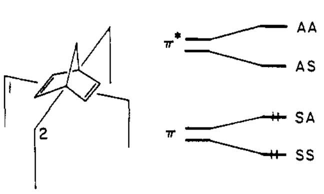


Figure 1. Norbornadiene levels before and after interaction through space. Levels are classified as symmetric (S) or antisymmetric (A) with respect to the mirror planes defined at left.

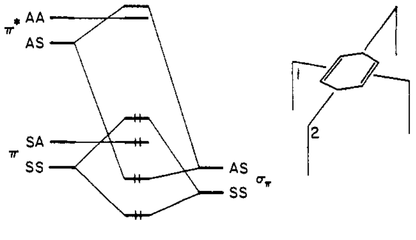


Figure 2. Interaction diagram for cyclohexadiene. The symmetry elements are the mirror planes defined at right. In the interaction diagram the π and π* levels are placed at left and the CH_2 σ orbitals of the correct symmetry to mix with the π levels are at right.

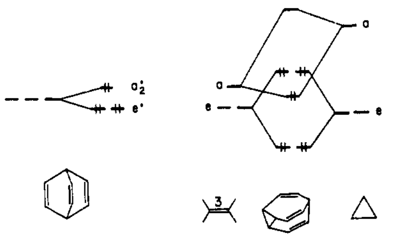
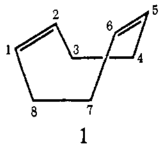


Figure 3. Interaction diagrams for barrelene (left) and bullvalene (right). For the latter we consider the mixing of the three ethylene π levels with the Walsh orbitals of the cyclopropane ring.

In 1,5-cyclooctadiene (**1**) the experimental splitting between the two π bands is less than 0.2 eV.[11] The



1

through-space interaction must be significant in the boat conformation,[12] as evidenced by a calculation on a model of two ethylenes positioned identically with the double bonds in **1**. The calculated splitting is 1.67 eV, with SS lower, as expected. In cyclooctadiene itself there is superimposed an interaction with the SS combination of the 3–4, 7–8 σ bonds, ideally oriented for coupling the two π-electron systems.[1d,13] This through-bond coupling destabilizes the π-SS combination, lowering the level splitting to a computed 0.48 eV. The latter value is sensitive to the geometry assumed for **1**. In a chair conformation the through-space interaction is absent and the through-bond coupling dominates.

Acknowledgment. This work was supported by the National Science Foundation (GP 8013), the National Institutes of Health (GM 13468), and the Schweizerische Nationalfonds Project No. 4651.[14]

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[11] E. Heilbronner, to be published.

[12] Cyclooctadiene conformations are discussed by J. D. Dunitz in "Perspectives in Structural Chemistry," Vol. II, J. D. Dunitz and J. A. Ibers, Ed., John Wiley & Sons, Inc., New York, N. Y., 1968, p 1.

[13] R. Hoffmann, A. Imamura, and W. J. Hehre, *J. Amer. Chem. Soc.*, 90, 1509 (1968).

[14] This is contribution No. 5 to Applications of Photoelectron Spectroscopy; for contribution No. 4 see E. Haselbach, J. A. Hashmall, E. Heilbronner, and V. Hornung, *Angew. Chem.*, **18**, 897 (1969).

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Metal Complexes As Ligands. A New Class of Polynuclear Dithiolate Complexes

Sir:

As an approach to the systematic synthesis of coordination oligomers we have been investigating[1] the possibility of using anionic coordination complexes as ligands for coordinatively unsaturated, metal-containing Lewis acids. We have noted that, in weakly coordinating solvents, solutions of the transition metal dithiooxalate complexes,[2–4] $M^{II}(Dto)_2^{2-}$ (I), where M = Ni, Pd, Pt, Cu, or Fe, react with the R_xSnCl_{4-x} species ($x = 0, 1, 2$; R = *n*-butyl). These reactions are always accompanied by pronounced color changes which occur as a result of a bathochromic shift of the first (low en-

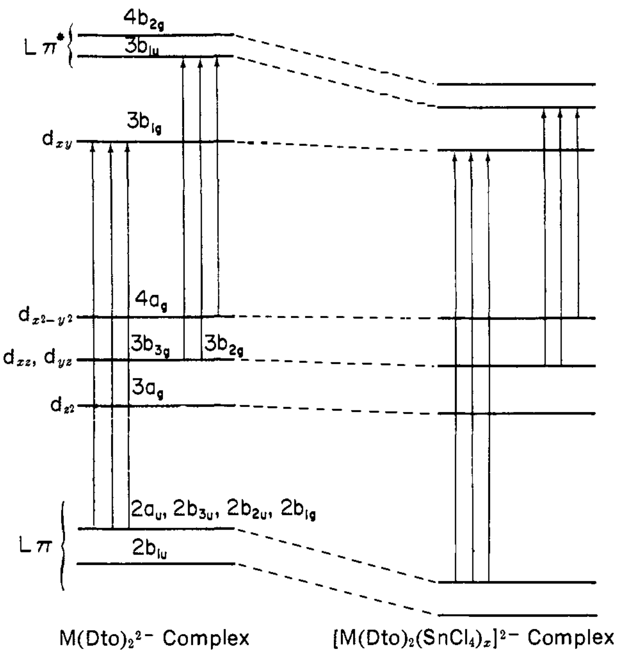

Figure 1. Energy level diagram for $M(Dto)_2^{2-}$ (ref 10) and $[M(Dto)_2(SnCl_4)_x]^{2-}$ complexes.

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[1] D. Coucouvanis, paper presented at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969.

[2] C. S. Robinson and H. O. Jones, *J. Chem. Soc.*, 62 (1912).

[3] F. A. Dwyer and A. M. Sargeson, *J. Amer. Chem. Soc.*, 81, 2335 (1959).

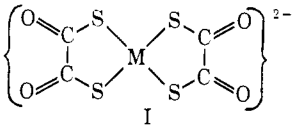
[4] (a) E. G. Cox, W. Wardlaw, and K. C. Webster, *J. Chem. Soc.*, 1475 (1935); (b) the benzyl triphenylphosphonium ($BzPh_3P^+$) salts of the Ni(II), Pd(II), Pt(II), and Cu(II) dithiooxalato complexes are X-ray isomorphous. The structure of the $K_2Ni(Dto)_2$ complex has been determined (ref 4a). The nickel(II) ion is four-coordinate and sulfur bonded in the rigorously planar complex anion.

Table I. Physical Properties of the $[M(Dto)_2(SnCl_{4x})]^{2-}$ Complexes

Complex	Mp, °C	% C, calcd (found)	% H, calcd (found)	ν_{C-O}, cm^{-1} [a,b]	E_{red}, V[c]	λ_{max}, cm^{-1} ($\epsilon \times 10^{-3}$)[d,e]
$(BzPh_3P)_2[Ni(Dto)_2(SnCl_4)_2]$	219–220	42.4 (42.37)	2.88 (2.86)	1480 (br)	−1.12 −1.48	16,000 (6.3) 18,750 (4.5) 20,400 (3.4)
$(BzPh_3P)_2[Pd(Dto)_2(SnCl_4)_2]$	219–221	41.2 (41.49) (41.10)	2.79 (2.96) (2.86)	1460 (br)	−1.39 −1.73	22,200 (7.8) 24,100 (12.8) 27,400 (8.2)
$(BzPh_3P)_2[Ni(Dto)_2SnCl_4]$	163–164	51.2 (51.13)	3.48 (3.28)	1629 (s) 1590 (w) 1488 (s) 1456 (s)	−0.85	15,150 (3.2) 15,900 (3.2) 18,200 (1.5)
$(BzPh_3P)_2[Pd(Dto)_2SnCl_4]$	168–169			1620 (s) 1580 (m) 1480 (s) 1450 (s)		
$(Ph_4As)_2[Pd(Dto)_2SnCl_4]$	201–202	45.4 (45.45)	2.91 (2.81)	1623 (s) 1580 (m) 1480 (s) 1450 (s)	−0.78	22,500 (5.3) 23,500 (5.2) 27,000 (3.6)

[a] Nujol mulls between sodium chloride plates. [b] Reference 6. [c] Cyclic voltammetry in CH_2Cl_2 *vs.* Ag|AgI. Reference 13, *n*-Bu_4NClO_4 was used as the supporting electrolyte. First oxidation wave of $Ni(MNT)_2^{2-}$ was observed at +0.19 V. The voltage scan rate was 0.5 V/sec. [d] Spectra obtained in CH_2Cl_2 solutions. [e] The first (low energy) absorptions occur at 17,700, 19,900, and 20,000 cm^{-1} in the $Ni(Dto)_2^{2-}$ complex, and at 25,100 cm^{-1} in the $Pd(Dto)_2^{2-}$ complex.

ergy) high intensity ($2{,}000 < \epsilon < 12{,}000$) absorption band found in the spectra of the $M(Dto)_2^{2-}$ complexes (Table I). We were able to isolate[5] solid crystalline

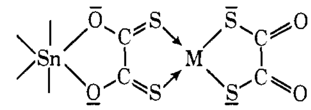


I

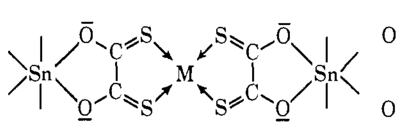
products of the composition $[M(Dto)_2SnCl_4]C_2$ (A) and $[M(Dto)_2(SnCl_4)_2]C_2$ (B) where M = Ni, Pd and C = $C_7H_7(C_6H_5)_3P^+$.

A typical synthetic procedure for the compounds of type B consists of the reaction between an acetone suspension of the $M(Dto)_2C_2$ complex and an acetone solution of $SnCl_4 \cdot 5H_2O$ in the appropriate molar ratios. The intensely colored acetone solutions thus obtained on dilution with either hexane or ether gave the crystalline products. Recrystallization could be affected from CH_2Cl_2–pentane mixtures. Compounds of type A were obtained in a similar manner, using acetonitrile as a reaction medium and ether as a diluent. Table I summarizes some of the physical properties of these complexes. The compounds A and B are diamagnetic, 2:1 electrolytes in nitromethane, and readily dissociate (as evidenced by color changes) in the presence of such donor solvents as pyridine, water, and dimethyl sulfoxide. The compounds of the type A are X-ray isomorphous and show two sets of carbonyl absorptions (Table I). The multiple carbonyl vibrational frequencies and their energies relative to those of the parent $M(Dto)_2^{2-}$ complexes[6] could indicate an asymmetric structure in which the $M(Dto)_2^{2-}$ complexes are chelated to the $SnCl_4$ molecule (IIa). The compounds of type B are also X-ray isomorphous; however, their infrared spectra show only one set of carbonyl absorptions (Table I). The compound $[Pd(Dto)_2(SnCl_4)_2](BzPh_3P)_2$ crystallizes as orange needles in space group $P2_1/c$ with two molecules in the unit cell. The experimentally determined density of 1.72 g/cm^3 requires a molecular weight of 1562 ± 20 for this compound (calcd mol wt, 1573.8).

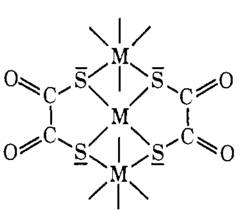
On the basis of the above data and space group symmetry requirements[7] the centrosymmetric planar structure IIb is proposed for the 2:1 complexes. The alternative structure IIc is not very likely, since a similar sulfur bonded structure thought to prevail in the $[Ag(PPh_3)_2]_2[Ni(Dto)_2]$ complex[8] shows the carbonyl absorptions at considerably higher frequencies (*ca.* 1660 cm^{-1}). Although the $M(Dto)_2^{2-}$ complexes formally can be classified with the 1,2-dithiolate complexes, they do not undergo the thoroughly studied,[9] *reversible* electron-transfer reactions typical of the 1,2-dithiolate complexes. To a large extent the redox properties of the 1,2-dithiolate complexes are centered on the ligands and have been rationalized in terms of a thiol–thione interconversion (III). The apparent anomaly found with the



IIa



IIb



IIc

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(5) A continuous variations study in acetonitrile showed that with *n*-$BuSnCl_3$ the $Ni(Dto)_2^{2-}$ and $Pd(Dto)_2^{2-}$ complexes formed 1:1 adducts. Solid products could not be obtained from these solutions, however, and all attempts to isolate the adducts produced viscous intensely colored oils.

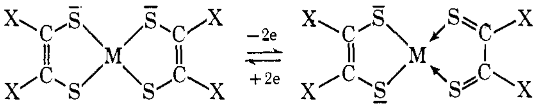
(6) (a) The C–O absorptions in $Ni(Dto)_2^{2-}$, $Cu(Dto)_2^{2-}$, and $Pd(Dto)_2^{2-}$ occur, respectively, at 1605, 1588; 1620, 1585; and 1618, 1590 cm^{-1}; (b) a dimeric structure similar to that found with many 1:1 oxo adducts of $SnCl_4$ (J. Lindquist, "Inorganic Adduct Molecules of Oxo-Compounds," Academic Press, New York, N. Y., 1963, p 50) cannot be ruled out at present.

(7) The space group P21/c requires that the two molecules in the unit cell occupy centers of symmetry.

(8) D. Coucouvanis and D. Piltingsrud, paper in preparation.

(9) J. A. McCleverty, *Progr. Inorg. Chem.*, 10, 49 (1968).

$M(Dto)_2{}^{2-}$ complexes could be due to the presence of the carbonyl groups which do not allow a formal thiol-thione interconversion. We have observed that the



III

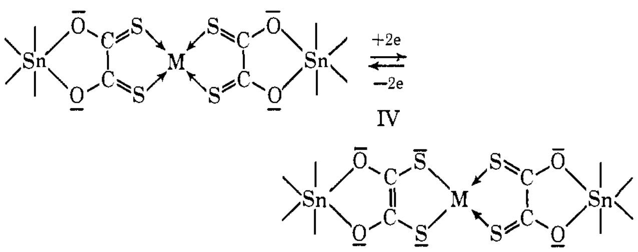
$SnCl_4$ adducts of the $M(Dto)_2{}^{2-}$ complexes undergo the following *reversible* one-electron reductions.

$$[M(Dto)_2(SnCl_4)_2]^{2-} \underset{-e}{\overset{+e}{\rightleftharpoons}} [M(Dto)_2(SnCl_4)_2]^{3-} \underset{-e}{\overset{+e}{\rightleftharpoons}} [M(Dto)_2(SnCl_4)_2]^{4-}$$

and

$$[M(Dto)_2SnCl_4]^{2-} \underset{-e}{\overset{+e}{\rightleftharpoons}} [M(Dto)_2SnCl_4]^{3-}$$

These results can be rationalized, by analogy to the 1,2-dithiolate complexes, if we consider the thioketonic form IV as a formal description for the structure of the adducts. The fact that only one one-electron reduction occurs with the 1:1 adducts, while two separate one-electron reductions occur with the 2:1 adducts, suggests that in addition to the ligands, the tin ions are also involved in the observed processes. More definitive information regarding the electronic structures of these complexes must await an epr study of the reduction products. The first set of low energy high intensity absorption bands in the visible spectra of the $M(Dto)_2{}^{2-}$ complexes (Table I) has been assigned by Gray and coworkers[10] to M→L charge-transfer processes. This assignment is consistent with the observed bathochromic shifts of these bands in the R_xSnCl_{4-x} adducts, since the introduction of additional metal ions to the $M(Dto)_2{}^{2-}$ complexes is expected primarily to lower the energy of the π and π^* ligand orbitals (Figure 1).[11] The hypsochromic shifts expected for the second set of L→M charge-transfer bands was also observed in the spectrum of the $Ni(Dto)_2{}^{2-}(SnCl_4)$ adduct. Electronic effects similar to the above have been reported by Shriver and coworkers[12] in a study of the BX_3 adducts (X = CH_3, Br, Cl, F) of the $Fe(phen)_2(CN)_2$ complex. Similar changes in the spectra of the $M(Dto)_2{}^{2-}$ complexes are also brought about with such Lewis acids as Cl_2SbR_3, R_3SiCl, $ZrCl_4$, $Ti(C_5H_5)_2Cl_2$, etc.[13] A detailed study of these compounds is currently in progress.



IV

Acknowledgment. This study was supported, in part, by a grant (PRF No. 1775-G3) from the Petroleum Research Fund, administered by the American Chemical Society.

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[10] A. R. Latham, V. C. Hascall, and H. B. Gray, *Inorg. Chem.*, **4**, 788 (1965).

[11] Shriver and coworkers (ref 12) have calculated the orbital energies of $CN^- + H^+$ as a function of the N-H distance and found a decrease of the σ, σ^*, π, and π^* orbital energies as the N-H distance decreased. The same workers reported that changes in the d-d transitions in Lewis acid adducts of cyanide complexes are at most about fourfold less than changes in the charge-transfer bands.

[12] (a) D. F. Shriver, S. A. Shriver, and S. E. Anderson, *Inorg. Chem.*, **4**, 725 (1965); (b) J. J. Rupp and D. F. Shriver, *ibid.*, **6**, 755 (1967), and references therein.

[13] F. Röhrscheid, A. L. Balch, and R. H. Holm, *ibid.*, **5**, 1542 (1966).

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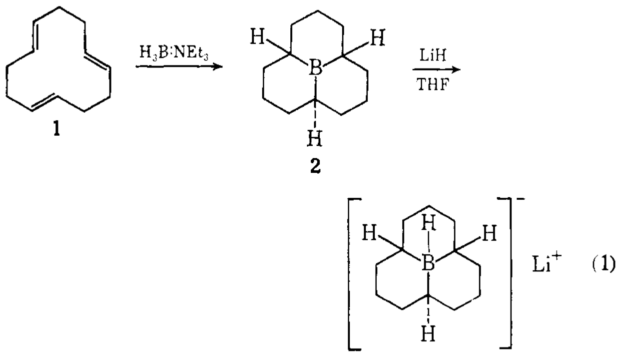
Lithium Perhydro-9b-boraphenalylhydride. An Active Reducing Agent of Unusually High Stereoselectivity for the Reduction of Cyclic and Bicyclic Ketones

Sir:

Lithium hydride readily reacts with *cis,cis,trans*-perhydro-9b-boraphenalene[1,2] in refluxing tetrahydrofuran (eq 1) to give the corresponding addition compound **3**. This unusual derivative of lithium borohydride, lithium perhydro-9b-boraphenalylhydride, is an active reducing agent which exhibits remarkably high stereoselectivity in the reduction of cyclic and bicyclic ketones, such as 2-methylcyclopentanone, 2-methylcyclohexanone, norcamphor, and camphor.



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Since their original discovery[3] relatively little research has been devoted to the trialkylborohydrides. In a brief study of the properties of lithium triethylborohydride[4] it was observed that this material is a stronger reducing agent than the parent compound. The enhanced reducing properties of the derivative presumably arise from the greater ease of transferring hydride ion from the weaker Lewis acid, triethylborane, than from the stronger Lewis acid, borane.[3] It was of interest to explore the hydride transfer ability of a polycyclic boron derivative, such as **3**, with that of a simple trialkylborane derivative, such as lithium triethylborohydride.[5]

In the course of these studies we observed that **3** possessed an unusual ability to introduce steric control into the reduction of ketones. Thus 2-methylcyclopenta-

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[1] G. W. Rotermund and R. Köster, *Ann. Chem.*, **686**, 153 (1965).

[2] Köster's configuration assignment (*cis,cis,cis*) has been revised: H. C. Brown and W. C. Dickason, *J. Amer. Chem. Soc.*, **91**, 1226 (1969).

[3] H. C. Brown, H. I. Schlesinger, I. Sheft, and D. M. Ritter, *ibid.*, **75**, 192 (1953).

[4] A. Khuri, Ph.D. Thesis, Purdue University, Lafayette, Ind., 1960.

[5] A detailed study of the reducing characteristics of these derivatives is now underway with S. Krishnamurthy.