also calculated CO_3 in which the unique CO bond length was 1.15 Å and the symmetry equivalent bond lengths were 1.40 Å (Moll's[3] parameters). The unique angle found by Gimarc and Chou occurred around 90°. We have also carried out INDO calculations for this CO_3 species with the results that the unique angle occurs in the vicinity of 60–55°, again consistent with a closed-ring structure for this compound.

Conclusions

The two quantum-mechanical methods used in this work confirm the deductions of Moll, *et al.*,[3] that the CO_3 molecule belongs to the C_{2v}-point group, although we have not investigated the stability of species IV–VI. On the basis of our calculations, one can relate the adoption of the C_{2v} structure to the Jahn–Teller effect; the trigonal (D_{3h}) arrangement is unstable because the singlet wave function is degenerate.

The bond populations provided by both methods suggest a closed-ring structure for the compound, similar to the one found experimentally for cyclopropanone.[13,14] The equilibrium bond angle calculated by the XHMO method appears somewhat large for such a structure, whereas the INDO angle is more reasonable; it is possible that the use of two different bond lengths for the two types of CO bonds would reduce the discrepancy between the two methods on this point.

Acknowledgments. A grant of computer time at the Courant Institute Computation Center of New York University is gratefully acknowledged. We also wish to express our sincere thanks to Dr. D. L. Beveridge for making available to us his INDO program.

Chelate Adducts of a Difunctional Lewis Acid. 1,2-Bis(difluoroboryl)ethane. III[1,2]

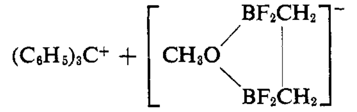
Michael J. Biallas

Contribution from the Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115. *Received June 23, 1969*

Abstract: Chelate adducts are formed when $F_2BCH_2CH_2BF_2$ reacts either with triphenylmethylamines in CH_2Cl_2 or with 1,3,5-cycloheptatrienyl-7 methyl ether; *e.g.*, see eq 5. Unchelated 1:1 adducts are formed when $F_2BCH_2CH_2BF_2$ reacts with triphenylmethylamines in a nonpolar solvent or with 1,3,5-cycloheptatrienyl-7-N,N-dimethylamine; *e.g.*, see eq 3.

The difunctional Lewis acid 1,2-bis(difluoroboryl)ethane reacts with triphenylmethyl ethers to produce "chelated" 1:1 adducts.[1] In these reactions a C–O bond is cleaved in order to form (a) a resonance-stabilized organic cation, and (b) an anion which has two boron atoms coordinated to a single oxygen atom. For example

$(C_6H_5)_3COCH_3 + BF_2CH_2CH_2BF_2 \longrightarrow$



(1)

The generality of this reaction has now been evaluated by examining the reactions of 1,2-bis(difluoroboryl)ethane with triphenylmethylamines, 1,3,5-cycloheptatrienyl-7 methyl ether, and 1,3,5-cycloheptatrienyl-7-N,N-dimethylamine. This group of Lewis bases allows variation in the identity of both organic cation and the donor atom.

Experimental Section

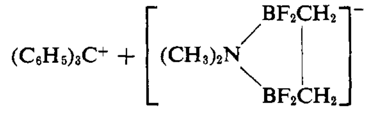
Materials. The following compounds were prepared according to procedures given in the literature: triphenylmethylamine, mp 103° (lit.[3] 103°); N,N-dimethyltriphenylmethylamine (*via* an analogous procedure) (*Anal.* Calcd: C, 87.76; H, 7.37, N, 4.87. Found: C, 87.67; H, 7.37; N, 4.52); 1,3,5-cycloheptatrienyl-7 methyl ether,[4] and 1,3,5-cycloheptatrienyl-7-N,N-dimethylamine,[5] (the latter two compounds were characterized *via* nmr[6]). All solvents were stored over molecular sieves and distilled before use.

Techniques. Most of the compounds used in these studies were air sensitive, so manipulations were performed on a vacuum line or in a glove bag. Tared samples of each donor were dissolved in the chosen solvent, and a known amount of the difunctional Lewis acid was added by means of a calibrated bulb. Solution mixing was done by a solenoid stirrer. After completion of the reaction, solvent and excess acid (if any) were removed and analyzed. Visible and ir spectra of the adducts (all were solids) were obtained as both hydrocarbon and halocarbon mulls on a Cary Model 14 and a Beckman IR-12 instrument, respectively. C, H, and N analyses were obtained on a Perkin-Elmer 240 analyzer, and nmr spectra were obtained on a Varian A-60 spectrometer.

Results and Discussion

Triphenylmethylamines. A chelate adduct is obtained exclusively when N,N-dimethyltriphenylmethylamine reacts with 1,2-bis(difluoroboryl)ethane in methylene chloride solvent, *i.e.*

$(C_6H_5)_3CN(CH_3)_2 + BF_2CH_2CH_2BF_2 \xrightarrow{CH_2Cl_2}$



(2)

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[1] Part II: D. F. Shriver and M. J. Biallas, *J. Amer. Chem. Soc.*, **89**, 1078 (1967).

[2] Presented in part at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., Spring 1969.

[3] C. A. Krause and R. Rosen, *J. Amer. Chem. Soc.*, **47**, 2739 (1925).

[4] W. von E. Doering and L. H. Knox, *ibid.*, **76**, 3203 (1954).

[5] W. von E. Doering and L. H. Knox, *ibid.*, **79**, 352 (1957).

[6] G. W. Borden, O. L. Chapman, R. Swindell, and T. Tezuka, *ibid.*, **89**, 2979 (1967).

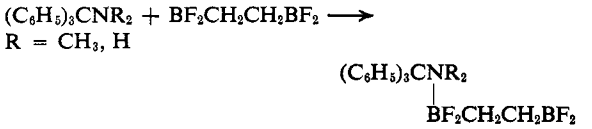
Table I. Acid–Base Stoichiometry

Base	Solvent	Amount, mmol	Acid added, mmol	Acid recovered,[a] mmol	Acid reacted,[b] mmol	Stoichiometry, acid–base
$(C_6H_5)_3CN(CH_3)_2$	CH_2Cl_2	0.0445	0.0574	0.0132	0.0450	1.00
$(C_6H_5)_3CN(CH_3)_2$	Toluene	0.1506	0.1817	0.0307		1.00
$(C_6H_5)_3CNH_2$	CH_2Cl_2	0.1214	0.1650	0.0407	0.1209	1.01
$(C_6H_5)_3CNH_2$	Toluene	0.0628	0.0839	0.0220		0.99
$C_7H_7OCH_3$	Pentane	0.1770	0.2500	0.0703		1.01
$C_7H_7OCH_3$	Pentane	0.0804	0.1074		0.0791	0.99
$C_7H_7N(CH_3)_2$	Pentane	0.0891	0.0955	0.0136		0.92
$C_7H_7N(CH_3)_2$	Pentane	0.0878	0.1051		0.0813	0.93

[a] As determined by weight of $(CH_3)_3N$ adduct of excess acid. [b] As determined by hydrolysis and subsequent boric acid–mannitol titration of products.

As previously, this is verified by the appearance of the yellow color due to the characteristic twin absorption peaks of the triphenylmethyl cation (410 and 430 mμ), as well as the shift of the B–F stretching frequencies characteristic of trigonally coordinated boron (1350–1380 cm^{-1}) to those characteristic of tetrahedrally coordinated boron (*ca.* 1000 cm^{-1}).[1] The stoichiometry of the reaction is also established by several other analytical methods (Table I).

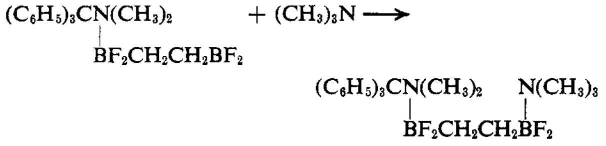
When triphenylmethylamine, a base with less severe steric requirements, reacts, the chelation reaction is incomplete; a second 1:1 adduct is also obtained. The second product can be obtained exclusively from either amine when a hydrocarbon is used as the solvent. The lack of color in the isolated adduct demonstrates that C–N bond cleavage does not occur, and the presence of absorption peaks in both B–F stretching regions indicated that only one boron atom per acid molecule is coordinated. The equation for this reaction is



$$(C_6H_5)_3CNR_2 + BF_2CH_2CH_2BF_2 \longrightarrow \underset{\textstyle BF_2CH_2CH_2BF_2}{(C_6H_5)_3CNR_2} \qquad R = CH_3, H \tag{3}$$

The yellow color of the triphenylmethyl cation can be generated in solution by cooling the reaction mixture.[7] Also, the colorless adduct gradually reverts to a yellow solid when allowed to stand at room temperature in the absence of solvent. These changes tend to indicate that the chelation reaction is favored in somewhat polar solvents, but it is not favored in nonpolar solvents. This is reasonable for a reaction in which a net gain of charged species occurs.

An additional demonstration that one end of the acid molecule remains uncoordinated is obtained by the addition of trimethylamine to the reaction mixture. The following reaction occurs.



$$\underset{\textstyle BF_2CH_2CH_2BF_2}{(C_6H_5)_3CN(CH_3)_2} + (CH_3)_3N \longrightarrow (C_6H_5)_3CN(CH_3)_2\ \ N(CH_3)_3 \text{ joined through } BF_2CH_2CH_2BF_2 \tag{4}$$

As expected, the product obtained *via* reaction 4 displays no ir absorption in the 1350–1380-cm^{-1} region.[8]

In the chelate formation reactions with triphenylmethylamines the yellow color of the triphenylmethyl cation appears only several minutes after the reaction mixture warms to room temperature. The color also increases in intensity over a period of hours. This behavior is in contrast to that of the triphenylmethyl ethers which appear to reach equilibrium within minutes.

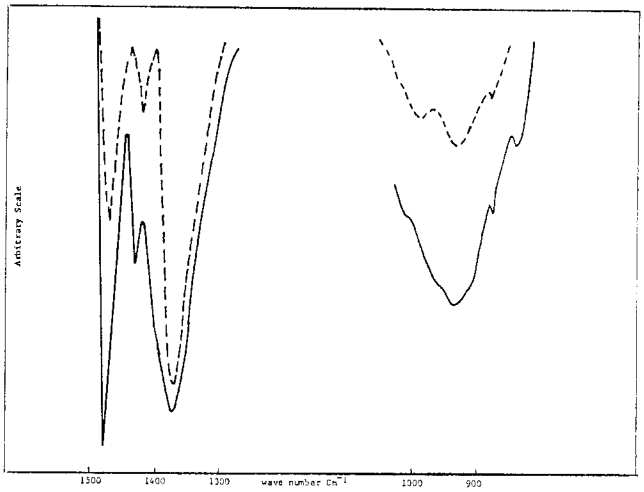
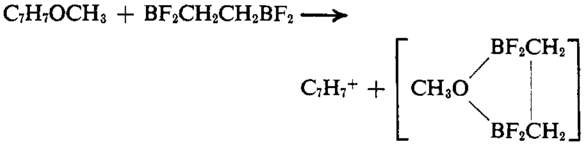


Figure 1. Partial ir spectrum of $BF_2CH_2CH_2BF_2$–$C_7H_7N(CH_3)_2$ adduct: $C_7H_7^+$ absorption, 1472 cm^{-1} (ref 10); trigonal B–F absorption, 1380 cm^{-1} (ref 1); tetrahedral B–F absorption, 940 cm^{-1} (ref 1); -----, 0.5 hr after mixing; ———, 16 hr after mixing.

1,3,5-Cycloheptatrienyl-7 Methyl Ether. A chelate adduct precipitates immediately from all nonreactive solvents when this ether reacts with the difunctional Lewis acid.[9] The reaction is



$$C_7H_7OCH_3 + BF_2CH_2CH_2BF_2 \longrightarrow C_7H_7^+ + \left[CH_3O \begin{matrix} \diagup BF_2CH_2 \\ \diagdown BF_2CH_2 \end{matrix} \right] \tag{5}$$

The ir spectrum showed the presence of tropenium ion[10] and tetrahedrally coordinated boron. The

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[7] Even though cooling the reaction mixture increases the $BF_2CH_2CH_2BF_2$ concentration in solution, the same 1:1 adduct is always isolated, provided that the mole ratio of acid–base is greater than 1:1.

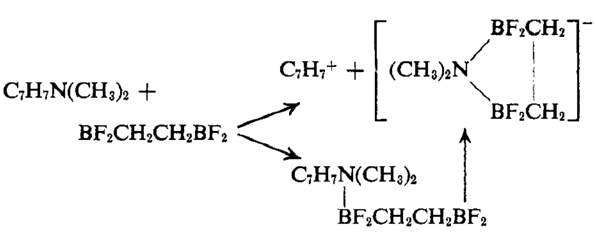
[8] Exact stoichiometric values were not obtainable for this reaction. Presumably this was due to the partial displacement of $(C_6H_5)_3CN(CH_3)_2$ by the more basic $(CH_3)_3N$. However, the salient features of the reaction, (a) a visible change in the appearance of the adduct, (b) an over-all gain in weight, (c) no change in boron atoms contained, and (d) the above-mentioned details of the ir spectrum, indicate the validity of eq 4.

[9] The preparation of this particular chelated adduct has been incorrectly reported in an earlier publication [M. J. Biallas and D. F. Shriver, *J. Amer. Chem. Soc.*, **88**, 375 (1966)]. A reinvestigation of the compound previously prepared showed it to be identical with an authentic sample of the thermally more stable compound, tropenium fluoroborate, $C_7H_7^+$ BF_4^- [prepared according to the method of H. J. Dauben, L. R. Hannen, and K. M. Harmon, *J. Org. Chem.*, **25**, 1442 (1960)].

[10] K. M. Harmon and S. Davis, *J. Amer. Chem. Soc.*, **84**, 4359 (1962).

chelate adduct was also characterized by stoichiometric measurements (Table I). The adduct decomposes above 0° to a blue-green gum over a period of hours.

1,3,5-Cycloheptatrienyl-7-N,N-dimethylamine. A colorless precipitate is formed when this base reacts with 1,2-bis(difluoroboryl)ethane in hydrocarbon solvents. (Decomposition occurs very rapidly in methylene chloride, precluding the use of this solvent.) The ir spectrum of this product showed peaks characteristic of the tropenium ion as well as both trigonal and tetrahedrally coordinated boron. Upon standing overnight at 0° the tropenium ion and tetrahedral B–F bands were enhanced, and the trigonal B–F bonds were diminished in relative proportions (Figure 1); thus, it appears that the adduct is a mixture of 1:1 adducts. These compounds are related by the equations



(6)

Thus, as noted previously with the triphenylmethyl compounds, the chelation reaction of the N donor is much slower than the corresponding reaction of the O donor. Presumably, this phenomenon occurs since the amide ions, R_2N^-, are poorer leaving groups than the alkoxide ions, RO^-.[11] This effect is currently under further study.

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(11) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York, N. Y., 1965, p 164.

Structural Characterization of a Tetranuclear Rhodium Complex, $[Rh_2Cl_2(CO)(C_2H_5C_2C_2H_5)_2]_2$, Containing a Coordinate–Covalent Electron-Pair Rhodium(I)–Rhodium(III) Bond

Linda R. Bateman,[1a,2] Peter M. Maitlis,[1b] and Lawrence F. Dahl[1a]

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706, and the Department of Chemistry, McMaster University, Hamilton, Ontario, Canada. *Received January 9, 1969*

Abstract: The rhodacyclopentadiene complex $[Rh_2Cl_2(CO)(C_2H_5C_2C_2H_5)_2]_2$, produced in the reaction of 3-hexyne with chlorodicarbonyl rhodium dimer, crystallizes with four molecules arranged in a triclinic unit cell of symmetry $B\bar{1}$ such that two half-molecules comprise the crystallographically asymmetric unit. The dimensions of this centrosymmetric B-centered cell are a = 16.78 Å, b = 20.45 Å, c = 9.60 Å, α = 96.4°, β = 89.5°, and γ = 102.7°. The structure consists of discrete $[Rh_2Cl_2(CO)(C_2H_5C_2C_2H_5)_2]_2$ molecules in which two *cis*-tetraethylbutadiene fragments (each arising from the polymerization of two diethylacetylene molecules) are each coordinated to a Rh(III) by two σ bonds to give a rhodacyclopentadiene ring system and to a Rh(I) by two μ-type bonds. Two symmetrically bridging chlorine atoms interconnect each Rh(III) of a rhodacyclopentadiene ring to the Rh(I) which is not μ-bonded to that ring. Each Rh(I) has a localized square-planar environment through linkage with the midpoints of the two olefinic groups and the two chlorine atoms, while each Rh(III) has a localized square-pyramidal environment through bonding with the apical carbonyl group and with the two basal terminal diene-carbon and two chlorine atoms. The resulting molecular configuration, required to have a crystallographic center of symmetry, ideally conforms to C_{2h} symmetry. The unprecedented structural feature found in this complex is a coordinate–covalent Rh(I)–Rh(III) bond which is necessitated in order for each of the two centrosymmetrically related Rh(III) atoms per molecule to attain a coordinatively saturated electronic configuration. This proposed electron-pair metal–metal bond is in accord not only with the short Rh(I)–Rh(III) distance of 2.70 Å being similar to rhodium–rhodium distances in other organorhodium complexes (where molecular stabilization by Rh–Rh bonds is obvious), but also with the stereochemical similarity of this complex to ferracyclopentadiene complexes which also possess coordinate–covalent metal–metal bonds. The chemical implications of the two Rh(I)–Rh(III) bonds in the $[Rh_2Cl_2(CO)(C_2H_5C_2C_2H_5)_2]_2$ molecule are discussed.

The reactions of metal carbonyls with acetylenes have resulted in a large variety of organometallic complexes with unusual structural features and novel types of bonding.[3-6] Maitlis, McVey, and Kang[6] found the reaction of diethylacetylene with chlorodicarbonylrho-

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(1) (a) University of Wisconsin; (b) McMaster University.

(2) This manuscript is based in part on the Ph.D. dissertation of L. R. B., University of Wisconsin, Jan 1969.

(3) M. L. H. Green, "Organometallic Compounds," Vol. 2, "The Transition Elements," Methuen and Co., London, 1968, pp 289–311, and references therein.

(4) W. Hübel, "Organic Synthesis *via* Metal Carbonyls," I. Wender and P. Pino, Ed., Interscience Publishers, New York, N. Y., 1968, pp 273–342, and references therein.

(5) F. L. Bowden and A. B. P. Lever, *Organometal. Chem. Rev.*, **3**, 227 (1968).

(6) (a) P. M. Maitlis, S. McVey, and J. W. Kang, Proceedings of the First International Symposium on New Aspects of the Chemistry of Metal Carbonyls and Derivatives, Venice, Italy, Sept 1968, D-2; (b) J. W. Kang, S. McVey, and P. M. Maitlis, *Can. J. Chem.*, **46**, 3189 (1968), and references contained therein.