to an attractive surface (or vice versa). Since the probability of this transition depends on the position of the crossing relative to r_0, changes in the magnetic flux density indirectly alter the net rate of reaction. Another commonly cited mechanism for magnetic effects, the so-called Δg mechanism, will not be considered here.[14]

It is widely believed that spin–orbit mixing of the singlet and triplet states provides an additional mechanism for electronic relaxation, thereby diluting the magnetic field effect.[20-22] Because spin–orbit coupling constants[23] are nearly always larger than nuclear hyperfine coupling constants[24] (particularly in heavy atoms),[25] one might conclude that heavy-atom magnetic field effects should be difficult to observe.[26] We believe that this view is false and misleading because it fails to recognize that, in the adiabatic limit, relaxation between spin–orbit states of heavy-atom radicals occurs only as a result of other perturbations (e.g., hyperfine or radiative coupling or rotation of the radicals).

Our study outlined above is one of a growing number in which heavy-atom magnetic field effects have been observed.[20,27-29] In this communication we present an explanation for the large magnetic effect involving reaction of Cl atom pairs. The argument is extended to explain the observation of magnetic effects in other heavy-atom systems.

A schematic diagram of potential energy surfaces relevant to reactive Cl atom pairs generated in reaction 1 is presented in Figure 2B. Photodissociation near 337 nm is known to occur mainly by excitation from the ground $^1\Sigma_g^+$ state to the repulsive $^1\Pi_u$ surface.[30,31] As the atoms separate and these two surfaces approach each other to within the spin–orbit coupling constant (about 900 cm^{-1}), spin and orbital angular momentum become ill-defined, and the surfaces are instead characterized by total spin–orbit angular momentum Ω, which is quantized along the interatomic axis. Thus, while the *characters* of the surfaces change, they nonetheless retain a distinct identity. Transitions between attractive and repulsive surfaces may be induced by nuclear hyperfine coupling[32] at crossing points such as that denoted by the circle in Figure 2B. This is analogous to the scheme represented by Figure 2A. The crossings depicted in Figure 2B are quite general for pairs of atoms having magnetic nuclei.[33] Therefore, magnetic effects in heavy-atom systems may be just as strong and prevalent as for light atoms.

In cases where a heavy-atom radical center is located in a molecule rather than an isolated atom, the electronic state is often orbitally nondegenerate (e.g., $^2A_1$ instead of ^2E), so that the asymptotic states are (essentially) degenerate despite the fact that spin and orbital motions of the unpaired electron are strongly coupled. The correlations of the asymptotic states with the valence states of the radical pair precursor are usually well-defined, and magnetic effects can be interpreted by the scheme represented by Figure 2A.

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(20) Buchachenko, A. L.; Khudyakov, I. V. *Acc. Chem. Res.* **1991**, *24*, 177.

(21) Podoplelov, A. V.; Leshina, T. V.; Sagdeev, R. Z.; Molin, Yu. N.; Goldanskii, V. I. *Pis'ma Zh. Eksp. Teor. Fiz.* **1979**, *29*, 419.

(22) Doubleday, C.; Turro, N. J.; Wang, J. *Acc. Chem. Res.* **1989**, *22*, 199.

(23) Lefebvre-Bion, H.; Field, R. W. *Perturbations in the Spectra of Diatomic Molecules*; Academic Press: Orlando, FL, 1986; p 214.

(24) Atkins, P. W.; Symons, M. C. R. *The Structure of Inorganic Radicals*; Elsevier: Amsterdam, 1967.

(25) The spin–orbit and nuclear hyperfine coupling constants in atomic chlorine are 587 and 0.02 cm^{-1}, respectively. These are the values for the separated atoms, and they should be relatively insensitive to the magnitude of internuclear separation in the Cl_2 molecule.

(26) Broomhead, E. J.; McLauchlan, K. A. *J. Chem. Soc., Faraday Trans. 2* **1975**, *74*, 775. These authors failed to observe a significant magnetic effect for a Br atom reaction, even in viscous solutions.

(27) Grissom, C. B.; Chagovetz, A. M.; Wang, Z. *Biochemistry* **1992**, *31*, 2202.

(28) Step, E. N.; Tarasov, V. F.; Buchachenko, A. L. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1988**, 200.

(29) Step, E. N.; Tarasov, V. F.; Buchachenko, A. L. *Nature* **1990**, *346*, 25.

(30) Wilson, K. R. In *Symposium on Excited State Chemistry*; Pitts, J. N., Ed.; Gordon and Breach: New York, 1970.

(31) Matsumi, Y.; Tonokura, K.; Kawasaki, M. *J. Chem. Phys.* **1992**, *97*, 1065.

(32) Both principal isotopes of chlorine atoms have non-zero nuclear spin and therefore may couple spin–orbit states within about 0.02 cm^{-1} of the crossing points through the nuclear hyperfine interaction. Nonadiabatic transitions are possible here because the hyperfine correlation time, $(0.02\ c)^{-1} = 1.7 \times 10^{-9}$ s, can be comparable to the time-of-passage through the crossing region, depending on the magnetic flux density.

(33) Herzberg, G. *Molecular Spectra and Molecular Structure*; Van Nostrand Reinhold: New York, 1950; Vol. I, p 311.

3-*o*-Carboranylcarbenes: Linear, Ground-State Triplets[†,1]

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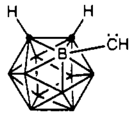
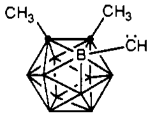
We have recently described the generation and reactions of the first boron-substituted carbenes, **1** and **2**.[2] In these papers we argue from considerations of reactivity for the special prominence of triplet-state reactions of these carboranylcarbenes.[3] Here we report the EPR spectra of **1** and **2** and show that the triplets are the ground states of these probably linear reactive intermediates.



1



2

Degassed solutions (~10 mM) of the diazo compound precursors[2] of **1** and **2** in methylcyclohexane were frozen at 10 K, and the glasses were irradiated through Pyrex in the EPR cavity with a 200-W high-pressure mercury arc for 30 min. The resulting spectra were persistent at low temperature, but disappeared irreversibly at about 32 K. For **1**, a plot of peak height vs $1/T$ was linear over the range 14–30 K. Thus the Curie law is obeyed, and the ground state of **1** (and presumably the other 3-carboranylcarbenes) is the triplet. At most, the triplet may lie only a few calories above the singlet.

The zero-field splitting parameter, $|D/hc|$, for **1** and **2** is 0.657 and 0.661 cm^{-1}, respectively. This matches well the values of 0.6860 and 0.6920 cm^{-1} reported by Hutton, Roth, and Chari for two carbon-substituted carboranylcarbenes, **3** and **4**.[4] $|D/hc|$ is

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[†] This paper is dedicated to the memory of Professor Gerhard L. Closs, 1928–1992.

[‡] Princeton University.

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(2) Li, J.; Jones, M., Jr. *J. Am. Chem. Soc.* **1992**, *114*, 1094. Li, J.; Caparrelli, D. J.; Jones, M., Jr. *J. Am. Chem. Soc.*, submitted for publication.

(3) (a) For general references on carborane chemistry, see: Bregadze, V. I. *Chem. Rev.* **1992**, *92*, 209. Olah, G. A.; Surya Prakash, G. K.; Williams, R. E.; Field, L. D.; Wade, K. *Hypercarbon Chemistry*; Wiley: New York, 1987. Muetterties, E. L. *Boron Hydride Chemistry*; Academic: New York, 1975. Grimes, R. N. *Carboranes*; Academic: New York, 1970. Onak, T. *Organoborane Chemistry*; Academic: New York, 1975. (b) For a review of the interactions between carbenes and carboranes, be alert for Jones, M., Jr. *Adv. Carbene Chem.* **1993**, *1*, in press.

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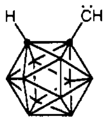
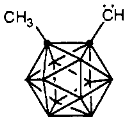


3



4

related to $1/r^3$, where r is the average distance between the two electrons.[5] For a carbene in which delocalization is impossible, methylene, $|D/hc| = 0.76$ cm^{-1}.[6] For dialkylcarbenes such as diadamantylcarbene or di-*tert*-butylcarbene in which delocalization is minimal, $|D/hc| = 0.6823$ and 0.689 cm^{-1}, respectively.[7,8] By contrast, for arylcarbenes in which one of the nonbonding electrons is well-delocalized over one or more aromatic rings, $|D/hc|$ is much smaller.[5] Phenylcarbene, for example, shows $|D/hc| = 0.51$ cm^{-1}.[5,9] Hutton, Roth, and Chari took their values of $|D/hc|$ to mean that there was little delocalization into the carborane cage,[4] and we see no reason to disagree with their evaluation. The nonbonding electrons of both carbenes **1** and **2** are strongly localized on the extra-cage carbon.

The other zero-field splitting parameter, $|E/hc|$, is a measure of the difference in magnetic properties along the x and y axes and will vanish for a linear molecule. Although a zero $|E/hc|$ is only consistent with a 180° angle at the divalent carbon, it has generally been taken as diagnostic for a linear species. Most simple triplet carbenes, including methylene,[6] diadamantylcarbene,[7] and phenylcarbene,[5,9] are bent, with $|E/hc| = 0.052$, 0.038, and 0.0249 cm^{-1}, respectively. Carbenes with cylindrical symmetry such as cyanocarbene[10] and a series of ethynylcarbenes[10] are linear ($|E/hc| \approx 0$). Although the carbon-substituted carboranylcarbenes **3** and **4** are bent ($|E/hc| = 0.0302$, 0.0293 cm^{-1}),[4] their boron-substituted relatives **1** and **2** are linear, as $|E/hc| < 0.002$ cm^{-1} in each case. Clearly, this is an important difference in the two kinds of intermediate. Equally clearly, rationalization is perilous, as very small energy differences may be involved.[12] We have calculated the structures of triplets **1** and **3** at the MNDO level. The B–C–H angle for carbene **1** is calculated to be nearly linear, 173°, whereas the related angle in **3** is only 155°. MNDO is known to overemphasize triplet linearity,[11] but the observed experimental trend is nicely reproduced.

Boron-substituted carbenes have been previously investigated computationally.[14] In H_2BCH, overlap of a filled carbene orbital with the empty 2p orbital on boron stabilizes the singlet state, but there is a competing σ effect in which the electronegativity difference between B and C acts to stabilize the triplet carbene. For H_2BCH, the two spin states emerge close in energy, with the singlet favored by 4–6 kcal/mol.[14] However, H_2BCH is not a good model for **1** and **2** as the 2p orbital that is so stabilizing to the singlet state is missing in the icosahedral species, occupied as it is in the network of three-center, two-electron bonding making up the cage frame. Perhaps better models would be silylcarbenes,[15] in which the carbene is also attached to a less electronegative atom.[16] Here, too, linear triplets are found, as $|E/hc| \approx 0$ for a series of alkylsilylcarbenes.[12,15]

In summary, the first boron-substituted carbenes are ground-state triplets and appear to be linear. It remains to verify linearity through an analysis of the ^{13}C hyperfine interactions and to examine the other possible isomers of **1** and **2**.

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Supplementary Material Available: EPR spectra of **1** and **2** and Curie plot data (3 pages). Ordering information is given on any current masthead page.

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(4) Hutton, R. S.; Roth, H. D.; Chari, S. *J. Phys. Chem.* **1981**, *85*, 753.

(5) Trozzolo, A. M.; Wasserman, E. Structure of Arylcarbenes. In *Carbenes*; Moss, R. A., Jones, M., Jr., Eds.; Wiley: New York, 1975; Vol. 2, p 185.

(6) Wasserman, E.; Hutton, R. S.; Kuck, V. J.; Yager, W. A. *J. Chem. Phys.* **1971**, *55*, 2593.

(7) Myers, D. R.; Senthilnathan, V. P.; Platz, M. S.; Jones, M., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 4232.

(8) Gano, J. E.; Wettach, R. H.; Platz, M. S.; Senthilnathan, V. P. *J. Am. Chem. Soc.* **1982**, *104*, 2326.

(9) Trozzolo, A. M.; Murray, R. W.; Wasserman, E. *J. Am. Chem. Soc.* **1962**, *84*, 4990.

(10) Bernheim, R. A.; Kempf, R. J.; Gramas, J. V.; Skell, P. S. *J. Chem. Phys.* **1965**, *43*, 196.

(11) Jackson, J. E.; O'Brien, T. A. *J. Phys. Chem.* **1988**, *92*, 2686. See, especially, Table I.

(12) A referee has quite rightly pointed out that a near-zero $|E/hc|$ value may be the result of rotational averaging in a bent structure with a very low barrier.[13] However, the carbon-substituted carbenes **3** and **4** show substantial $|E/hc|$ values,[4] not the zero values of **1** and **2**. We calculate (MNDO) a tiny 5-fold barrier to rotation about the extra-cage C–C bond of 1-methyl-*o*-carborane (ca. 0.2 kcal/mol), and there seems little chance that there would be a substantial barrier in the carbon-substituted carbenes. Accordingly, unless the carbon-substituted carbenes and the boron-substituted carbenes fortuitously find themselves in substantially different matrix sites, we think our near-zero $|E/hc|$ values are significant. We hope to resolve this point through a determination of the ^{13}C hyperfine interactions in a suitable labeled carbene.

(13) See for example, the discussion in Hehre, W. J.; Pople, J. A.; Lathan, W. A.; Radom, L.; Wasserman, E.; Wasserman, Z. R. *J. Am. Chem. Soc.* **1976**, *98*, 4378.

(14) Luke, B. T.; Pople, J. A.; Krough-Jespersen, M.-B.; Apeloig, Y.; Karni, M.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1986**, *108*, 270. Schleyer, P. v. R.; Luke, B. T.; Pople, J. A. *Organometallics* **1987**, *6*, 1997.

(15) Chedekel, M. R.; Skoglund, M.; Kreeger, R. L.; Shechter, H. *J. Am. Chem. Soc.* **1976**, *98*, 7846.

(16) Allen, L. C. *J. Am. Chem. Soc.* **1989**, *111*, 9003.

Direct Coupling of Aniline and Nitrobenzene: A New Example of Nucleophilic Aromatic Substitution for Hydrogen

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The majority of reactions between nucleophiles and electron-deficient aromatic compounds can be separated into two classes. The most common is nucleophilic aromatic substitution for halide and, in particular, the reaction of nucleophiles with halogenated nitroaromatics.[1] The second is nucleophilic aromatic substitution for hydrogen, which formally requires the replacement of a hydride ion. This reaction is often promoted by the addition of an external oxidant such as oxygen.[2] Both of these reactions are believed to proceed via attack of a nucleophile on the nitroarene generating an anionic σ-complex, **1**, followed by departure of the leaving group and rearomatization.[3] More recently, the removal of a proton and two electrons from σ-complexes has been shown to be facilitated in a new class of reaction referred to as vicarious nucleophilic substitution (VNS).[4] These reactions require a good leaving group, such as sulfoxonium ion,[5] halide,[6] triazole,[7] or

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(1) Rondestvedt, C. S., Jr. *J. Org. Chem.* **1977**, *42*, 1786–1790.

(2) (a) Wohl, A. *Chem. Ber.* **1903**, *36*, 4135. (b) Montmollin, G.; Montmollin, M. *Helv. Chem. Acta* **1924**, *6*, 94. (c) Bradley, W.; Robinson, R. *J. Chem. Soc.* **1932**, 1254.

(3) Chupakhin, O. N.; Charushin, V. N.; van der Pas, H. C. *Tetrahedron* **1988**, *44*, 1–34.

(4) Makosza, M.; Winiarski, J. *Acc. Chem. Res.* **1987**, *20*, 282–289 and references therein.

(5) Traynelis, V. J.; McSweeney, J. V. *J. Org. Chem.* **1966**, *31*, 243–247.

(6) (a) Makosza, M.; Glinka, T. *Tetrahedron Lett.* **1978**, 3495. (b) Makosza, M.; Glinka, J. *J. Org. Chem.* **1983**, *48*, 3860. (c) Makosza, M.; Golinski, J.; Baran, J. *J. Org. Chem.* **1984**, *49*, 1488. (d) Makosza, M.; Wojciechowski, K. *Tetrahedron Lett.* **1984**, 4791.

(7) (a) Katritzky, A. R.; Laurenzo, K. S. *J. Org. Chem.* **1986**, *51*, 5039. (b) Katritzky, A. R.; Laurenzo, K. S. *J. Org. Chem.* **1988**, *53*, 3978.

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