 kcal/mol compared to $PhNH^+$, apparently due to the same steric interaction discussed above for the analogous carbene systems. The large singlet stabilization in **3**$^+$ compared to **1**$^-$ and **2** is a particularly dramatic manifestation of how different the effects of substitution on otherwise isoelectronic systems can be.

Surprisingly, perhaps, solvent effects on the state splitting are predicted to be smaller for ionic **3**$^+$ than for neutral **2**. This appears to derive from a subtle cancellation of effects associated with overall polarity and local polarity. The singlet state of **3**$^+$ has a partial charge on the CH_3N fragment of only +0.03 while the triplet state fragment charge is +0.37; thus, charge transfer to the N atom acting as an acceptor is more efficient in the singlet state. One might expect, then, that the triplet would be better solvated, since it concentrates more positive charge on the smaller fragment, as opposed to spreading it over the aromatic ring. However, the *local* polarization in the singlet is higher, by comparison to the triplet. For example, the singlet aromatic ring shows the *ortho/para* localization of positive charge expected[95] from simple resonance theory. The triplet, on the other hand, distributes positive charge over the aromatic ring much more uniformly (i.e., the charge stabilization is more from volume polarizability than from resonance). This, combined with differences in geometry that also affect the solvation free energies, coincidentally leads to a cancellation of effects.

Hydrogen Migrations. The 1,2-hydrogen shift is also sensitive to the degree of conjugative stabilization. Focusing first on the carbene, we calculate the gas-phase barrier to be 5.4 kcal/mol, a value quite consistent with those found for simple alkylidenes.[40,76] Tomioka et al. examined the analogous hydrogen migration in 1,2-diphenyl-1-propylidene in several low-temperature glassy and polycrystalline matrices.[24] Because the kinetics for this process were strongly influenced by

interactions of the carbene with different matrix sites, they were unable to determine an activation barrier. McMahon and Chapman examined 1,2-hydrogen migration in **2** itself in a soft xenon matrix.[27] Monitoring the decay of the triplet carbene by IR spectroscopy, they demonstrated that the process follows simple first-order kinetics with an Arrhenius activation energy of 4.7 kcal/mol at 65 K.

Solution studies have also been carried out for the 1,2-hydrogen shift in **2**. Sugiyama et al. measured this process by laser flash photolysis in *n*-heptane at 298 K and determined a lower limit for the activation free energy of 4.3 kcal/mol.[10] The calculated barrier when *n*-heptane solvation is accounted for via the SM5.4/AM1 model is 5.1 kcal/mol (Table 1), in excellent agreement with the solution measurement (and with the matrix measurement, assuming solvation effects from the xenon matrix to be similar to those for a nonpolar solvent like *n*-heptane, thermal differences to be small, and that one can compare barrier heights to activation energies). Sugiyama et al. also determined the hydrogen shift in acetonitrile to have an activation free energy of 2.3 kcal/mol, i.e., a reduction of 2 kcal/mol compared to *n*-heptane. The SM5.4/AM1 model also predicts barrier lowering in the more polar acetonitrile, but by only 0.7 kcal/mol (Table 1).

Sugiyama et al.[10] speculated that the acceleration by polar solvent indicated a charge separation in the transition state. Based on observing additional acceleration in the propylidene compared to the ethylidene, they concluded that the carbon adjacent to the carbene center develops a partial positive charge in the transition state (substitution stabilizes this charge by hyperconjugation). Based on seeing little effect on the rate when the aromatic ring was substituted with electron donors or acceptors, they concluded that the required buildup of balancing negative charge must take place on the hydrogen atom in flight (since if it were on the carbene carbon, one might expect the reaction to be sensitive to the ability of the aromatic ring to stabilize such charge). The calculations permit some interesting comparisons to these conclusions.

First, it is noteworthy that when the gas-phase charge distribution is used (the NOPOL lines in Table 1), no acceleration of the hydrogen shift is predicted in either solvent. Acceleration arises purely from relaxation effects (i.e., charge redistribution in response to the surrounding solvent) and is a manifestation of the greater polarizability of the transition state (TS) compared to the singlet equilibrium structure. The gas-phase charge distributions in the TS and the singlet equilibrium structure are, in fact, quite similar. The DFT ESP charges for the carbene carbon are predicted to be −0.72 in the reactant and −0.68 in the TS. The overall charge on the methyl group in the reactant is predicted to be +0.33, while the methylene group in the TS has an overall charge of +0.29 (the H in flight has a charge of +0.11). Relaxation of the wave function, however, *does* increase the positive charge on the methylene carbon by 0.07 unit in the TS (the relaxation change in the reactant is only 0.02 unit). This observation, then, is consistent with the hypothesis of Sugiyama et al. regarding positive charge increase at this position.

The in-flight hydrogen is predicted to have a partial *positive* charge in the gas phase, and that charge is predicted to become more positive upon relaxation of the wave function with respect to solvent. The balancing negative charge is supplied by the carbene carbon plus a very small amount from the aromatic ring. This contrasts with the inference of Sugiyama et al.[10] We suggest that the insensitivity of the rearrangement to substitution of the aromatic ring by electron withdrawing groups indicates simply that in the TS most of the conjugation between the aromatic ring and the carbene carbon has been lost. As can be

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seen in Figure 1, the new C—H bond is already well formed in the transition state (1.390 Å) and the carbene p orbital is effectively removed from conjugation.

We conclude this discussion of the carbene by noting that some caution should be applied in comparing the various measured activation (free) energies and calculated barrier heights. For instance, the experimental results of McMahon and Chapman[27] are based on the disappearance of *triplet* carbene, and thus the measured activation energy is influenced by the singlet—triplet splitting and/or surface-crossing effects. The activation free energies of Sugiyama et al.[10] were derived from the solution of a fairly complex set of kinetic equations that included several processes for which rate constants were estimated by one means or another. Furthermore, possible effects on the measured activation energies from quantum mechanical tunneling cannot be evaluated with the presently available information. Dix et al. demonstrated significant tunneling in low-temperature 1,2-hydrogen migrations in me-thylchlorocarbene.[96] Storer and Houk calculated that tunneling reduces the activation energy in methylchlorocarbene by 3.2 kcal/mol at 298 K.[97] In this instance, however, a 6 kcal/mol difference between the measured activation energy and a computationally predicted barrier had been noted. The *good* agreement between the measured activation energies and computed barrier for methylphenylcarbene rearrangement may either result from tunneling effects being small at the measured temperatures or from tunneling effects being significant with the theoretical barriers being too low.

For borenide **1**$^-$, the gas-phase migration barrier is 10.5 kcal/mol, which is larger than that for the carbene; such an increase is consistent with the electrostatic cost of migration moving delocalized negative charge density out of the aromatic system and localizing it onto the HB=CH$_2$ fragment. The DFT ESP charges suggest that localization on this fragment is only 0.04 electron more in the TS structure than in the reactant, so phenomena such as differing C—H (breaking) and B—H (forming) bond strengths probably also affect the barrier height. Solvent effects on the hydrogen migration in **1**$^-$ are small and consistent with the trends observed for the carbene.

Finally, in **3**$^+$ it is *positive* charge density that hydrogen migration concentrates on the heteroatom, and in this case the barrier is much higher (21.5 kcal/mol) because migration takes place using the orbital of the divalent center that is conjugated with the aromatic system, i.e., π donation from the aromatic ring is greatly diminished in the transition state. Note that in **1**$^-$, migration occurs to the orbital *not* in conjugation with the aromatic system, so the interaction of the borenide with the aromatic ring is less perturbed in the transition state. Further, an unsubstituted phenyl ring is a much better π donor than it is an acceptor. Thus, the trend in hydrogen shift barriers for **1**$^-$, **2**, and **3**$^+$ is consistent with the degree to which the shift affects conjugative stabilization. The reaction exothermicities for 1,2-hydrogen migration are also consistent with these differential conjugative stabilization effects, being −43, −63, and −33 kcal/mol for **1**$^-$, **2**, and **3**$^+$, respectively.

The concentration of positive charge in **3**$^+$‡ relative to **3**$^+$S leads to the prediction of a very large solvent effect on the barrier height for rearrangement. Using the SM5.4/AM1 continuum solvation model for acetonitrile as solvent,[80,81] we calculate the barrier to be reduced by about 3 kcal/mol when the unrelaxed gas-phase DFT geometries and charge distributions are solvated (NOPOL in Table 1). Evaluating the effects of relaxing the solute geometries and electronic wave functions

with respect to solvation at the AM1 level indicates that solvation by acetonitrile (i) lengthens the migrating hydrogen's bond lengths to both N and C in **3**$^+$‡ by about 0.2 Å compared to the gas phase, (ii) increases the (positive) charge on this atom by about 0.3 units, and (iii) reduces the overall barrier height to 13 kcal/mol. The relaxation of the electronic wave function accounts for 5.1 kcal/mol of the reduction, while the geometric relaxation, in spite of the rather large change in C—H and N—H bond lengths, accounts for only 0.7 kcal/mol. The resulting low barrier in acetonitrile is consistent with the experimental observation of products arising from 1,2-hydrogen migration when alkylarylnitrenium ions are generated in acetonitrile solution.[67] While not explicitly addressed here, we speculate that similar effects are operative in 1,2-alkyl migrations in substituted nitrenium ions, these migrations being better studied experimentally for reasons outlined in the introduction.[53,98]

The coupling of the solvation and relaxation effects in stabilizing **3**$^+$‡ relative to **3**$^+$S results from the high dielectric constant of acetonitrile ($\epsilon = 37.5$[99]). Using the SM5.4/AM1 model for *n*-heptane[80,81] ($\epsilon = 1.91$[99]), we predict the barrier height to be reduced by only about 1 kcal/mol for unrelaxed gas-phase geometries and wave functions, and full relaxation further reduces the barrier by only another 1 kcal/mol (relaxed barrier of 19.4 kcal/mol). Thus the migration in **3**$^+$ is very sensitive to solvent and, to the extent that solvent induces geometric changes in the transition state structure and barrier width, may further exhibit interesting kinetic isotope and/or tunneling effects.

Conclusions

The interaction of a divalent center with a conjugating substituent is intimately dependent on the electron donating or withdrawing nature (and power) of the hypovalent atom; isoelectronic analogies are dangerous for systems having different formal charges. In the case of the isoelectronic series **1**$^-$, **2**, and **3**$^+$, fundamental differences are predicted for singlet state geometries, singlet—triplet state splittings, barriers to singlet 1,2-hydrogen migration, and sensitivity of 1,2-hydrogen migration to solvent effects, and these differences are differentially modulated by the solvent in a way that further depends on charge state. Using gas-phase energies calculated at the BPW91/cc-pVDZ level and solvation effects calculated at the SM5.4/AM1 level, good agreement with experiment is noted for the singlet—triplet splitting and 1,2-hydrogen shift barriers of methylphenylcarbene (**2**). Solvent effects on these quantities are also well predicted, and the calculations rationalize the observed trends as being due to different charge distributions and polarizabilities for singlets, triplets, and hydrogen-shift transition state structures. The barrier-lowering effect of polar solvation is predicted to be particularly large in methylphenylnitrenium (**3**$^+$).

Supporting Information Available: Cartesian coordinates (Å), electronic energies (au), and solvation free energies (kcal/mol) for all structures (5 pages). See any current masthead page for ordering and Internet access insructions.

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