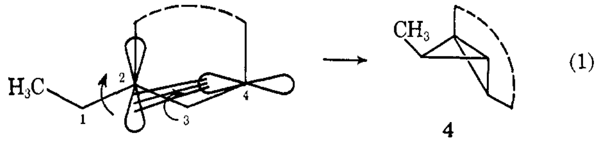
brational relaxation with twisting of the internal double bond must be highly preferred. Assuming that the cyclization is initiated from this twisted species, *i.e.*, **7** or **8**, R_1 = ring, R_2 = Me, one expects and finds retention of the stereochemical integrity of the methyl group. However, because the fourth p orbital is orthogonal there are no orbital symmetry requirements for 2,4 bonding. Thus, for example, clockwise rotation in



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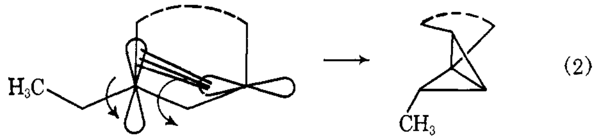
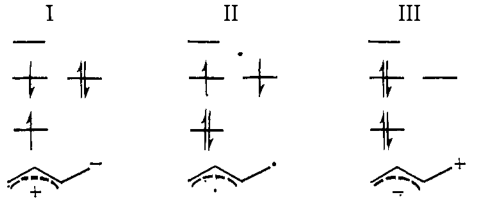


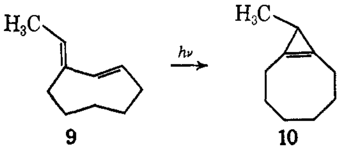
5

a conrotatory closure of the allyl system (eq 1) (with 2,4 closure as indicated to avoid a *trans*-bicyclobutane) would give **4**, while counterclockwise rotation (eq 2) (requiring use of the alternate lobe at C-2) would produce **5**. Given free rotation about the 3,4 bond, both pathways should be of equal probability. In the system under study, the restraint induced by the eight-membered ring accounts for the preferential *cis* stereochemistry of the fused ring (eq 1).

From the stereochemistry found for the methyl group, the 1,3 closure of the allyl system is conrotatory as suggested above, thus requiring that the orthogonal singlet have one of the following three electronic configurations.[10]



To evaluate further these possible electronic configurations some additional experimental results must be considered: first, cyclopropene **10** [ir (CCl_4) 1880 cm^{-1}; nmr (δ CCl_4) 0.96 (3 H, d, J = 4.5 Hz), 2.4 (4 H, m)] is formed (10%) during the irradiation of **2** and it arises from the subsequent irradiation of the initially formed *endo-trans* isomer **9**.[11] Second, direct, but *not* sensitized excitation of 3-methylenecycloalkenes in methanol yields methyl ethers.[12]



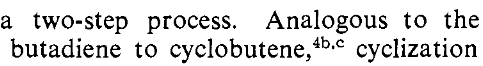
9 **10**

Considering now the three possible electronic configurations of the orthogonal singlet, the first, the excited allyl cation–methyl anion, is rejected as being too high in energy to be formed from the spectroscopic singlet of a diene and as not accounting for cyclopropene formation and the observed direction of solvent addition.

The second species, the diradical, besides having a high activation energy for closure,[10,13] does not account for the observed type of solvent addition.

The third species, allyl anion–methyl cation, is consistent with cyclopropene formation occurring *via* a 1,2-hydride shift during the ring closure and also correctly predicts the position and direction of solvent addition. Such a species does not require the excited state to be fully 90° nonplanar to remove 2,4 orbital symmetry bonding requirements.

The next question to consider is whether the cyclization to bicyclobutanes is a concerted or two-step process. One can envision a cyclopropyl anion–carbinyl cation (eq 3), analogous to the diradical postulated by Srinivasan[14] for a two-step process. Analogous to the cyclization of butadiene to cyclobutene,[4b,c] cyclization cannot proceed from the S_1^0 state of butadiene to the S_1^0 state of bicyclobutane because of the high endothermicity. In a two-step cyclization, internal conversion could occur during the second closure; however, this requires that the first closure produce an excited state of bicyclobutane, an unlikely endothermic process. Both the diradical and zwitterion two-step closures must be rejected on this basis.



In a concerted cyclization of the third species, it is possible that electrostatic interaction between the methyl cation and the developing anion might lower the energy of the transition state and allow progress along the reaction path to a point of *facile internal conversion* and collapse to ground-state bicyclobutane, such as has been calculated for the butadiene–cyclobutene closure.[15] We suggest that bicyclobutane formation from conjugated dienes occurs in a concerted fashion from a vibrationally relaxed singlet having an allyl anion–methyl cation electronic configuration,[16] that orbital symmetry controls the stereochemistry of the allylic system cyclization, and that internal conversion occurs during the closure.

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[10] H. C. Longuet-Higgins and E. W. Abrahanson, *J. Amer. Chem. Soc.*, **87**, 2045 (1965).

[11] The *endo-trans* isomer is assigned an *s-cis* configuration (**9**) since photolysis of this isomer produces as the major product a cyclobutene; bicyclobutane **3** is also formed, consistent with our predicted stereochemistry.

[12] W. G. Dauben and C. D. Poulter, unpublished observations.

[13] O. P. Strausz, P. J. Kozak, G. N. C. Woodall, A. G. Sherwood, and H. E. Gunning, *Can. J. Chem.*, **46**, 1317 (1968).

[14] R. Srinivasan, *J. Amer. Chem. Soc.*, 90, 4498 (1968).

[15] (a) W. Th. A. M. van der Lugt and L. J. Osterhoff, *ibid.*, **91**, 6042 (1969); (b) G. Feler, *Theor. Chim. Acta*, **12**, 412 (1968).

[16] Extended Hückel calculations[8b] on singlet diene also support this configuration. We thank Professor Hoffmann for communicating this result to us.

[17] National Science Foundation Predoctoral Fellow, 1966–present.

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Received January 26, 1970

Multiple Chromium(II)–Chromium(II) and Rhodium(II)–Rhodium(II) Bonds

Sir:

It has been noted elsewhere[1] that the binuclear, carboxylato-bridged species, I, (where the end groups,

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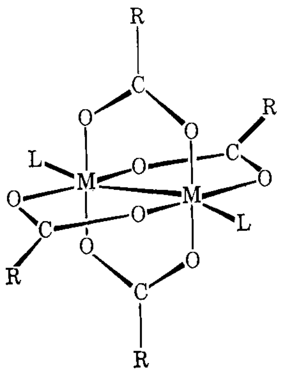
[1] F. A. Cotton, *Rev. Pure Appl. Chem.*, **17**, 25 (1967).



I

L, may be neutral molecules or anions, or may be absent), provide circumstances well suited to the study of the strength and nature of metal-to-metal (M–M) interactions as a function of electron configuration, formal charge, and position in the periodic table. The metal atoms are relatively free to move over fairly wide limits along the fourfold axis in accord with the magnitude and sign of the interaction between them. Thus, in a variety of copper(II) complexes the Cu–Cu distances[2,3] are in the range 2.62–2.71 Å, indicative of only slight interaction. Magnetic studies[3] confirm that only weak antiferromagnetic spin couplings occur. In $Mo_2(O_2CCH_3)_4$[4] and several $Re_2(O_2CR)_4X_2$ species,[5,6] on the other hand, extremely short distances (Mo–Mo, 2.11 Å; Re–Re, 2.24 Å) imply very strong M–M interactions which can be formulated as quadruple bonds.[1,7]

Chromous acetate, $Cr_2(O_2CCH_3)_4(H_2O)_2$, has always been regarded as exhibiting very weak M–M interaction. The structure was reported[8] to be similar to that of $Cu_2(O_2CCH_3)_4(H_2O)_2$ with a Cr–Cr distance of 2.64 Å. Even though the compound is diamagnetic,[9] such a distance has been regarded[1,9,10] as too long to allow for substantial M–M bonding. Thus Figgis and Martin[9] concluded that "since the internuclear Cr–Cr distance is identical to that observed in copper acetate, the bonds (*i.e.*, σ, π and δ components of a quadruple interaction) are unlikely to be strong. This conclusion is supported by evaluation of the overlap integrals." Of course, at the distance of 2.64 Å the overlap integrals had to be very small. Similarly, Cotton[1] wrote: "Is there any more involved (in $Cr_2(O_2CCH_3)_4(H_2O)_2$) than just interionic coupling of spins? Is there actually a Cr–Cr bond? The structural parameters (*i.e.*, Cr–Cr = 2.64 Å) indicate clearly that there is no bond."

More recently, however, various considerations led us to question the reasonableness of the *seemingly* proved weakness of the Cr–Cr interaction. A critical examination of the report on the structure[8] raised grave doubts as to its reliability; the reported distance appeared to be only a rough estimate, arbitrarily equated to that reported earlier for the copper compound. A single-crystal structural study[11] has now shown that the Cr–Cr distance is 2.362 (1) Å.[12] The quadruple M–M interaction is thus a strong one and the electronic structure and spectrum of the molecule must be (and are being) reconsidered on the basis of new MO calculations. This result has far-reaching significance because it implies that strong M–M bonds may be important in the chemistry of the metals of the first transition series as well as for the heavier metals.[13]

We have also reinvestigated the structure of $Rh_2(O_2CCH_3)_4(H_2O)_2$, which was reported[19] in 1962 to have a structure of type I with a Rh–Rh distance of about 2.45 Å. This number was, apparently, an estimate based on inspection of two electron density projections. Because the nature of the M–M bond in this compound is of much importance in understanding the electronic structures of a number of structurally homologous compounds in the same region of the periodic table, accurate structure parameters were needed. A fresh crystallographic study[20] has shown that the M–M bond is significantly shorter than previously implied, namely, 2.386 (3) Å; the mean Rh–O (acetate) distance is 2.04 ± 0.01 and the Rh–OH_2 distance is 2.308 (3) Å. We believe that these dimensions are in accord with the previous proposals[7,21] of a multiple (as opposed to single) Rh–Rh bond in this compound.

Full reports on both structures as well as detailed discussions of the M–M bonds are in preparation.[22]

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(2) L. Manojlovic-Muir, *Chem. Commun.*, 1057 (1967).

(3) D. M. L. Goodgame, *et al.*, *ibid.*, 629 (1969).

(4) D. Lawton and R. Mason, *J. Amer. Chem. Soc.*, **87**, 921 (1965).

(5) M. J. Bennett, W. K. Bratton, F. A. Cotton, and W. R. Robinson, *Inorg. Chem.*, **7**, 1570 (1968).

(6) C. Calvo, N. C. Jayadevan, C. J. L. Lock, and R. Restwo, *Can. J. Chem.*, **48**, 219 (1970).

(7) F. A. Cotton, *Accounts Chem. Res.*, **2**, 240 (1969).

(8) J. N. van Niekerk, F. R. L. Schoening, and J. F. de Wet, *Acta Crystallogr.*, **6**, 501 (1953).

(9) B. N. Figgis and R. L. Martin, *J. Chem. Soc.*, 3837 (1956).

(10) L. Dubicki and R. L. Martin, *Inorg. Chem.*, **5**, 2203 (1966).

(11) The intensities of 1313 independent reflections were collected on a counter diffractometer with Mo Kα radiation. The structure has been refined to $R_1 = 4.6\%$ and $R_2 = 5.0\%$ with anisotropic temperature parameters.

(12) The mean Cr–O (acetate) is 2.02 ± 0.02 Å; the Cr–OH_2 distance is 2.284 (3) Å.

(13) Recent data[14-16] on three binuclear nickel(II) complexes also point in this direction. Also, the reports[17,18] of a very short Cr–Cr bond (1.95 Å) in $Cr_2(C_3H_5)_4$ become more credible in light of the structure reported here; the bond in that compound must be formulated as a quadruple one though the relatively low symmetry makes the picture less simple than it is for species of D_{4h} symmetry, such as $M_2X_8{}^{n-}$ or $M_2(O_2CR)_4L_2$.

(14) M. Corbett and B. F. Haskins, *Chem. Commun.*, 1602 (1968).

(15) M. Borramico, G. Dessy, and V. Fares, *ibid.*, 697 (1969).

(16) M. Borramico, G. Dessy, and V. Fares, *ibid.*, 1106 (1969).

(17) T. Aoki, *et al.*, *Bull. Chem. Soc. Jap.*, **42**, 545 (1969).

(18) G. Albrecht and D. Stock, *Z. Chem.*, **7**, 321 (1967).

(19) M. A. Porai-Koshits and A. S. Antschishkina, *Dokl. Chem.*, **146**, 902 (1962).

(20) The intensities of 1644 independent reflections were collected on a counter diffractometer with Mo Kα radiation. The structure is currently refined to $R_1 = 3.4\%$ and $R_2 = 4.3\%$ with anisotropic temperature parameters.

(21) K. G. Caulton and F. A. Cotton, *J. Amer. Chem. Soc.*, **91**, 6517 (1969).

(22) This research was supported in part by the U. S. Atomic Energy Commission.

(23) NDEA Predoctoral Fellow.

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Reaction of Carbonyl Groups with Perchloric Acid. *gem*-Diperchlorates[1]

Sir:

Superacid media that have received wide attention in carbonium ion chemistry,[2] such as combinations of

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(1) This work was supported by the Office of Naval Research.

(2) See, for example, R. J. Gillespie, *Accounts Chem. Res.*, **1**, 202