ORGANIC LETTERS

2000
Vol. 2, No. 20
3059−3062

A DFT and PM3 Study of a Hypothetical Silicon-Based σ-Allyl Cation and σ-Allyl Radical and Higher Homologues

Leif P. Olson

Eastman Kodak Company, Rochester, New York 14650

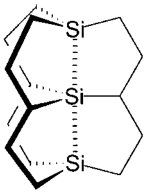
leif.olson@kodak.com

Received July 7, 2000

ABSTRACT

1-Si$_3^+$ (cation) or

1-Si$_3^•$ (radical)



DFT and PM3 calculations were used to model the hypothetical σ-allyl cation 1-Si$_3^+$ and σ-allyl radical 1-Si$_3^•$. For both the cation and the radical, the structure with equal Si–Si bond lengths and σ-delocalized charge or spin is predicted to be favored relative to a bond-localized "capped" triquinane alternative. Higher homologues of 1-Si$_3^+$ and 1-Si$_3^•$ were also modeled; they likewise are predicted to prefer σ-delocalized structures.

Stabilization of charge or unpaired spin via allylic delocalization through a π system is a well-known and commonly observed phenomenon.[1] The π-allyl cation (Figure 1a), for example, is formed from an olefin and an empty adjacent p orbital, when the atomic 2p orbitals are parallel to each other. It has been pointed out that there is another possible bonding orientation which is highly analogous but where delocalization could instead occur by overlap of a carbon−carbon σ bond with a collinear empty p orbital, to give the so-called σ-allyl cation (Figure 1b).[2] Recently, Baldridge et al. published an ab initio Hartree−Fock and density functional theory (DFT) study[3] of the triquinane cation **1** (Figure 2). This species had been proposed earlier by Lipkowitz et al.,[2] as possibly arising from solvolysis of an alkyl halide precursor. The cage structure should enforce collinear p orbitals as well as a tethering constraint on the central carbon atoms. This might favor the symmetric cation with delocalized charge, rather than a localized cation-capped triquinane with an intact central carbon−carbon bond. However, DFT (B3PW91/cc-pvdz) calculations[3] indicated that the symmetric delocalized conformation of **1** is not a minimum but a transition state that interconverts two mirror-image localized-charge structures. This transition state was predicted to be ca. 14 kcal/mol higher in energy than a localized cation, so the σ-allyl cation of this type still should remain elusive as an intermediate.

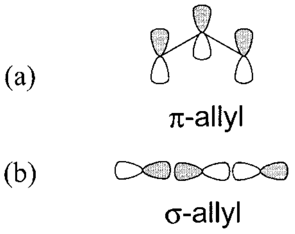


Figure 1. Examples of π-allyl (a) and σ-allyl (b) cations.

There are reasons why **1** might not favor the σ-allyl cation form, even though the underlying orbital symmetry concepts appear to be sound. First, the central C−C distances in C_3h-symmetric **1** (2.250 Å at the B3PW91/cc-pvdz level)[3] are probably too great for the orbitals to overlap effectively. Second, while formation of a five-coordinate carbon (such as the central carbon atom in C_3h-symmetric **1)** is undoubt-

---

[1] Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper & Row: New York, 1987; p 33 ff.

[2] Lipkowitz, K. B.; Larter, R. M.; Boyd, D. B. *J. Am. Chem. Soc.* **1981**, *102*, 85.

[3] Baldridge, K. K.; Leahy, J.; Siegel, J. S. *Tetrahedron Lett.* **1999**, *40*, 3503.

10.1021/ol0063003 CCC: $19.00

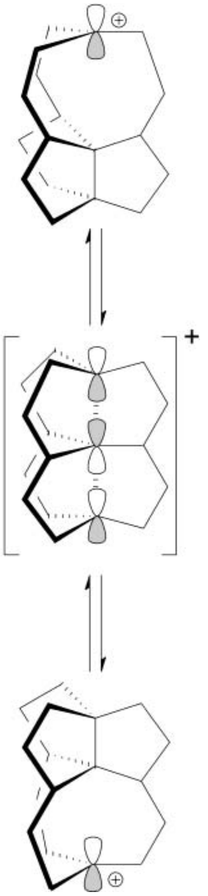


Figure 2. Earlier proposed σ-allyl cation **1**.

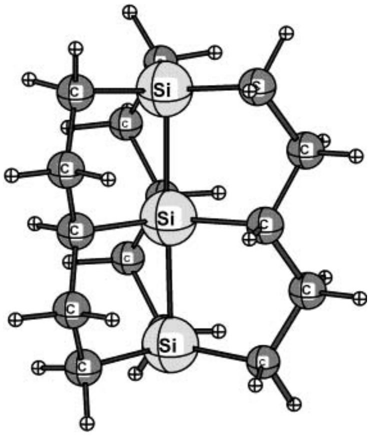


Figure 3. Proposed silicon-substituted σ-allyl cation **1-Si**$_3^+$. The structure shown is the only minimum found at the HF/PM3, B3LYP/6-31G*, and B3LYP/cc-pVDZ levels.

edly possible,[4] it may not be favorable. Compared to carbon, silicon has longer bond lengths (e.g., Si−Si longer than C−C); also it has been shown that silicenium ions (R_3Si^+) can be stabilized by pairs of donor ligands, resulting in a trigonal-bipyramid coordination environment.[5] For these reasons, the silicon-substituted ion **1-Si**$_3^+$ (Figure 3) was expected to have a better chance of existing as a ground-state σ-allyl cation than the hydrocarbon parent **1**, and this expectation was confirmed by DFT and PM3 calculations.

The geometry of **1-Si**$_3^+$ was optimized at the PM3 SCF-MO semiempirical level,[6] the B3LYP/6-31G* ab initio DFT level,[7] and the B3LYP/cc-pVDZ ab initio DFT level.[7] The B3LYP/cc-pVDZ calculations are at a similar level to those performed previously on **1**.[3] All calculations were carried out in the gas phase. Only one minimum was found (Figure 2), corresponding to C_3h or very near C_3h symmetry.[8] **1-Si**$_3^+$ was proven by vibrational frequency calculations[9] to be a true minimum.

The analogy of σ-delocalization with π-delocalization was carried further with higher homologues of **1-Si**$_3^+$. The principle of extension of a π-delocalized chain by iterative addition of conjugating vinyl groups (pentadienyl, heptatrienyl, etc.) was extended to the σ-allyl cation, resulting in **1-Si**$_5^+$, **1-Si**$_7^+$, and **1-Si**$_9^+$ (Figure 4). These higher homologues of **1-Si**$_3^+$ are predicted to be σ-delocalized, at the B3LYP/6-31G* and/or PM3 levels (Figures 4 and 5). The largest ions **1-Si**$_7^+$ and **1-Si**$_9^+$ were only computationally accessible at the PM3 level.

---

[4] Reference 1, p 448 ff.

[5] Berlekamp, U.-W.; Jutzi, P.; Mix, A.; Neumann, B.; Stammler, H.-G.; Schoeller, W. W. *Angew. Chem., Int. Ed.* **1999**, *38*, 2048.

[6] (a) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209. (b) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 221. The minimal basis set PM3 theoretical method does not include d orbitals, yet it still predicts a delocalized structure for **1-Si**$_3^+$ (while still predicting a localized charge structure for the parent hydrocarbon **1**, which is in agreement with the previously reported DFT calculations[3]). Low-lying d orbitals of silicon might be expected to aid in expansion of its coordination sphere, but the PM3 results suggest that d orbitals are not required for delocalization in **1-Si**$_3^+$. This points to poor carbon 2p orbital overlap as the reason **1** is not delocalized.

[7] (a) DFT: Becke, A. D. *J. Chem. Phys.* **1996**, *104*, 1040. (b) All restricted B3LYP calculations were done using *Jaguar 3.0*: Schrodinger, Inc., Portland, Oregon, 1997. (c) All UB3LYP calculations were done using *Gaussian 98*, *Revision A.7*: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; L Andres, J.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A.; Gaussian, Inc., Pittsburgh, PA, 1998. (d) Semiempirical geometry optimizations were done using *GAMESS*: Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. *J. Comput. Chem.* **1993**, *14*, 1347 (*PC GAMESS version 5.0, build number 1465*; Alex A. Granovsky, Moscow State University). (e) Some semiempirical properties calculations were done using *Spartan 3.0*, Wavefunction, Inc., Irvine, CA, 1994. (f) For example, one possibly relevant concern with DFT methods is "inverse symmetry breaking", observed in some radical ions: Bally, T.; Sastry, G. N. *J. Phys. Chem. A* **1997**, *101*, 7923.

[8] This structure was not a minimum at the AM1 semiempirical level, which found a preference for a C_3-symmetric bond-localized cation-capped triquinane instead. The AM1 structure collapsed back to C_3h symmetry when re-minimized using PM3 or DFT. From this comparison to the higher-level DFT results, AM1 was judged an unreliable method for **1-Si**$_3^+$ and related structures, while PM3 was judged probably reliable. AM1: Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

[9] All species described in this paper were shown to be true minima by vibrational frequency calculations: Hehre, W. J.; Radom, L.; v. R. Schleyer, P.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986; p 227.

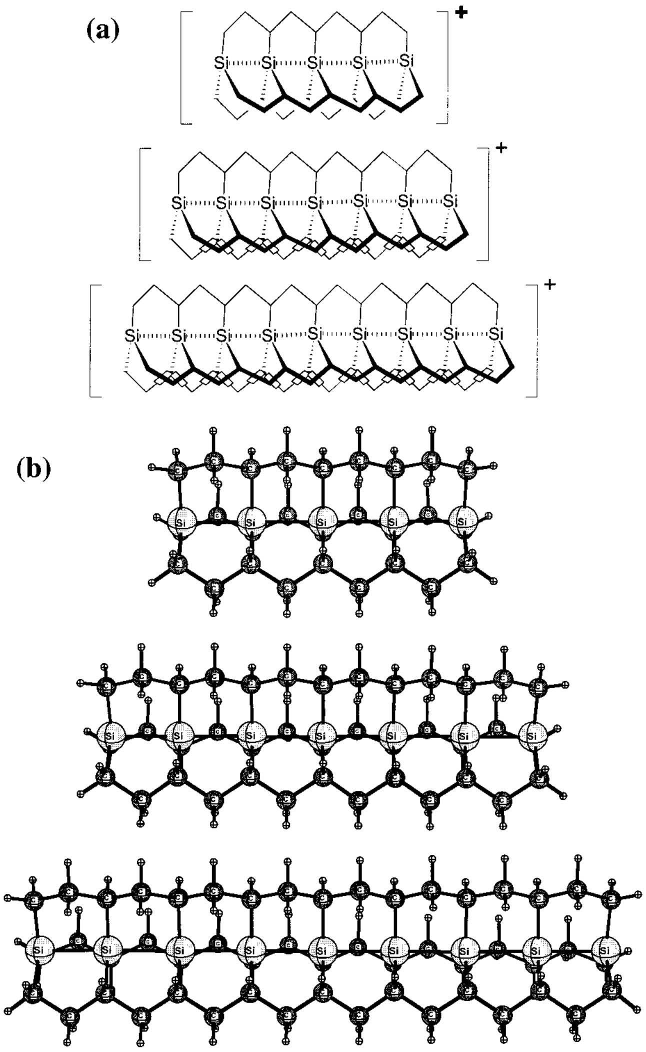


Figure 4. (a): structures of higher homologues of **1-Si$_3$$^+$**: **1-Si$_5$$^+$** (top), **1-Si$_7$$^+$** (middle), **1-Si$_9$$^+$** (bottom). (b) B3LYP/6-31G* structure of **1-Si$_5$$^+$** and HF/PM3 structures of **1-Si$_7$$^+$** and **1-Si$_9$$^+$**.

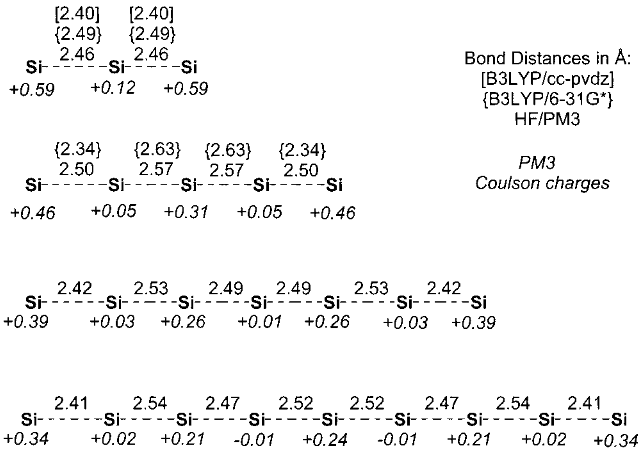


Figure 5. Si−Si bond lengths for **1-Si$_3$$^+$** to **1-Si$_9$$^+$**, computed at several levels of theory, and computed charges for the silicon atoms in each cation (because the combined C and H atoms in these structures are computed to have an overall negative charge, the combined charge on the Si atoms is greater than 1).

The homologous series **1-Si$_3$$^+$** to **1-Si$_9$$^+$** shows the same type of charge alternation for the atoms involved in the delocalization as in the π-delocalized allyl, pentadienyl, heptatrienyl, and nonatetraenyl cation series of hydrocarbons.[10] PM3 Coulson charges are listed for **1-Si$_3$$^+$** through **1-Si$_9$$^+$** in Figure 5.[11] More positive charge resides on the silicon atoms bearing large LUMO coefficients than on the intervening silicon atoms, which have small LUMO coefficients. This can be seen in a qualitative diagram of the MO's of interest for **1-Si$_5$$^+$** (HOMO-1 through LUMO+2; Figure 6a), where the first, third, and fifth silicon atoms have large LUMO coefficients. The qualitative diagram is in fact a reasonable depiction; the HF/PM3 HOMO and LUMO of **1-Si$_5$$^+$** are plotted as examples (Figure 6b).

The analogy of σ-delocalization with π-delocalization is not restricted to a specific redox state, which means for example that if an electron were to be added to **1-Si$_3$$^+$** or its

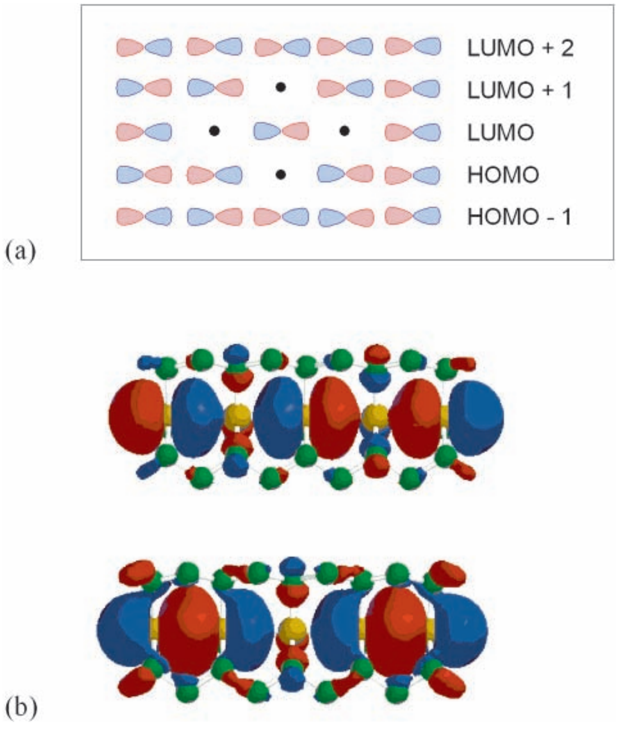


Figure 6. (a) Qualitative MO diagram for the silicon chain in **1-Si$_5$$^+$**. (b) Plot of LUMO and HOMO of **1-Si$_5$$^+$**, computed at the HF/PM3 level. Hydrogen atoms have been removed for clarity; carbon atoms are green, and silicon atoms are orange.

---

[10] PM3-computed data for well-known π-delocalized carbocations (allyl, pentadienyl, etc.) not shown.

[11] Due to the "buried charge" nature of the σ-delocalized cations, atomic charge calculations using electrostatic potential fitting techniques gave unphysical results, while the results from the less complicated Mulliken and Coulson atomic charge schemes were reasonable. (a) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833. (b) Armstrong, D. R.; Perkins, P. G.; Stewart, J. J. P. *J. Chem. Soc., Dalton Trans.* **1973**, 838. (c) Pople, J. A.; Beveridge, D. L. *Approximate Molecular Orbital Theory*; McGraw-Hill: New York, 1970; p 67.

homologues, the resulting radicals (i.e., **1-Si$_3^\bullet$** **1-Si$_5^\bullet$**, etc.) should also be σ-delocalized. Analysis of the frontier MOs (Figure 6) indicates that unpaired spin density in such radicals should largely reside on alternating silicon atoms in the SOMO (i.e., the LUMO of the closed-shell cation). Geometry optimizations and spin density analyses at the UB3LYP/cc-pVDZ level on **1-Si$_3^\bullet$** and the UB3LYP/6-31G* level on **1-Si$_5^\bullet$** confirmed these expectations (Figure 7). As in the case of the cations, the symmetric delocalized radicals were the only minima which were found, regardless of the starting structure. The radical structures are not greatly changed from the cations and were proven to be minima by vibrational frequency calculations.[9a]

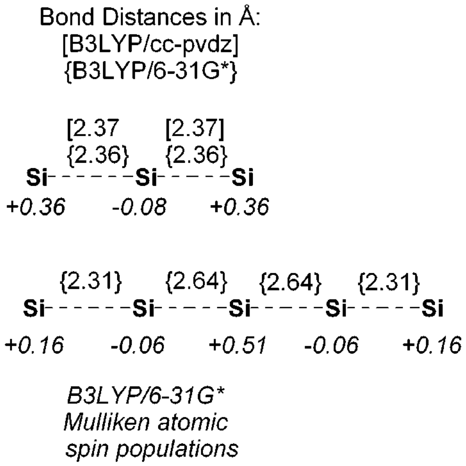


Figure 7. Si−Si bond lengths for **1-Si$_3^\bullet$** and **1-Si$_5^\bullet$**, computed at one or two levels of UB3LYP theory, and spin populations for the silicon atoms of each radical.

UHF calculations on the radicals were plagued by serious spin contamination (whether UHF/PM3 or UHF/6-31g*, etc.). Fortunately, spin contamination was insignificant for the UB3LYP calculations.[12,13] (This is important because other correlated methods, such as UMP2, are highly unreliable when spin contamination is severe, which gives a distinct advantage to UB3LYP in such cases,[13] although some caveats are still required concerning DFT methods[7f]). This DFT method was too computationally demanding to be used with the hypothetical σ-delocalized radicals **1-Si$_7^\bullet$** and **1-Si$_9^\bullet$**. Although these larger radicals were not examined theoretically, the principle of more than one redox state of σ-delocalized species is at least established for the **1-Si$_3^+$**/**1-Si$_3^\bullet$** and **1-Si$_5^+$**/**1-Si$_5^\bullet$** pairs. One might anticipate σ-delocalization in the analogous anions as well (e.g., **1-Si$_3^-$**, **1-Si$_5^-$**, etc.), but this possibility has not been explored.

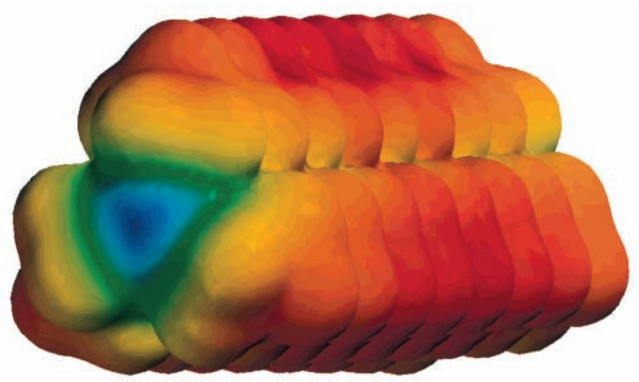


Figure 8. Electrostatic potential of **1-Si$_9^+$**, mapped onto the electron density (computed at the HF/MNDO//HF/PM3 level). Regions in blue are relatively electropositive, and those in red are relatively electronegative. Although delocalized, the positive charge is largely buried in the interior of the ion.

It is interesting to note that these molecules seem to possess characteristics which might be desirable for "molecular wires".[14] In traditional π-delocalization, the relevant orbitals are exposed to the surrounding medium due to their orientation perpendicular to the long axis of the chain (Figure 1a). This means that if a π-delocalized chain (e.g., a polyene) is used as a molecular wire, there is a possibility of undesired interactions with the environment, such as nucleophilic or radical attack, along its entire length. Therefore, a practical molecular wire based on a π system might require a separate molecular sheath (or "insulator") to be associated with the wire,[15] which could be a disadvantage. A σ-delocalized species such as those presented here has a linear core, which is surrounded radially by substituents that might be expected to shield the interior from interactions with the surrounding medium (Figure 8).[16] While synthesis of cage molecules such as those modeled here would very likely be nontrivial, they do provide an interesting hypothetical example of a class of molecular wire which is inherently "insulated".

Acknowledgment. Drs. David Giesen and Stephanie Chacon provided helpful discussions.

OL0063003

---

[12] (a) Baker, J.; Scheiner, A.; Andzelm, J. *J. Chem. Phys. Lett.* **1993**, *216*, 380. (b) Cramer, C. J.; Dulles, F. J.; Falvey, D. E. *J. Am. Chem. Soc.* **1994**, *116*, 9787.

[13] While calculations using the ROHF formalism would not be subject to spin contamination, such calculations were deemed untrustworthy, due to the problem of ROHF symmetry breaking. This is a well-known phenomenon in ROHF calculations on π-allyl radical, and it leads (incorrectly) to localization of spin density: Bally, T.; Borden, W. T. In *Reviews in Computational Chemistry*, Vol. 13; Lipkowitz, K. B.' Boyd, D. B., Eds.; Wiley: New York, 1999; p 17 ff.

[14] (a) *Atomic and Molecular Wires*; Joachim, C., Roth, S., Eds.; Kluwer: Dordrecht, 1997; Vol. 341, p 232. (b) Bumm, L. A.; Arnold, J. J.; Cygan, M. T.; Dunbar, T. D.; Burgin, T. P.; Jones, L.; Allara, D. L.; Tour, J. M.; Weiss, P. S. *Science* **1996**, *271*, 1705.

[15] (a) Anderson, S.; Aplin, R. T.; Claridge, T. D. W.; Goodson, T., III; Maciel, A. C.; Rumbles, G. *J. Chem. Soc., Perkin Trans.* **1998**, 2383. (b) http://chemistry.about.com/education/chemistry/library/weekly/aa030899a.htm.

[16] The MNDO electrostatic potential (ESP) surface is shown in Figure 8 rather than the PM3 ESP because MNDO has been shown superior to PM3 for reproducing ab initio computed ESPs: (a) Besler, B. H.; Merz, K. M.; Kollman, P. A. *J. Comput. Chem.* **1990**, *11*, 431. (b) Merz, K. M. *J. Comput. Chem.* **1992**, *13*, 749. MNDO: (c) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899. (d) Dewar, M. J. S.; Grady, G. L.; Friedheim, J.; Healy, E. F.; Stewart, J. J. P. *Organometallics* **1986**, *5*, 375.