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A COMPUTATIONAL STUDY OF M–M MULTIPLE BONDING IN $Ph_2MMPh_2^{n-}$, WHERE M = B OR Al, AND n = 0, 1, OR 2

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Abstract

We have completed Hartree-Fock *ab initio* electronic structure calculations on the series of compounds $Ph_2MMPh_2^n$, where M = B or Al, and n = 0, 1-, or 2-. The results show that the added one and two electrons upon reduction of the neutral compounds go into the M–M π bond, as expected. The canting of the rings in D_2 symmetry is related to the degree of steric repulsion in the compounds. There is no evidence for preferential population of an Al–Al $\sigma*$ orbital in the dianion of the aluminum compound, and hence we nave no ready explanation as to why this ion has so far proved impossible to detect experimentally. The charge distribution in the compounds is examined with Natural Population Analysis.

Introduction

Whereas multiple bonding is common in Group 14 (especially carbon chemistry), it is very rare in Group 13. Brothers and Power[1] have recently summarized the known data involving multiple bonding of the heavier main-group metallic elements Al, Ga, In, and Tl, and compared the results to those known for B chemistry. The reason for the rarity of homonuclear multiple bonds involving Group 13 elements is simply that the electron count demands a monoanion or dianion for compounds of formula R_2MMR_2 in order to have a π bond order of 1/2 and 1, respectively. This requires that we begin with a neutral compound and carry out a one- and two-electron reduction. But the neutral compounds have a vacant valence orbital on M, and hence are susceptible to donor coordination of, for example, a solvent molecule. Such four coordination of the Group 13 atom inhibits the necessary reduction needed to form multiple bonds. To circumvent these problems synthetic chemists have resorted to bulky R groups such as R = $CH(SiMe_3)_2$ and R = Trip = $2,4,6-i-Pr_3C_6H_2$, or R = Mes = $2,4,6-Me_3C_6H_2$. These bulky substituents protect the vacant orbital in the neutral compound, leaving it available for reduction to form the multiple bond.

In this work we focus on a computational study of B–B and Al–Al bonds in $Ph_2MMPh_2^n$, where M = B or Al, and n = 0, 1-, or 2-, and Ph refers to the phenyl ring. We have chosen this set of molecules because it has a close connection with the experimental work as summarized by Brothers and Power. The Ph substituents are large enough to capture the essence of the electronic features of the experimental Trip and Mes substituents, but simple enough to be computationally tractable.

In the experimental work there is structural data for both neutral and dianion compounds analogous to our model molecule, $Ph_2BBPh_2^n$. When we began our work there was only indirect EPR evidence for the monoanion of a tetraalkyl species.[2a] Later an X-ray study of $Mes_2BBMes(Ph)^-$ was reported by Grigsby and Power.[2b] For aluminum compounds there is structural data for both the neutral and monoanion, but attempts to prepare the dianion have been unsuccessful.

The purpose of our computational work is threefold. First, to examine trends in pertinent structural features that indirectly provide evidence of the electronic structure. The main structural features are the M–M distance, the M–C distance, and the dihedral angles C–M–M–C and M–M–C–C. Second, to examine the hypothesis that the inability to detect the dianions of the aluminum compounds is due to the occupation of a low-lying Al–Al $\sigma*$ orbital, causing the molecule to dissociate. Third, to examine the nature of charge

distribution upon one- and two-electron reduction of the neutral compounds. For example, how much of the charge is delocalized onto the phenyl rings?

The idealized structure of these molecules corresponds to D_2 symmetry. The symmetry elements in this point group are E, $C_2(x)$, $C_2(y)$, and $C_2(z)$. The structure can be described as a "propeller". The torsional angle M–M–C–C must be nonzero in order for the molecule to take on the propeller shape, i.e., the phenyl rings are canted so as to reduce steric repulsion among the rings. We display two forms of the formula Ph₂MMPh₂. In the first, **1**, the dihedral angle C–M–M–C is near 90°. In the second, **2**, this dihedral angle is near 0°.

1   **2**
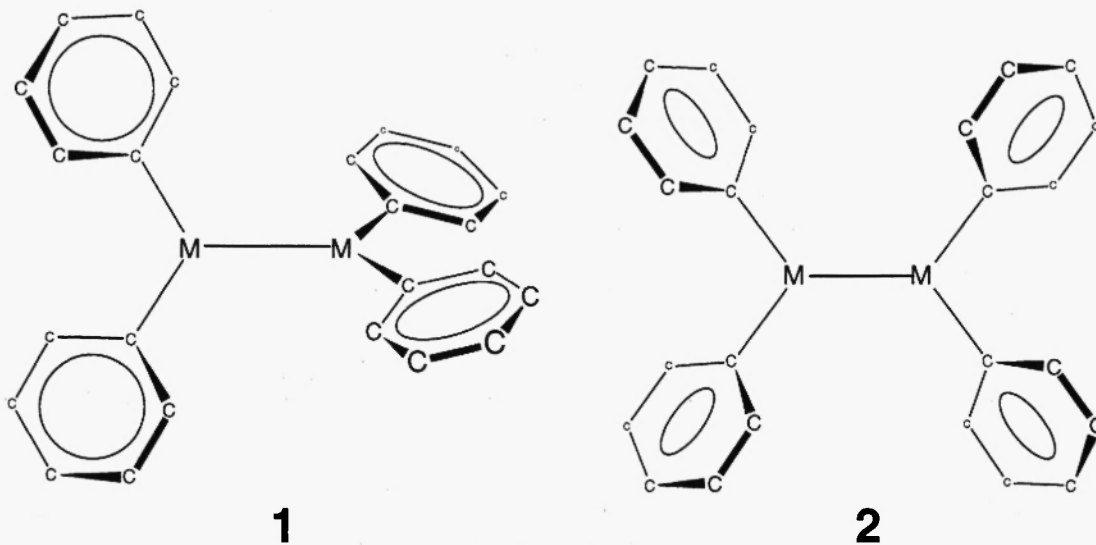
Theoretical Methods

We have performed ab initio electronic structure calculations using restricted Hartree-Fock (RHF) theory for the neutral and dianion molecules and unrestricted Hartree-Fock theory (UHF) for the monoanions.[3] The basis set that we have employed is 3-21+G*.[4] This is a split valence basis set, with added diffuse functions on the B, C, and Al atoms, and added polarization (d) functions on the same atoms. The diffuse functions are needed to accurately describe the electron density distribution of the mono- and dianion.

We have utilized the Gaussian 94 code[5] running on the SGI Power Challenge Array at the National Center for Supercomputing Applications (NCSA) at the University of Illinois in Champaign-Urbana. Selected Gaussian 94 calculations also were performed on the SGI Indigo II and IBM RS/6000 at Calvin College. The monoanion of the boron compound was completed using the Mulliken 2.0.1 code,[6] since we had difficulty obtaining SCF convergence in Gaussian 94.

We performed additional theoretical studies on the simplified model compound $H_2AlAlH_2^{2-}$ in order to test the effects of altering the basis set on the question related to occupancy of the Al–Al σ* orbital vs. the π orbital in the dianions of the aluminum compounds. These studies employed the 3-21G*, 6-31+G*, and 6-311G* basis sets, in addition to the 3-21+G* work. This additional work was done using Mulliken.

Population analysis was performed using Natural Bond Orbital (NBO) version 3.1,[7,8] which is part of the Gaussian 94 package. These populations are referred to as Natural Population Analysis, NPA.

Results and Discussion

We present pertinent geometric data in Table 1 for all six compounds. We first discuss the M–M distances. For the boron compounds there is an incremental shortening of the B–B distances by 0.05 Å and 0.04 Å for the first and then the second one-electron reductions. This is as expected in that the formal B–B bond order goes from 1, to 1.5, to 2 in this series. Each of these changes amounts to about 3% of the original length. The corresponding bond length shortening for the Al–Al compounds is 0.14 Å and 0.04 Å, amounting to 5% and 1.6%, respectively.

Table 1. Geometric data for the six compounds

Compound	M–M, Å	M–C, Å	M–M–C, degrees	τ(C–M–M–C) degrees	ϕ(M–M–C–C) degrees
B_2Ph_4	1.713	1.578	119.1	78.6	25.9
$B_2Ph_4^-$	1.661	1.605	122.7	14.0	38.6
$B_2Ph_4^{2-}$	1.622	1.625	123.9	8.3	39.6
Al_2Ph_4	2.614	1.979	119.0	85.1	4.1
$Al_2Ph_4^-$	2.478	2.016	124.4	6.3	30.9
$Al_2Ph_4^{2-}$	2.443	2.047	126.2	3.5	30.9

The experimental B–B bond lengths for the neutral, monoanion, and dianion of $Mes_2BB(Mes)Ph$ are 1.706 Å, 1.649 Å, and 1.636 Å, respectively.[2b, 9] The theoretical results for our model compounds $Ph_2BBPh_2^n$ compare well with these, Table 1. We error in computing a B–B bond length decrease of 0.04 Å in going from the monoanion to the dianion, whereas the experimental decrease is only 0.01 Å. For the aluminum compounds, the experimental shortening for one-electron reduction of $Trip_2AlAlTrip_2$ is 0.17 Å,[10] compared to our value of 0.14 A.

A brief discussion of the expected change in the M–M bond length upon one- and two-electron reduction is in order. First, on the basis of simple change in bond order from 1, to 1.5, to 2, one would predict the bond distance to decrease. But at the same time there will be a build up of electronic charge on the M atoms, causing the overall electron density to expand and tne effective radius of the atom to increase. This will tend to offset the expected bond length decrease due to bond order increase. Second, there will be secondary effects on the M–M distance brought about by changes in the nature of the M–C bonding. Given these complications, we cannot provide a simple explanation as to why the computed incremental changes in B–B length are about 3% for each step, but are 5% and 1.6% for Al–Al.

We look next at the M–C distances. For both series of compounds we see that as the compound is further reduced, the M–C distances increase. Each step of reduction causes an increase of about 2.5% for B–C and about 3.5% for Al–C. These results too are in good agreement with experiment;[2b, 9] the B–C bond lengths in the neutral, monoanion, and dianion of $Mes_2BB(Mes)Ph$ are 1.576 Å, 1.61 Å, and 1.637 A, respectively. Similarly the average Al–C bond lengths increase upon one-electron reduction of $Trip_2AlAlTrip_2$ by 0.025 Å,[10] compared to a computed change of 0.037 Å in our model compound with phenyl substituents.

The M–M–C bond angles increase slightly upon one- and two-electron reduction. In all cases the angles are near 120°, ranging from 119.0° to 126.2°. Again, the agreement with experiment is excellent. There are much larger changes in the torsional angles, τ(C–M–M–C) and ϕ(M–M–C–C). These angles will be more susceptible to distortion by the experimental substituents (Mes and Trip) on the phenyl rings, than were the lengths and

angles considered previously. It is necessary to keep that in mind when we compare theory to experiment.

Consider τ first. We compute a value of about 85° for Al_2Ph_4; this drops to less than 7° for the monoanion and the dianion. Similarly for $B_2Ph_4{}^n$, the computed values are 78.6°, 14.0°, and 8.3°, for the neutral, monoanion, and dianion, respectively. These large changes in τ are expected. In the neutral there is only a formal B–B single bond, and the computed structure of B_2H_4 shows a staggered structure of D_{2d} symmetry ($\tau = 90°$),[11,12] whereas the dianion shows[13] a planar structure of D_{2h} symmetry ($\tau = 0°$), as predicted. The situation with our model compounds, $M_2Ph_4{}^n$, is not quite so straightforward in that there is steric interaction between the phenyl rings, and there is delocalization of the phenyl π electrons into the π orbitals of M–M. Nonetheless, the predicted values of $\tau = 90°$ and $\tau = 0°$, are quite closely followed in these compounds. The startling change is from the neutral to the monoanion, showing that a π bond order of 0.5 is sufficient to twist the phenyl substituents substantially toward $\tau = 0°$.

A comparison of the τ values with those obtained experimentally shows that in $Trip_2AlAlTrip_2$ the value is 44.8°; in its monoanion τ has decreased to 1.4°. The value of 44.8° is quite far from our computed value of 85°, but that is not unexpected given what we said about the importance of the phenyl substituents related to the value of τ (see above). There is better agreement in the case $Mes_2BB(Mes)Ph^n$; 79.1°, 6.9°, and 7.3° for the neutral, monanion, and dianion, respectively. These compare to our values of 78.6°, 14.0°, and 8.3°, respectively. Part of the reason for the good agreement in the case of the Mes substituent, and poor for the Trip substituent, might have to do with the large size of the *i*-Pr subsituent in Trip compared to the relatively small Me substituent in Mes.

We next examine the torsion angles $\phi(M–M–C–C)$. This torsion angle is related to the cant of phenyl rings or the degree of "pitch" of the propeller blade. These angles control the degree of steric interaction between the two phenyl rings on a given M atom, and also the steric interaction between phenyl rings on different M atoms if they are in a *cis* or *gauche* configuration. The larger the value of ϕ, the smaller the steric interaction. At the same time smaller values of ϕ allow for greater delocalization of π electrons through the M–M framework. Our computed values are 25.9° for B_2Ph_4, increasing to 38.6° for the monoanion and 39.6° for the dianion. The corresponding values for the Al compounds are 4.1°, 30.9°, and again 30.9°. The trends in these values are as expected. First, we would expect larger angles for the B–B compounds than the Al–Al compounds, since there is more steric interaction among phenyls in tne B compounds than in the Al compounds for a given value of ϕ. Second, we anticipate that the value of ϕ would be very dependent upon the value of τ. Larger values of τ should lead to smaller values of ϕ and vice versa, for steric reasons. When τ is large we need only concern ourselves with steric interactions of phenyl rings on a given M atom. As τ decreases steric interaction amongst all the phenyl substituents becomes important and hence ϕ will tend to increase. The angles ϕ display considerable variability in the experimental results. For example, in $Mes_2BB(Mes)Ph$ the four values are 39.3°, 43.1°, 56.5°, and 65.7°. Just as in the case of τ, we expect ϕ to be very dependent upon substituents on the phenyl ring, and so we do not further compare experiment with theory.

We now focus on the electronic structure of $Al_2Ph_4{}^{2-}$; this is the one member of our six compounds for which synthetic attempts have proved fruitless. Brothers and Power[1] speculate that perhaps the reason for the nonexistence of the dianion is that the Al–Al σ^* orbital may be occupied, rather than the π orbital. We do not find any evidence for a lowlying Al–Al σ^* orbital in our computational study. Whether we look at the neutral or the dianion, we find an eigenvalue gap between the energy of the Al–Al π orbital and the Al–Al σ^* orbital to be at least 2 eV (~200 kJ/mol). Hence, it is unlikely that a molecule with the Al–Al σ^* orbital doubly occupied would be more stable than with the π orbital occupied.

In order to examine this point further we completed additional theoretical studies on the simplified model compound $H_2AlAlH_2{}^{2-}$. These studies employed the 3-21G*, 6-

31+G*, and 6-311G* basis sets, in addition to the 3-21+G* basis set work. We found that in all cases the dianion with the π orbital occupied (b_1 symmetry) was more stable than one with the σ^* orbital occupied (b_3 symmetry).[14] For example, in both the 3-21+G* and 6-31+G* studies the former is about 350 kJ/mol more stable than the latter. We found that without the diffuse functions, 3-21G* and 6-311G*, occupation of the b_3 orbital symmetry resulted in scission of the Al–Al bond. Hence the computed electronic structure of the dianion is sensitive to the level of basis set employed. But in no instance do we find that occupation of the Al–Al σ^* orbital is more stable than that of the Al–Al π orbital.

We did not complete computational studies on dianions with a triplet ground state, e.g., one electron in an orbital of b_1 symmetry and one in b_3 symmetry. Further computational studies are ongoing.

Finally, we examine the population analysis as obtained by NPA. These results are presented in Table 2. We look first at the boron results. The neutral compound has a computed charge on B of about 0.68, which is reduced to 0.31 in the monoanion, and to 0.00 in the dianion. Hence, of the two electrons in the reduction, about 1.36 electrons reside on the B atoms. The remainder 0.64 electron are distributed 0.16 electron on each Ph ring. The carbon atoms which absorb the most charge are C_2, C_4, and C_6. The largest amount of charge is absorbed by C_4. It is noteworthy that in the NPA analysis C_1 actually becomes more positive. (The carbon attached to M is C_1, and the other atoms are numbered clockwise around the ring, see **1** and **2**.)

In the two-electron reduction of the Al compounds, the Al atom charge changes from about 1.25 to 0.45. So 1.60 of the two electrons reside on the two aluminum atoms, and 0.10 electron is delocalized onto each of the phenyl rings. Hence, somewhat less of the charge is delocalized onto the Ph rings than in the case of the boron compounds. The comments made about the carbon atoms in the Ph rings of the B compounds also hold for the Al compounds.

Table 2. Natural Population Analysis

Compound	M	C_1	C_2 H_2	C_3 H_3	C_4 H_4	C_5 H_5	C_6 H_6
B_2Ph_4	0.676	–.447	–.183 0.236	–.257 0.245	–.218 0.244	–.260 0.244	–.185 0.244
$B_2Ph_4^-$	0.313	–.326	–.206 0.238	–.257 0.222	–.264 0.219	–.260 0.220	–.222 0.230
$B_2Ph_4^{2-}$	0.003	–.216	–.245 0.245	–.262 0.211	–.341 0.206	–.268 0.207	–.266 0.227
Al_2Ph_4	1.265	–.651	–.216 0.232	–.254 0.244	–.229 0.244	–.254 0.245	–.219 0.226
$Al_2Ph_4^-$	0.854	–.558	–.239 0.240	–.259 0.230	–.270 0.227	–.261 0.228	–.246 0.232
$Al_2Ph_4^{2-}$	0.447	–.482	–.252 0.245	–.265 0.217	–.308 0.212	–.268 0.214	–.265 0.229

Acknowledgments

References

1) Brothers, P. J.; Power, P. P. *Advances in Organometallic Chemistry;* Stone, F. G. A.; West, R., Eds.; Academic Press: New York, 1996; Vol. 39, pp 1-69.

2) a. Klusik, H.; Berndt, A. *Angew. Chem. Int. Ed. Engl.* 1981, **20**, 870. b. Grigsby, W. J.; Power, P. *Chem. Eur. J.* 1997, **3**, 368.

3) Szabo, A.; Ostlund, N. S. *Modern Quantum Chemistry*; Dover Publ.: New York, 1996.

4) Feller, D.; Davidson, E. R. *Reviews in Computational Chemistry*; Lipkowitz, K.; Boyd, D. B., Eds.; VCH: New York, 1990; Vol. 1, pp 1-44.

5) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*; Revision D.1, D.3, and D.4; Gaussian, Inc.: Pittsburgh, PA, 1995.

6) Lengsfield, B. H., III; Horn, H.; Swope, W. C.; Carter, J. T.; McLean, A. D.; Carter, J. T.; Replogle, E. S.; Rice, J. E.; Barnes, L. A.; Maluendes, S. A.; G.C. Lie; Gutowski, M.; Rudge, W. E.; Sauer, S. P. A.; Lindh, R.; Andersson, K.; Chevalier, T. S.; Widmark, P.-O.; Bouzida, D.; Nesbet, R.; Singh, K.; Gillan, C. J.; Carnevali, P.; Liu, B.; Pacansky, J. *Mulliken*; 2.0; IBM Research Division, Scientific & Technical Application Software, Almaden Research Center: San Jose, CA, 1996.

7) Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. *NBO*; Version 3.1.

8) Bachrach, S. M. *Reviews in Computational Chemistry*; Lipkowitz, K.; Boyd, D. B., Eds.; VCH: New York, 1994; Vol. 5, pp 171-228.

9) Power, P. P. *Inorg. Chim. Acta* 1992, **198**, 443.

10) Wehmschulte, R. J.; Ruhlandt-Senge, K.; Olmstead, M. M.; Hope, H.; Sturgeon, B. E.; Power, P. P. *Inorg. Chem.* 1993, **32**, 2983.

11) Lammertsma, K.; Ohwada, T. *J. Am. Chem. Soc.* 1996, **118**, 7247.

12) Mo, Y.; Lin, Z. *J. Chem. Phys.* 1996, **105**, 1046.

13) Kaufman, E.; Rague-Schleyer, P. *Inorg. Chem.* 1988, **27**, 3987.

14) Strictly speaking we should not say that the Al–Al σ^* orbital was occupied, but rather that we occupied an orbital of the correct symmetry to be Al–Al σ^*. If the molecule lies in the xy plane with the x axis along the Al–Al bond, then in D_2 symmetry the b_3 irreducible representation has the correct symmetry for the σ^* orbital, and b_1 has the correct symmetry for the π orbital.