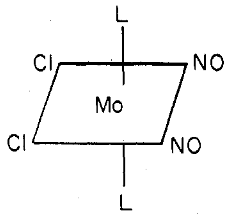
similar to that obtained by the sequential *in situ* reaction of $MoCl_5$ with NO and Ph_3P.

Oxidation of the triphenylphosphine in the above reactions could be effected either by the NO or the NOCl generated in the $MoCl_5$-NO reaction.[7,8]

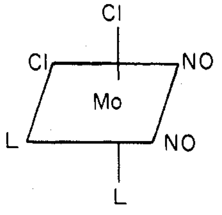
The apparent presence of $MoOCl_3(Ph_3PO)_2$ in the reaction products was surprising since we had found that $MoOCl_3$ is readily reduced by NO. To illuminate this point, we examined the reaction of $MoOCl_3(Ph_3PO)_2$ with NO in C_6H_5Cl. After a reaction period of 5 hr at room temperature, 67% of the complex was recovered. Under the same conditions, $MoOCl_3$ is essentially completely consumed. Apparently, some slow reaction does occur since not all the $MoOCl_3(Ph_3PO)_2$ was recovered. Indeed, a yellow solid was isolated in a small amount from the reaction. This material was not identified; however, the ir spectrum clearly indicated the absence of nitrosyl groups. This result indicates that the Ph_3PO ligands stabilize the $MoOCl_3$ toward reduction by NO and that the limited extent of reaction that does occur follows a different course. This would also explain why a higher proportion of $MoCl_2(NO)_2(Ph_3PO)_2$ (derived from $MoCl_2(NO)_2$) was present in the mixture obtained when the Ph_3P was added after the NO.

At present, we do not know the identity of the species exhibiting the N-O stretching vibration at 1698 cm^{-1}; it is possibly due to a molybdenum-mononitrosyl derivative. The complex $[MoCl_3(NO)]_n$, prepared by the reaction of $[MoCl_2(CO)_4]_2$ with NOCl, has been reported[9] but no details concerning its properties were given.

The Ph_3P complexes obtained from either $MoCl_5$- or $MoOCl_3$-derived $[MoCl_2(NO)_2]_n$ show two strong N-O stretching vibrations at 1789 and 1672 cm^{-1} in $CHCl_3$ solution. This suggests that the NO groups are mutually cis. Cotton and Johnson reported values for ν_{NO} of 1790 and 1670 cm^{-1} (in CH_2Cl_2) for the Ph_3P complex derived from $[MoCl_2(NO)_2]_n$ prepared by the reaction of $Mo(CO)_6$ with NOCl.[5] Our Ph_3P complexes exhibit splitting of the ν_{NO} bands in Nujol with absorptions appearing at 1790, 1775, and 1670, 1660 cm^{-1}. In the far-ir spectra of the Ph_3P complexes we find only two absorptions in the 200-400-cm^{-1} region at 288 and 306 cm^{-1}. These we attribute to the Mo-Cl stretching vibrations of cis chloro ligands. Two isomers, **1** and **2**, are possible which possess cis NO and cis Cl groups.



1



2

To assist in differentiating between **1** and **2** we prepared the diphenylmethylphosphine complex $MoCl_2(NO)_2(Ph_2PCH_3)_2$. This complex shows two strong ν_{NO} bands at 1788 and 1677 cm^{-1} (in $CHCl_3$) and two ν_{Mo-Cl} vibrations at 281 and 303 cm^{-1}. The similarity of the ν_{NO} and ν_{Mo-Cl} frequencies between the Ph_3P and Ph_2PCH_3 complexes suggests that the NO and Cl ligands are in similar environments in the two complexes. The 60-MHz ^1H nmr spectrum of the Ph_2PCH_3 complex contains a well-defined 1:2:1 triplet in the methyl proton region (δ 2.26, 4-Hz spacings). As shown by Jenkins and Shaw, this pattern is characteristic of mutually trans methylphosphine ligands.[10] The combined ir and nmr data strongly suggest a cis Cl, cis NO, trans phosphine geometry (**1**) for the Ph_2PCH_3 and, because of the similarity in its ir spectrum, the Ph_3P complex.[11]

Registry No. $MoCl_2(NO)_2(Ph_3PO)_2$, 14095-87-5; $MoCl_5$, 10241-05-1; NO, 10102-43-9; $MoCl_2(NO)_2$, 30731-17-0; $MoCl_2(NO)_2(Ph_3P)_2$, 37402-68-9; $MoCl_2(NO)_2(C_5H_5N)_2$, 14024-95-4; $MoOCl_3$, 13814-74-9; Ph_3P, 603-35-0.

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(7) M. Halmann and L. Kugel, *J. Chem. Soc.*, 3272 (1962).

(8) D. Klamann and P. Weyerstahl, *Angew. Chem.*, **75**, 574 (1963).

(9) B. F. G. Johnson, K. H. Al-Obaidi, and J. A. McCleverty, *J. Chem. Soc. A*, 1668 (1969).

(10) J. M. Jenkins and B. L. Shaw, *Proc. Chem. Soc., London*, 279 (1963).

(11) Note Added in Proof. A single-crystal X-ray diffraction study has established the cis-dichloro, cis-dinitrosyl, trans-bisphosphine configuration for $MoCl_2(NO)_2(Ph_3P)_2$ [M. O. Visscher and K. G. Caulton, *J. Amer. Chem. Soc.*, 94, 5923 (1972)].

Contribution from the Department of Chemistry, University of Western Ontario, London, Ontario, Canada

Ab Initio Calculations for the Boron-Nitrogen Analog of Cyclobutadiene[1]

N. Colin Baird

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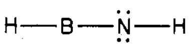
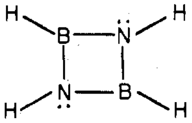
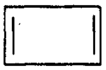
In a previous publication, *ab initio* calculations were reported for iminoborane (**1**), the boron-nitrogen analog of acetylene.[2] Dimerization of **1** can yield several interesting molecules, one of which—1,3,2,3-diazadiboretidine (**2**)—would correspond to the boron-nitrogen analog of the antiaromatic hydrocarbon cyclobutadiene **3**.[3] To determine the similarities and differences in properties between the "inorganic" and "organic" cyclobutadiene systems, *ab initio* STO-*N*G calculations have been performed for **2**.[4,5]



1



2



3

In contrast to cyclobutadiene itself, the D_{2h} planar form of **2** in which all four ring bond lengths are equal is *not* subject to Jahn-Teller distortion in the lowest singlet state and may well correspond to the optimum geometry. In fact, the D_{2h} structure may well be more stable than the "alternating" C_{2h} geometry for all type **4** ring systems in which the elec-

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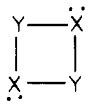
(1) Research supported by the National Research Council of Canada.

(2) N. C. Baird and R. K. Datta, *Inorg. Chem.*, **11**, 17 (1972).

(3) Other possible dimers would be the B-N analog of tetrahedrane and a planar four-membered ring with one B-B, one N-N, and two B-N bonds. The latter could also be considered an analog of **3**.

(4) (a) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969). (b) *Ab initio* calculations for a variety of B-N systems, including **2** have recently been reported: D. R. Armstrong and D. T. Clark, *Theor. Chim. Acta*, **24**, 307 (1972).

(5) The B-H and N-H bond lengths, as well as the STO exponents for the σ and π atomic orbitals, used in the calculations were taken from ref 1. Only planar structures in which all NBH angles are equal (and similarly for the BNH angles) were considered.



4

tronegativity of X is greater than that of Y to the extent that each X formally contributes two π electrons and each Y no π electrons, to the conjugated network. In particular, the highest occupied (lowest unoccupied) π MO is completely localized on the X(Y) π atomic orbitals and has energy equivalent to an X(Y) nonbonding orbital in such systems. When X = Y (as in cyclobutadiene), an exact degeneracy occurs between these two MO's, resulting in an "alternating" geometry for the lowest singlet state and in a small energy gap between the lowest singlet and triplet state.[6]

To establish the optimum geometry for 2, STO-2G calculations were performed first for a square ring; the optimum B-N distance found of 1.47 Å is 0.07 Å longer than predicted for BH_2NH_2 itself and 0.04 Å longer than for an N-B-N chain.[7] Subsequent calculations for the rectangular form of 2 and using an *average* B-N separation of 1.47 Å indicate that the D_{2h} form is stable relative to such displacements, in agreement with the arguments advanced above. Finally, calculations (again with a B-N distance of 1.47 Å) indicate that the optimum NBN angle for the D_{2h} form of 2 is 93°. These structural predictions agree reasonably well with X-ray diffraction results[8] for the hexakis(trimethylsilyl)2,4-diamino derivative of 2, in which the four almost-equal ring B-N distances are 1.45 ± 0.02 Å, and the ring NBN angle is 98°.

Although the $(BHNH)_2$ ring is expected to be destabilized by both strain and antiaromaticity effects, the optimum energy calculated[9] for 2 is some 74.3 kcal/mol more bonding than for two iminoborane monomers, in good agreement with the value of 63.3 kcal/mol calculated by Armstrong and Clark.[4b] In contrast, *ab initio* calculations predict that $(BH_2NH_2)_2$ is only $\sim$3 kcal/mol more stable than two aminoborane monomers.[10] It is evident from these results that both B-N coordinate covalent and π bonds are weak relative to the "normal" σ bonds formed between trivalent boron and nitrogen atoms.

To test the Huckel method prediction that the antiaromaticity of type 4 four-membered rings decreases as the electronegativity difference between X and Y increases,[11] SCF wavefunctions and energies were redetermined for 2 and for BH_2NH_2 using a basis set which does *not* include a $2p_\pi$ orbital on boron (and thus localizes the π electrons on the nitrogen atoms). In contrast to cyclobutadiene, for which the delocalization energy is predicted by semiempirical calculations to be zero or even negative,[11,12] the π-bonding energy calculated for 2 is predicted to be 11 kcal/mol more stabilizing than for two isolated boron-nitrogen π bonds. Thus, the residual antiaromaticity for 2 must be slight.

A crude estimate of 53 kcal/mol for the σ-bond strain energy in 2 was deduced by comparison of the total bonding energy in the $(BHNH)_2$ ring (calculated with the π electrons localized on N) with the effective energies for four B-N, two B-H, and two N-H σ bonds; the latter were obtained from total energies for BH_2NH_2, $NH_2B(H)NH_2$, and $BH_2N(H)BH_2$ (again calculated with localized π electrons) by assuming that each type of σ-bond energy remains the same in the different molecules.[13] While the rather high strain energy calculated for 2 gains some support from the value of 55.4 kcal/mol (deduced from semiempirical calculations and the experimental heat of formation) for the cyclobutadiene derivative biphenylene,[14] previous experience with the STO-3G method indicates that strain energies are usually overestimated.[15]

As expected from the orbital energy arguments above, the highest occupied MO for 2 is localized on the nitrogen $2p_\pi$ orbitals and has a rather low stabilization (predicted ionization potential 8.1 eV, compared to 11.1 eV for BH_2NH_2).[16] The vertical excitation energy to the lowest triplet state T_1 is also relatively low at 119 kcal/mol (compare to 157 for BH_2NH_2) since the transition involved is from a nonbinding N to a nonbonding B π orbital. The predicted S_0-T_1 split for *square* cyclobutadiene is only $\sim$15 kcal/mol.[6]

Registry No. $(BHNH)_2$, 18464-81-8.

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[6] *Ab initio* calculations for various geometries and states of cyclobutadiene have been reported: R. J. Buenker and S. D. Peyerimhoff, *J. Chem. Phys.*, **48**, 354 (1968).

[7] N. C. Baird, to be submitted for publication. Calculations for BH_2NH_2 indicate that bond lengths calculated at the STO-2G level are $\sim$0.01 Å longer than those predicted by STO-3G expansions. See also N. C. Baird, *Chem. Phys. Lett.*, **6**, 61 (1970).

[8] V. H. Hess, *Acta Crystallogr., Sect. B*, **25**, 2342 (1969).

[9] All energy values quoted henceforth are based upon STO-3G calculations using the optimum calculated geometry for the ring (R_{BN} = 1.47 Å, NBN angle = 98°). The total energy for 2 is −158.6912 au.

[10] (a) D. R. Armstrong and P. G. Perkins, *J. Chem. Soc. A*, 2748 (1970). (b) Although the errors in the total bonding energies for both 1 and 2 are expected to be rather large due to correlation effects, the calculated dimerization energy should be of the correct order of magnitude since both 1 and 2 are closed-shell species and since the total number of bonds does not change in the dimerization process.

[11] See for example the calculations in (a) N. C. Baird and M. A. Whitehead, *Can. J. Chem.*, **45**, 2059 (1967); (b) D. P. Craig, *J. Chem. Soc.*, 997 (1959).

[12] According to the Huckel method including overlap integrals *S*, the total π-bonding energy for two ethylenes is $4\beta/(1 + S)$ whereas that for D_{4h} cyclobutadiene is only $4\beta/(1 + 2S)$.

[13] This assumption is supported by the calculated overlap populations[7] which do not vary significantly from one chain to another.

[14] See C. de Llano, Ph.D. Thesis, University of Texas, Austin, Texas, 1968, p 134. The strain energy quoted by de Llano has been corrected in the present study on the basis of the revised heat of vaporization reported by E. Morawetz, *J. Chem. Thermodynamics*, 4, 455 (1972).

[15] W. J. Hehre, R. Ditchfield, L. Radom, and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 4796 (1970).

[16] Armstrong and Clark[4b] predicted an ionization potential of 10.9 eV for 2.

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Kinetics of Copper Incorporation into Porphyrins in Acetic Acid

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Acetic acid has been used as a solvent to study the kinetics of incorporation of Cu, Fe, Co, Ni, and Mn species into porphyrin molecules.[1-3] In two separate studies, the rate laws for copper acetate insertion were found to be first order in porphyrin (either hematoporphyrin[1] or tetrapyridylpor-

[1] D. J. Kingham and D. A. Brisbin, *Inorg. Chem.*, **9**, 2034 (1970).

[2] D. A. Brisbin and R. J. Balahura, *Can. J. Chem.*, **46**, 3431 (1968).

[3] E. I. Choi and E. B. Fleischer, *Inorg. Chem.*, **2**, 94 (1963).