

possibility involving no hydride permutation gave a slightly better fit to the data and was, therefore, marginally preferred.

The physical mechanisms that correspond to the experimentally established permutations considered were examined by employing a quasi-least-motion simulation. We have concluded that the most probable mechanism involves a simultaneous exchange of the two axial phosphorus ligands with two of the equatorial phosphorus ligands. The hydride ligands simply move to the new equatorial edges. In the (distorted) distal pentagonal-bipyramidal structure that is favored as the equilibrium geometry, this corresponds to permutation of the CrP<sub>5</sub> framework via a "Berry pseudorotation" type process.

Line-shape analysis in a seven-spin system is a complex problem; the NMR line-shape study of CrH<sub>2</sub>[P(OCH<sub>3</sub>)<sub>3</sub>]<sub>5</sub> described in this paper involves an analysis of the most complex spin system yet treated in detail and further illustrates the power of a systematic analysis of the basic permutations to clarify and eliminate mechanistic possibilities.

**Acknowledgment.** We wish to acknowledge the fine technical assistance of M. A. Cushing, Jr., G. Watunya, and F. N. Schock.

### Appendix

In order to facilitate the visualization of dynamical processes such as mutual exchange in coordination complexes, electrocyclic reactions, and intramolecular Diels-Alder reactions, we have developed a methodology for

mapping an initial atomic configuration into a final one. The first step is to assure maximum coincidence of the (labeled) atoms in the initial and final arrangements. This is accomplished by requiring that the mass-weighted residual be at a minimum

$$m^i[R^i(\text{final}) - R^i(\text{initial})]^2$$

where the  $R^i$ 's are particle position vectors. It is generally convenient to operate in a center-of-mass coordinate system, though with simple coordination complexes it may be acceptable to place the origin at the central atom. The second step involves motion along some pathway leading from the initial to the final configuration. Least-motion pathways defined in Cartesian coordinates are generally unsuitable, giving physically unreasonable intermediate structures. *Quasi-least-motion* pathways may be mapped, either in spherical polar coordinates (suitable for simple coordination complexes) or in internal coordinates (the most general case). While these pathways will not in general correspond to the lowest energy route from starting material to products, they should represent qualitative approximations of the actual pathways.

We have used the spherical polar model for the rearrangement mechanisms for the distal isomer of CrH<sub>2</sub>[P(OCH<sub>3</sub>)<sub>3</sub>]<sub>5</sub>. The trimethyl phosphite ligands were replaced by points of equal mass displaced outward along the Cr-P bond direction to the center-of-mass for the phosphite group.

**Registry No.** Cr[P(OMe)<sub>3</sub>]<sub>5</sub>H<sub>2</sub>, 92842-95-0; Cr[P(OMe)<sub>3</sub>]<sub>6</sub>, 70948-62-8.

## Trinuclear Clusters of Early Transition Metals: Jahn-Teller Distortions and Electronic Structure<sup>†</sup>

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A detailed theoretical study of a trinuclear eight-electron cluster with a distorted metal core, Mo<sub>3</sub>S<sub>2</sub>Cl<sub>9</sub><sup>3-</sup>, leads to some general conclusions about the role of different capping, bridging, and terminal ligands in determining the electronic and geometrical structure of trinuclear clusters of the early transition metals.

The early transition-metal cluster compounds are distinguished from similar clusters involving 8B elements by the typically high oxidation state of the metal component and by halogens or other electronegative atoms as ligands. A variety of oxidation states or electron counts exists. During the past few years, much research has been carried out on and much attention has been paid to the trinuclear metal cluster systems, one of the representative species of experimental and theoretical importance.<sup>1</sup> Dozens of complexes of this type have been prepared and structurally

characterized.<sup>2-43</sup> At the same time, theoretical investigations were also developing.<sup>44-49</sup>

(1) Müller, A.; Jostes, R.; Cotton, F. A. *Angew. Chem., Int. Ed. Engl.* 1980, 19, 875.

(2) Cotton, F. A.; Mague, J. T. *Inorg. Chem.* 1965, 3, 1402.

(3) Goldberg, S. Z.; Spinack, B.; Stanley, G.; Eisenberg, R.; Braitsch, D. M.; Muller, J. S.; Abkowitz, M. *J. Am. Chem. Soc.* 1977, 99, 110.

(4) King, R. B.; Braitsch, D. M.; Kapoor, P. N. *J. Am. Chem. Soc.* 1975, 97, 60.

(5) Fisher, E. O.; Rohrscheid, F. *J. Organomet. Chem.* 1966, 6, 53.

(6) Churchill, M. R.; Chang, S. W. *J. Chem. Soc., Chem. Commun.* 1974, 248.

(7) Müller, A.; Ruck, A.; Dartmann, M.; Reinsch-Vogell, U. *Angew. Chem., Int. Ed. Engl.* 1981, 20, 483.

<sup>†</sup>Dedicated to the memory of our friend and colleague Earl Muetterties.

Table I. Some Trinuclear Clusters and Their Selected Properties

compound	type	electron count	M-M, Å	ref
Re <sub>3</sub> Cl <sub>9</sub>	U <sub>3</sub>	12	2.489	2
[Nb <sub>3</sub> Cl <sub>6</sub> (C <sub>6</sub> Me <sub>6</sub> ) <sub>3</sub> ] <sup>2+</sup>	U <sub>6</sub>	7		3
[Ta <sub>3</sub> Cl <sub>6</sub> (C <sub>6</sub> Me <sub>6</sub> ) <sub>3</sub> ] <sup>+</sup>	U <sub>6</sub>	8		4, 5
[Nb <sub>3</sub> Cl <sub>6</sub> (C <sub>6</sub> Me <sub>6</sub> ) <sub>3</sub> ] <sup>+</sup>	U <sub>6</sub>	8	3.334	4-6
[Nb <sub>3</sub> Br <sub>6</sub> (C <sub>6</sub> Me <sub>6</sub> ) <sub>3</sub> ] <sup>+</sup>	U <sub>6</sub>	8	3.335	4, 5
[Mo <sub>3</sub> O <sub>4</sub> F <sub>9</sub> ] <sup>5-</sup>	M <sub>3</sub>	6	2.502	7
[Mo <sub>3</sub> S <sub>4</sub> Cp <sub>3</sub> ] <sup>+</sup>	M <sub>3</sub>	6	2.812	8
[Mo <sub>3</sub> S <sub>4</sub> (CN) <sub>9</sub> ] <sup>5-</sup>	M <sub>3</sub>	6	2.766	9
[Mo <sub>3</sub> O <sub>4</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub> ] <sup>2-</sup>	M <sub>3</sub>	6	2.486	10
Mo <sub>3</sub> O <sub>4</sub> (acac) <sub>3</sub> (EtO) <sub>3</sub>	M <sub>3</sub>	6	2.47	11
[Mo <sub>3</sub> S <sub>13</sub> ] <sup>2-</sup>	M <sub>3</sub>	6	2.77	12
[W <sub>3</sub> O <sub>4</sub> F <sub>4</sub> ] <sup>5-</sup>	M <sub>3</sub>	6	2.514	13
W <sub>3</sub> O <sub>3</sub> Cl <sub>2</sub> (Oac)(PBU <sub>3</sub> ) <sub>3</sub>	M <sub>3</sub>	6	2.609	14
[Mo <sub>3</sub> O <sub>3</sub> S(Hnta) <sub>3</sub> ] <sup>2-</sup>	M <sub>3</sub>	6	2.589	15
[Mo <sub>3</sub> S <sub>4</sub> (SCH <sub>2</sub> CH <sub>2</sub> S) <sub>3</sub> ] <sup>2-</sup>	M <sub>3</sub>	6	2.78	16
Zn <sub>2</sub> Mo <sub>3</sub> O <sub>8</sub>	M <sub>3</sub>	6	2.524	17
LiZn <sub>2</sub> Mo <sub>3</sub> O <sub>8</sub>	M <sub>3</sub>	7	2.578	18
Mo <sub>3</sub> S <sub>4</sub> Cp <sub>3</sub>	M <sub>3</sub>	7		19
Nb <sub>3</sub> Cl <sub>8</sub>	M <sub>3</sub>	7	2.81	20
Nb <sub>3</sub> Br <sub>8</sub>	M <sub>3</sub>	7	2.88	21
Nb <sub>3</sub> I <sub>8</sub>	M <sub>3</sub>	7	3.00	21
[Mo <sub>3</sub> OCl <sub>3</sub> (Oac) <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub> ] <sup>2+</sup>	M <sub>3</sub>	8	2.550	22
[Mo <sub>3</sub> OCl <sub>3</sub> (Oac) <sub>3</sub> Cl <sub>3</sub> ] <sup>-</sup>	M <sub>3</sub>	8	2.579, 2.585, 2.567	23
Zn <sub>3</sub> Mo <sub>3</sub> O <sub>8</sub>	M <sub>3</sub>	8	2.58	18
[V <sub>3</sub> O(Oac) <sub>6</sub> (CH <sub>3</sub> COOH) <sub>2</sub> (THF)] <sup>+</sup>	M <sub>6</sub>	6	3.307	24
V <sub>3</sub> O(CF <sub>3</sub> CO <sub>2</sub> ) <sub>6</sub> (THF) <sub>3</sub>	M <sub>6</sub>	7	3.357	24
[W <sub>3</sub> O(Oac) <sub>6</sub> (H <sub>2</sub> O) <sub>3</sub> ] <sup>2+</sup>	M <sub>6</sub>	8	2.701, 2.715	25
[Cr <sub>3</sub> O(Oac) <sub>6</sub> (H <sub>2</sub> O) <sub>3</sub> ] <sup>+</sup>	M <sub>6</sub>	9	3.274	26
Cr <sub>3</sub> O(CHF <sub>2</sub> CO <sub>2</sub> ) <sub>6</sub> (4-CNC <sub>5</sub> H <sub>4</sub> ) <sub>3</sub>	M <sub>6</sub>	10	3.336	27
Cr <sub>3</sub> O(CHF <sub>2</sub> CO <sub>2</sub> ) <sub>6</sub> (C <sub>2</sub> H <sub>5</sub> N) <sub>3</sub>	M <sub>6</sub>	10	3.356	27
Mn <sub>3</sub> O(Oac) <sub>6</sub> (HOac)(Oac) <sub>2/2</sub>	M <sub>6</sub>	12	3.27	28
Mn <sub>3</sub> O(Oac) <sub>6</sub> (C <sub>5</sub> H <sub>5</sub> N) <sub>3</sub>	M <sub>6</sub>	13		29
Mn <sub>3</sub> O(Oac) <sub>6</sub> (3-ClC <sub>5</sub> H <sub>4</sub> N) <sub>3</sub>	M <sub>6</sub>	13	3.363	30
[Fe <sub>3</sub> O(Oac) <sub>6</sub> (H <sub>2</sub> O) <sub>3</sub> ] <sup>+</sup>	M <sub>6</sub>	15	3.29	31
[Mo <sub>3</sub> S <sub>2</sub> Cl <sub>9</sub> ] <sup>3-</sup>	B <sub>3</sub>	8	2.556, 2.641, 2.653	32
[Nb <sub>3</sub> O <sub>2</sub> (Me <sub>3</sub> CCO <sub>2</sub> ) <sub>6</sub> (C <sub>4</sub> H <sub>8</sub> O) <sub>3</sub> ] <sup>+</sup>	B <sub>6</sub>	4	2.842	33
Mo <sub>3</sub> O(OR) <sub>10</sub>	B <sub>6</sub>	4	2.53	34
[Nb <sub>3</sub> O <sub>2</sub> (SO <sub>4</sub> ) <sub>6</sub> (H <sub>2</sub> O) <sub>3</sub> ] <sup>5-</sup>	B <sub>6</sub>	4	2.875, 2.892	35
[Mo <sub>3</sub> (CCH <sub>3</sub> ) <sub>2</sub> (Oac) <sub>6</sub> (H <sub>2</sub> O) <sub>3</sub> ] <sup>2+</sup>	B <sub>6</sub>	4	2.883-2.891	36
[Mo <sub>3</sub> (CCH <sub>3</sub> ) <sub>2</sub> (Oac) <sub>6</sub> (H <sub>2</sub> O) <sub>3</sub> ] <sup>+</sup>	B <sub>6</sub>	5	2.815, 2.807, 2.820	36
[Mo <sub>3</sub> O <sub>2</sub> (Oac) <sub>6</sub> (H <sub>2</sub> O) <sub>3</sub> ] <sup>2+</sup>	B <sub>6</sub>	6	2.766	37, 38
[Mo <sub>3</sub> O <sub>2</sub> (O <sub>2</sub> C <sub>2</sub> Et) <sub>6</sub> (H <sub>2</sub> O) <sub>3</sub> ] <sup>2+</sup>	B <sub>6</sub>	6	2.752	37
Mo <sub>3</sub> O <sub>2</sub> (Oac) <sub>6</sub> (H <sub>2</sub> O)(OH) <sub>2</sub>	B <sub>6</sub>	6	2.796, 2.773	39
[Mo <sub>3</sub> O(CCH <sub>3</sub> )(Oac) <sub>6</sub> (H <sub>2</sub> O) <sub>3</sub> ] <sup>+</sup>	B <sub>6</sub>	6	2.752	40
[W <sub>3</sub> O <sub>2</sub> (Oac) <sub>6</sub> (H <sub>2</sub> O) <sub>3</sub> ] <sup>2+</sup>	B <sub>6</sub>	6	2.747	41, 42
[W <sub>3</sub> O <sub>2</sub> (O <sub>2</sub> C <sub>2</sub> Et) <sub>6</sub> (H <sub>2</sub> O) <sub>3</sub> ] <sup>2+</sup>	B <sub>6</sub>	6	2.745	41, 42
[W <sub>3</sub> O <sub>2</sub> (Oac) <sub>6</sub> (Oac) <sub>3</sub> ] <sup>-</sup>	B <sub>6</sub>	6	2.769	41
W <sub>3</sub> O <sub>2</sub> (O <sub>2</sub> CCMe <sub>3</sub> ) <sub>6</sub> (O <sub>2</sub> CCMe <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O)	B <sub>6</sub>	6	2.76	41
[Mo <sub>3</sub> O <sub>2</sub> (Oac) <sub>6</sub> (OCH <sub>3</sub> ) <sub>3</sub> ] <sup>-</sup>	B <sub>6</sub>	6	2.76, 2.81	43

Müller, Jostes, and Cotton<sup>1</sup> have reviewed in a systematic way the main achievements in this field prior to 1980.

They classified these compounds into three categories according to the number of capping ligands ( $\mu_3$ -type) in-

(8) Vergarmini, P. J.; Vahrenkamp, H.; Dahl, L. F. *J. Am. Chem. Soc.* **1971**, *93*, 6327.

(9) Müller, A.; Reinsch, U. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 72.  
(10) Bino, A.; Cotton, F. A.; Dori, Z. *J. Am. Chem. Soc.* **1978**, *100*, 5252; **1979**, *101*, 8842.

(11) Scanicar, S.; Herceg, M. *Acta Crystallogr.* **1966**, *21*, A151.

(12) Müller, A.; Pohl, S.; Dartmann, M.; Cohen, J. P.; Bennett, J. M.; Kirchner, R. M. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1979**, *B34*, 434.

(13) Mattes, R.; Mennemann, K. *Z. Anorg. Allg. Chem.* **1977**, *437*, 175.

(14) Sharp, P. R.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 1430.  
Cotton, F. A.; Felthouse, T. R.; Lay, D. G. *J. Am. Chem. Soc.* **1980**, *102*, 1431.

(15) Shibahara, T.; Hattori, M.; Kuroya, M. *J. Am. Chem. Soc.* **1984**, *106*, 2710.

(16) Halbert, T. R.; McGavley, K.; Pan, W.-H.; Czernuszewicz, R. S.; Stiefel, E. I. *J. Am. Chem. Soc.* **1984**, *106*, 1849.

(17) (a) McCarroll, W. H.; Katz, L.; Ward, R. *J. Am. Chem. Soc.* **1951**, *79*, 5410. (b) Ansell, G. B.; Katz, L. *Acta Crystallogr.* **1966**, *21*, 482.

(18) Torardi, C. C.; McCarley, R. E. *Inorg. Chem.* **1984**, *23*, 0000.

(19) Beck, W.; Danzer, W.; Thiel, G. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 582.

(20) Schnering, H.-G.; Wöhrle, H.; Schäfer, H. cited in: Schäfer, H.; Schnering, H.-G. *Angew. Chem.* **1969**, *76*, 833.

(21) Simon, A.; Schnering, H.-G. von *J. Less-Common Met.* **1966**, *11*, 31.

(22) Bino, A.; Cotton, F. A.; Dori, Z. *Inorg. Chim. Acta* **1979**, *33*, L133.

(23) Huang, J.; Shang, M.; Huang, J.; Zhang, H.; Lu, S.; Lu, J. *J. Struct. Chem. (Engl. Transl.)* **1982**, *1*, 1.

(24) Cotton, F. A.; Lewis, G. E.; Mott, G. N. *Inorg. Chem.* **1982**, *21*, 3316.

(25) Ardon, M.; Cotton, F. A.; Dori, Z.; Fang, A.; Kapon, M.; Reisner, G. M.; Shaia, M. *J. Am. Chem. Soc.* **1982**, *104*, 5394.

(26) Chang, S. C.; Jeffrey, G. A. *Acta Crystallogr., Sect. B.* **1970**, *B26*, 673.

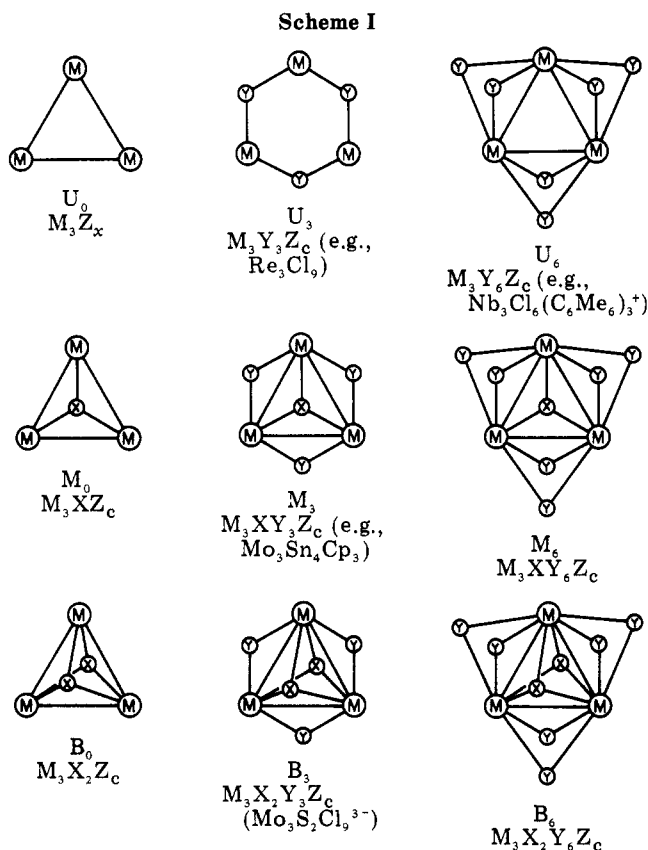
(27) Cotton, F. A.; Wang, W. *Inorg. Chem.* **1982**, *21*, 2675.

(28) Hessel, L. W.; Romers, C. *Recl. Trav. Chim. Pays-Bas* **1669**, *88*, 545.

(29) Baikie, A. R. E.; Hursthouse, M. B.; New, D. B.; Thornton, P. J. *Chem. Soc., Chem. Commun.*, **1978**, 62.

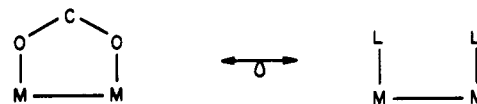
(30) Baikie, A. R. E.; Hursthouse, M. B.; New, D. B.; Thornton, P.; White, R. G. *J. Chem. Soc., Chem. Commun.*, **1980**, 684.

(31) Anzenhofer, K.; de Boer, J. J. *Recl. Trav. Chim. Pays-Bas* **1969**, *88*, 286.



involved and designated them by capital letters A, B, and C, corresponding to zero, one, or two  $\mu_3$ -ligands contained, respectively. For the purpose of the present investigation, it seems instructive to classify them in terms of the number of capping and bridging atoms simultaneously. We will use symbols M, B, and U to describe the number of capping or  $\mu_3$  ligands (M = mono-, B = bi-, and U = uncapped) and a subscript (0, 3, 6) to count the number of bridging or  $\mu_2$  atoms. The  $\mu_3$  or capping ligand will be called generally X, the  $\mu_2$  ligand Y, and the terminal ligands Z. Some typical examples are shown in Scheme I, where no atten-

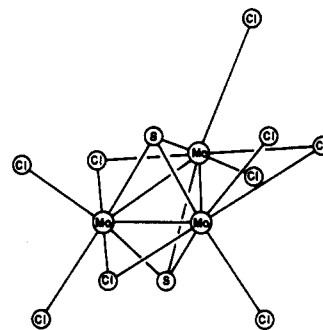
tion is paid to drawing out the stereochemistry of the  $\mu_2$  ligands in detail, nor are the  $\mu_1$  or terminal ligands drawn in. We have tentatively skirted the nontrivial issue of whether a bidentate polyatomic ligand that bridges two metals, e.g., acetate or sulfate, is really  $\mu_2$  or two  $\mu_1$  ligands (1). For the moment we count it as the equivalent of two



1

terminal ligands but, as our subsequent calculations will show, the detailed nature of the bidentate ligand cannot be ignored. Also note that this MXYZ nomenclature puts the terminal Z ligands in a subsidiary role. This is something we will discuss in some detail later. It is not a simple matter, for some  $\mu_1$  ligands in these systems are labile, weakly bound, but in other cases (e.g., terminal oxo groups) very strongly held. Finally, we will give primacy to electronic considerations rather than simple ligand or atom counting in deciding where a ligand fits in. Thus a terminal arene or cyclopentadienyl will be classified as  $Z_3$ . Table I lists some of the compounds known.

It can be seen from Table I that most of these compounds have electron counts from 6 to 8 with respect to the metal core except  $Re_3Cl_9$ , a  $U_3$  compound, and those  $M_6$  compounds with electron counts ranging from 7 to 13 and characterized by unusually long M-M distances. The effective symmetries of the cluster cores are either  $D_{3h}$  or  $C_{3v}$ , with a few exceptions showing tiny distortion. However, one novel compound of the  $M_3$ -type, whose molecular formula is  $[Mo_3S_2Cl_9]^{3-}$ , with eight electrons in the metal core, interestingly exhibits unequal M-M bond distances relative to its idealized  $D_{3h}$  symmetry.<sup>32</sup> The structural details of this molecule are shown in 2 and the Appendix.



2

Of the three Mo-Mo bonds, two are approximately equal but longer than the third, with the maximum difference equal to 0.097 Å. Similarly, a couple of the Mo-S bonds located between the two longer Mo-Mo bonds are shorter than the remaining four. Their maximum difference is 0.11 Å. The molecule also contains two kinds of Mo-Cl bonds, one involving  $\mu$ -Cl and the other involving terminal chlorine atoms, which also show unequal lengths with smaller differences of 0.025 and 0.045 Å, respectively. Such a significant distortion in the cluster skeleton must have electronic origins and formed the initial stimulus to this study.

We have carried out extended Hückel calculations of the electronic structure of  $Mo_3S_2Cl_9^{3-}$ , in order to gain a better

(32) Huang, J.; Shang, M.; Lui, S.; Lu, J. *Sci. Sin. (Engl. Transl.)* **1982**, *25*, 1270.

(33) Cotton, F. A.; Duraj, S. A.; Roth, W. J. *J. Am. Chem. Soc.* **1984**, *106*, 3527.

(34) R =  $CH_2$ -*t*-Bu, *i*-Pr: Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kirkpatrick, C. C. *Inorg. Chem.* **1984**, *23*, 1021.

(35) Bino, A. *Inorg. Chem.* **1982**, *21*, 1917.

(36) Ardon, M.; Bino, A.; Cotton, F. A.; Dori, Z.; Kapon, M.; Kolthammer, B. W. S. *Inorg. Chem.* **1981**, *20*, 4082.

(37) Ardon, M.; Bino, A.; Cotton, F. A.; Dori, Z.; Kaftory, M.; Reisner, G. *Inorg. Chem.* **1982**, *21*, 1912.

(38) Cotton, F. A.; Dori, Z.; Marler, D. O.; Schwotzer, W. *Inorg. Chem.* **1983**, *22*, 3104.

(39) Birnbaum, A.; Cotton, F. A.; Dori, Z.; Marler, D. O.; Reisner, G. M.; Schwotzer, W.; Shaia, M. *Inorg. Chem.* **1983**, *22*, 2723.

(40) (a) Bino, A.; Cotton, F. A.; Dori, Z. *J. Am. Chem. Soc.* **1981**, *103*, 243. (b) Bino, A.; Cotton, F. A.; Dori, Z.; Kolthammer, B. W. S. *J. Am. Chem. Soc.* **1981**, *103*, 5779. (c) Bino, A.; Cotton, F. A.; Dori, Z.; Falvello, L. R.; Reisner, G. M. *Inorg. Chem.* **1982**, *21*, 2750.

(41) Bino, A.; Cotton, F. A.; Dori, Z.; Koch, S.; Küppers, H.; Millar, M.; Sekutowski, J. C. *Inorg. Chem.* **1978**, *17*, 3245.

(42) Bino, A.; Hesse, K. F.; Küppers, H. *Acta Crystallogr., Sect. B* **1980**, *B36*, 723.

(43) Birnbaum, A.; Cotton, F. A.; Dori, Z.; Kapon, M. *Inorg. Chem.* **1984**, *23*, 1617.

(44) Cotton, F. A.; Haas, T. E. *Inorg. Chem.* **1964**, *3*, 10.

(45) Cotton, F. A. *Inorg. Chem.* **1964**, *3*, 1217.

(46) Bursten, B. E.; Cotton, F. A.; Stanley, G. G. *Isr. J. Chem.* **1980**, *19*, 132.

(47) Bursten, B. E.; Cotton, F. A.; Hall, M. B.; Najjar, R. C. *Inorg. Chem.* **1982**, *21*, 302.

(48) Chisholm, M. H.; Cotton, F. A.; Fang, A.; Kober, E. M. *Inorg. Chem.* **1984**, *23*, 749.

(49) Fang, A. Ph.D. Dissertation, Texas A&M University, 1982.

Table II. Symmetry-Adapted Linear Combinations for Mo<sub>3</sub>

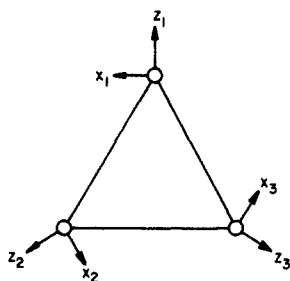
atomic orbitals	molecular orbitals
$z^2$	$a'_1 + e'$
$xz$	$a'_2 + e'$
$yz$	$a''_2 + e''$
$xy$	$a''_1 + e''$
$x^2 - y^2$	$a'_1 + e'$

understanding of the causes of the distortion existing in this anion. Interactions between the metal core and various ligand fragments are compared by displaying a series of correlation diagrams that present a qualitative picture of the role that each kind of ligand is playing as well as their couplings. General relationships between geometry and electron count are analyzed in terms of energy level sequences. These lead to an understanding of the geometrical trends not only of the eight-electron B<sub>3</sub> cluster Mo<sub>3</sub>S<sub>2</sub>Cl<sub>9</sub><sup>3-</sup> but also of the other molecules displayed in Table I. In particular we will find a significant role for a Jahn-Teller distortion for certain specific electron counts.

### The Electronic Structure of Mo<sub>3</sub>S<sub>2</sub>Cl<sub>9</sub><sup>3-</sup>

We began with a calculation on this trinuclear cluster in idealized *D*<sub>3h</sub> symmetry, the bond lengths and angles averaged from the experimental structure. The geometrical details and particulars of the extended Hückel calculations are given in the Appendix. With the normal oxidation state assignments of 1- for Cl and 2- for S one obtains a deficit of 10 electrons for the Mo<sub>3</sub> core or a total of 8 electrons distributed over the three metals.

Though this is not the way the computer program operates, it is convenient to work in a coordinate system adapted to local symmetry, i.e. one with radial (*z*), tangential (*x*), and perpendicular (*y*) orbitals, as shown in 3,



3

where all the *y* axes are parallel to one another and perpendicular to the triangle plane, the *z* axes intersect at and point away from the center of the triangle, and the tangential *x* axes are fixed by requiring a right-handed coordinate system. If  $\chi_1$ ,  $\chi_2$ , and  $\chi_3$  represent an equivalent atomic orbital set defined with respect to each of the three Mo atoms, then the following transformation will construct symmetry orbitals of species *a* and *e*, namely

$$\begin{pmatrix} \psi_a \\ \psi_{e_a} \\ \psi_{e_b} \end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} \\ \frac{2}{\sqrt{6}} & -\frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{6}} \\ 0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{pmatrix} \begin{pmatrix} \chi_1 \\ \chi_2 \\ \chi_3 \end{pmatrix}$$

where *a* denotes one of the four species  $a'_1$ ,  $a'_2$ ,  $a''_1$ , and  $a''_2$  and *e* represents  $e'$  or  $e''$ . The five 3d orbitals at each center will combine in the way indicated in Table II.

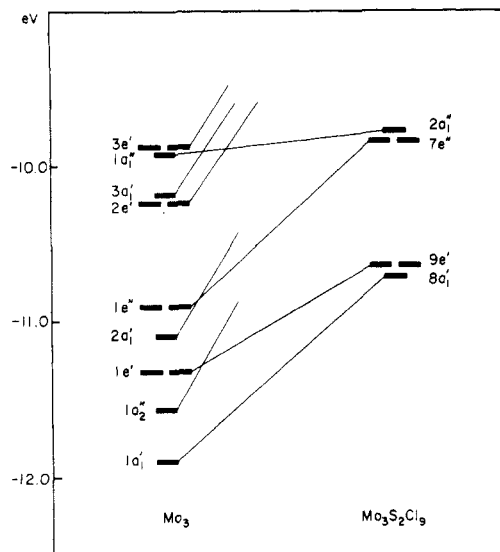
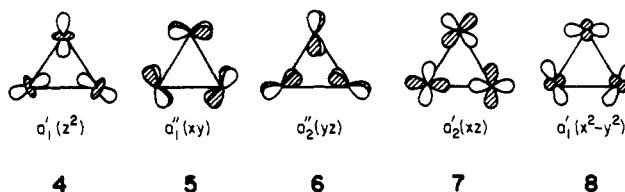


Figure 1. Lower d block levels of the Mo<sub>3</sub> core and the related frontier levels in the [Mo<sub>3</sub>S<sub>2</sub>Cl<sub>9</sub>] cluster.

Within each orbital set the topology of the interactions then sets the level ordering. In some cases the nondegenerate orbital is at low energy, in some cases the degenerate *e* orbitals. It is easy to decide which pattern it should be. For instance 4-8 show the nondegenerate combinations. These are clearly bonding for  $z^2$ ,  $yz$ , and  $x^2 - y^2$  but antibonding for  $xy$  and  $xz$ .



In Figure 1 we show the lower levels of the Mo<sub>3</sub> core and the Mo<sub>3</sub>S<sub>2</sub>Cl<sub>9</sub> cluster. The ten lowest levels of the Mo<sub>3</sub> cluster core are exactly as anticipated, the bonding combinations  $a'_1(z^2) + a''_2(yz) + e'(xz) + a'_1(x^2 - y^2) + e''(xy)$ . Not all of these survive the perturbation impressed by the S and Cl ligands in Mo<sub>3</sub>S<sub>2</sub>Cl<sub>9</sub><sup>3-</sup>. The geometry of the incoming donors clearly destabilizes all the d block levels (except  $1a''_1$  which has too many nodes to interact with any S or Cl  $\sigma$ -bonding combination). However  $1a''_2$  and  $2a'_1$ , which "point" toward the sulfurs and chlorines, are clearly affected most, pushed up and out of the frontier region.

Note the nice closed-shell configuration for a six-electron count ( $8a'_1 + 9e'$  filled). One is perfectly well justified in characterizing the six-electron system as possessing three metal-metal  $\sigma$  bonds, for the set of three such localized bonds would transform as  $a'_1 + e'$ . The composition of the  $a'_1 + e'$  set is also consistent with a set of three  $\sigma$  bonds.

For an eight-electron count, two electrons enter the degenerate  $7e''$  orbital. One would expect either a symmetrical (*D*<sub>3h</sub>) ground-state triplet or a distorted low-spin state. We will return to a general discussion of the M<sub>3</sub> clusters and the effect of substituents on the level ordering, but before we do that we wish to discuss the potential deformation of the eight-electron system in some detail.

### The Jahn-Teller Distortion in Mo<sub>3</sub>S<sub>2</sub>Cl<sub>9</sub><sup>3-</sup>

Given two electrons in an *e* orbital of a threefold symmetric system, the Jahn-Teller theorem<sup>50,51</sup> tells us that

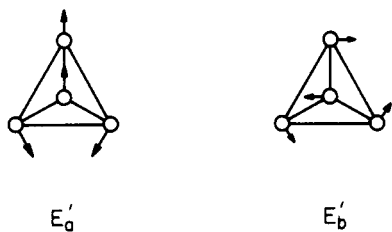
(50) Jahn, H. A.; Teller, E. *Proc. R. Soc. London, Ser. A* 1937, 161, 220.  
 (51) Longuet-Higgins, H. C.; Öpik, U.; Pryce, M. H. L.; Sack, R. A. *Proc. R. Soc. London, Ser. A* 1958, 244, 1.

Table III. Computed Energy Minima for  $[\text{Mo}_3\text{S}_2\text{Cl}_9]^{3-}$ 

	minimum 1	minimum 2
Mo-Mo, Å	2.637,	2.583,
	2.578	2.680
Mo-S, Å	2.407,	2.347,
	2.313	2.435
$\alpha$ , deg	117	125
$\beta$ , deg	3	-3
stabilization, <sup>a</sup> eV	0.115	0.138
HOMO stabilization, eV	0.105	0.133

<sup>a</sup> Relative to  $D_{3h}$  form:  $\alpha = 120^\circ$  and  $\beta = 0^\circ$ .

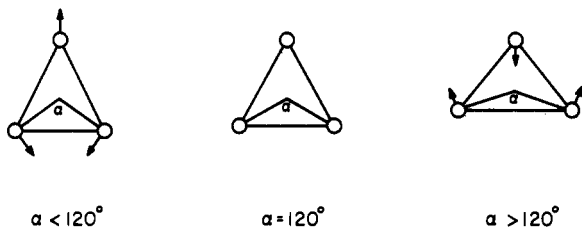
a vibrational mode of e symmetry exists that will remove this symmetry. One such mode is  $E'$ , shown in 9.<sup>52</sup> The



9

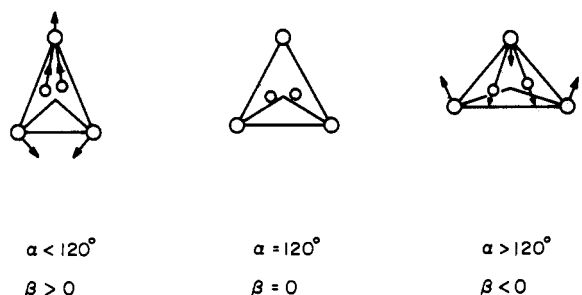
$E'_a$  component maintains  $C_{2v}$  symmetry, which is convenient. Let us assume that the Cl atoms remain fixed and only the Mo and S atoms move. This assumption is based on a fragment calculation which shows that the partly filled HOMO ( $e''$ ) is 95% on the  $\text{Mo}_3\text{S}_2$  core.

The molybdenum motion may be measured by the angle  $\alpha$  spanned by the lines connecting the center of the triangle and the two bottom Mo atoms, as in 10. The sulfur



10

motion can be followed by an angle  $\beta$  between the lines connecting the center of the molecule to the initial and final positions of a moving capped atom. If  $\beta > 0$ , the S atoms move toward the upper Mo, and if  $\beta < 0$ , the S atoms move toward the midpoint of the bottom Mo-Mo line. The combined motions are shown in 11.



11

(52) Herzberg, G. (1) "Infrared and Raman of Polyatomic Molecules"; Van Norstrand: Princeton, NJ, 1945. (2) "Molecular Spectra and Molecular Structure"; Van Norstrand-Rinhold: New York, 1966; Vol. III.

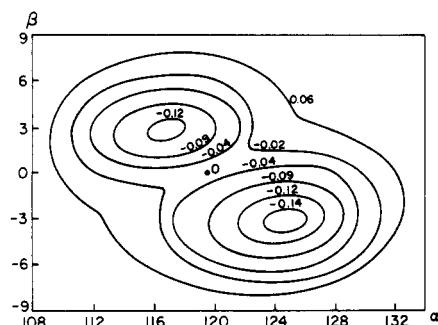


Figure 2. Energy surface of the Jahn-Teller distortion, with respect to the variation of  $\alpha$  and  $\beta$ .

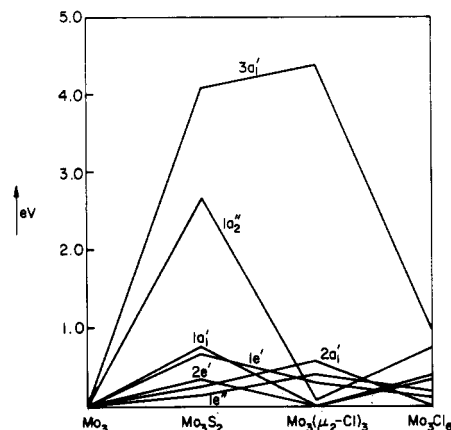


Figure 3. Destabilization of the lower d block levels relative to the unperturbed  $\text{Mo}_3$  core.

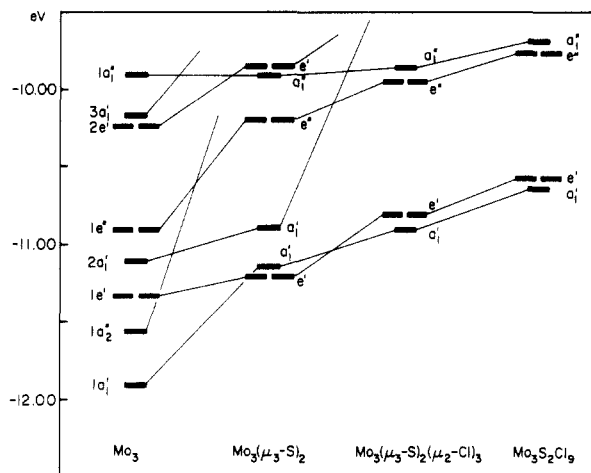
A potential energy surface is calculated varying  $\alpha$  and  $\beta$ . This is presented in Figure 2. There is a double minimum, as expected, for the combined  $\alpha$  and  $\beta$  variation. The computed minima occur with the geometrical parameters specified in Table III. Minimum 1 agrees well with the dimensions of the observed structure, which has Mo-Mo distances of 2.647 and 2.556 Å and Mo-S distances of 2.399 and 2.326 Å. The energy of stabilization of the molecule and the HOMO ( $e''$ ) are listed also in Table III. It is clear that the partly filled  $e''$  HOMO is the prime contributor to the stabilization of the molecule.

### Influence of the Ligands

Let us now return to the symmetrical  $\text{Mo}_3\text{S}_2\text{Cl}_9$  system and see if we can glean the relative importance of the interactions with the different types of ligands present—the  $\mu_3\text{-S}$ , the  $\mu\text{-Cl}$ , and the terminal Cl. We carry out a calculation on  $\text{Mo}_3(\mu_3\text{-S})_2$ ,  $\text{Mo}_3(\mu\text{-Cl})_3$ , and  $\text{Mo}_3\text{Cl}_6$ , i.e., the  $\text{Mo}_3$  core plus each type of ligand separately. The  $\text{Mo}_3$  d orbitals are destabilized by any interaction with additional ligands, the extent of such destabilization being a rough measure of the stabilizing interaction that must occur in low-lying bonding levels. This is essentially an angular overlap model argument. Figure 3 collects these destabilizations for the lower d block levels, all relative to the unperturbed  $\text{Mo}_3$  core.

One would not expect the destabilizations to be entirely uniform for each pattern of substitution (capping vs. bridging vs. terminal) carries its own symmetry constraints. Nevertheless, a general ordering does obtain:  $(\mu_3\text{-S})_2 > (\mu\text{-Cl})_3 > (\text{Cl})_6$ ; i.e., the capping ligands play the leading role and the terminal ligands influence the d block least.

Next let us apply the perturbations of these ligands in sequence. Figure 4 shows the energy levels of  $\text{Mo}_3$ ,  $\text{Mo}_3(\mu_3\text{-S})_2$ ,  $\text{Mo}_3(\mu_3\text{-S})_2(\mu\text{-Cl})_3$ , and the complete  $\text{Mo}_3\text{S}_2\text{Cl}_9$  complex. The sequence is instructive because it shows that



**Figure 4.** Correlation of d block levels of  $\text{Mo}_3$ ,  $\text{Mo}_3(\mu_3\text{-S})_2$ ,  $\text{Mo}_3(\mu_3\text{-S})_2(\mu\text{-Cl})_3$ , and  $\text{Mo}_3(\mu_3\text{-S})_2(\mu\text{-Cl})_3\text{Cl}_6$ .

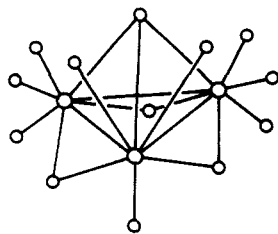
while the capping S ligands are energetically most important, they are not sufficient to set the final level order. The  $2a'_1$  orbital of the  $\text{Mo}_3$  cluster needs the ligand field of the bridging halides to be destabilized. The terminal ligands are not important to the level sequence, as the last stage of substitution shows. In this case, the good closed-shell electron counts for the metal core should be 6, 8, or 12. This is in agreement with the known  $U_3$ -type compound  $\text{Re}_3\text{Cl}_9$ .

It is clear that both the capping and bridging ligands are important in setting the level sequence. The caps destabilize  $1a''_2$  of the  $\text{Mo}_3$  cluster, the bridges  $2a'_1$ . In a general  $\text{M}_3(\mu_3\text{-A})_2(\mu\text{-B})_3\text{C}_6$  cluster if A or B are weak  $\sigma$  donors, then a different level sequence could result, with either  $1a''_2$  or  $2a'_1$  below the  $e''$  MO which is responsible for the Jahn-Teller distortion of the eight-electron cluster. Such eight-electron systems would not half-fill a degenerate level and so should maintain threefold symmetry.

We note here that there is evidence for seven- and eight-electron bicapped clusters in the electrochemistry of the  $\text{Mo}_3\text{O}(\text{OR})_{10}$  clusters of Chisholm and co-workers.<sup>48</sup> These authors have also presented molecular orbital calculations for their clusters that also indicate an  $e''$  level filled by the seventh and eighth electrons, and they recognize clearly the possibility of Jahn-Teller distortions in such complexes.<sup>48</sup>

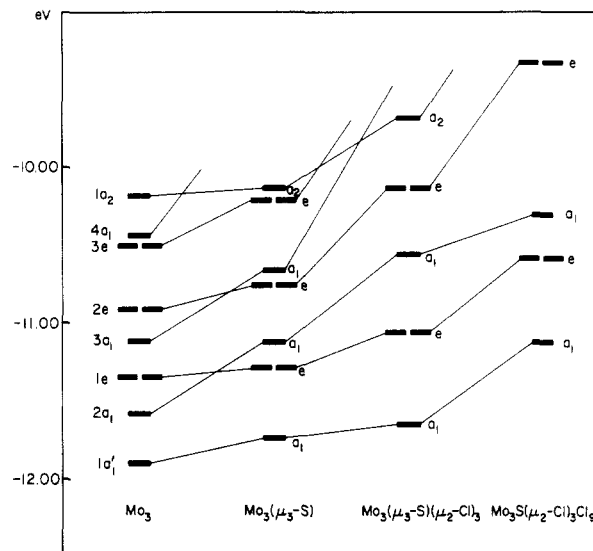
### Monocapped Clusters

There are a number of trinuclear metal clusters with only one capping ligand, classified as  $\text{M}_3$  in Table I. These compounds have six, seven, or eight metal-core electrons and show no distortion, or insignificant distortion, from  $C_{3v}$  symmetry. A typical geometry is shown in 12.



12

The adherence to threefold symmetry in the seven- and eight-electron systems is interesting. We chose as a model



**Figure 5.** Evolution of the orbitals from  $\text{Mo}_3$  to  $\text{Mo}_3(\mu_3\text{-S})$  to  $\text{Mo}_3(\mu_3\text{-S})(\mu\text{-Cl})_3$  to  $\text{Mo}_3(\mu_3\text{-S})(\mu\text{-Cl})_3\text{Cl}_9$ .

system  $\text{Mo}_3(\mu_3\text{-S})(\mu\text{-Cl})_3\text{Cl}_9^{2-}$  with bond lengths and angles in the  $\text{Mo}_3(\mu_3\text{-S})(\mu\text{-Cl})_3$  core equal to those in  $\text{Mo}_3\text{S}_2\text{Cl}_9^{2-}$ . In the monocapped clusters the three bridging atoms move down away from the single capping ligand. The angle  $\theta$  from the center of the  $\text{Mo}_3$  triangle to a  $\mu\text{-Cl}$  and the threefold axis optimizes at  $60^\circ$ . The terminal chlorides also adjust their position in the cluster. We next carried out a sequence of fragment calculations, just as we did in the bicapped cluster. The evolution of the orbitals from  $\text{Mo}_3$  to  $\text{Mo}_3(\mu_3\text{-S})$  to  $\text{Mo}_3(\mu_3\text{-S})(\mu\text{-Cl})_3$  to  $\text{Mo}_3(\mu_3\text{-S})(\mu\text{-Cl})_3\text{Cl}_9$  is shown in Figure 5.

There is now no crossing of levels between  $\text{Mo}_3\text{S}$  and  $\text{Mo}_3\text{SCl}_3$  and between  $\text{Mo}_3\text{SCl}_3$  and  $\text{Mo}_3\text{SCl}_{12}$ . This is a consequence of the lower symmetry and most importantly the different geometrical location of  $\mu\text{-Cl}$  atoms. In the bicapped trimers these bridging chlorides pushed  $2a'_1$  way up. In the monocapped trimers the same orbital is less destabilized.

The important consequence is that the monocapped trinuclear clusters  $\text{M}_3\text{XY}_3\text{Z}_6$  should be undistorted low-spin complexes for 6, 8, and 12 electrons. This is in agreement with the known experimental results. For electron counts greater than 8, but less than 12, a Jahn-Teller distortion should be observed.

### Other Trimers

In recent years, Bino, Cotton, Dori, and co-workers have synthesized a number of bicapped clusters mostly with O caps, three terminal ligands, and six bridging acetate units. There is an inherent ambiguity in the way these bridges can be considered, for is an acetate a single  $\mu$  ligand (13) or the equivalent of two terminal ligands (14)? Either



13

14

view could be defended, and either will produce a level sequence similar to that of  $\text{Mo}_3\text{S}_2\text{Cl}_9^{3-}$ , but the nature of some of the frontier MO's is quite dependent on the model used. This means we must not ignore the specific nature of each bidentate ligand if we are to deduce reliable con-



ployed by Bursten, Cotton, Hall, and co-workers. In their preceding published work dealing with trinuclear metallic clusters,<sup>46-49</sup> they emphasized the investigation of how the Mulliken population of the canonical valence orbitals of the metallic cluster varied with different ligand environments and analyzed the possible trend of metal-metal bond lengths. Many of our conclusions are similar. For instance, we have both deduced that the role of the terminal ligands is less important. Our study complements that of Bursten, Cotton, Hall, et al. These simplified models must be used with care. For instance, when each bidentate ligand is replaced by two terminal ligands, some frontier MO's, predominantly of ligand character, are automatically eliminated. Some fragment MO's that in the carboxylate were in the frontier MO region here are missing.

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### Appendix

The experimental and idealized model geometrical parameters of  $\text{Mo}_3\text{S}_2\text{Cl}_9^{3-}$  are listed in Table V.

Our calculations used the extended Hückel method,<sup>53</sup> with weighted  $H_i$ 's.<sup>54</sup> The Coulomb integrals and wave functions are specified in Table VI.<sup>55</sup>

Registry No. 2, 92844-13-8.

(53) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397.

(54) (a) Ammeter, J. H.; Bürgi, H.-B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686. (b) Hoffmann, R.; Hoffmann, P. *Ibid.* **1976**, *98*, 598.

(55) Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 7240.

## Mechanisms of the Carbon-Hydrogen Bond-Forming Binuclear Reductive Elimination Reactions of Benzyl- and Hydridomanganese Carbonyls<sup>†</sup>

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The reactions between  $\text{RMn}(\text{CO})_4\text{L}$  [ $\text{R} = p\text{-MeOC}_6\text{H}_4\text{CH}_2$ ;  $\text{L} = \text{CO}$  (**1a**),  $\text{L} = (p\text{-MeOC}_6\text{H}_4)_3\text{P}$  (**1c**)] and  $\text{HMn}(\text{CO})_4\text{L}$  [ $\text{L} = \text{CO}$  (**2a**),  $\text{L} = (p\text{-CH}_3\text{OC}_6\text{H}_4)_3\text{P}$  (**2c**)] exhibit diverse stoichiometries and mechanistic pathways, depending upon the solvent and CO concentration and on whether  $\text{L} = \text{CO}$  or  $(p\text{-CH}_3\text{OC}_6\text{H}_4)_3\text{P}$ . The following reactivity patterns were identified: (1) In benzene: **1a**  $\rightleftharpoons$   $\text{RMn}(\text{CO})_4 + \text{CO}$ , followed by  $\text{RMn}(\text{CO})_4 + 2\text{a} \rightarrow \text{RH}$ . (2) In acetonitrile or acetone (S): **1a**  $\rightleftharpoons$   $\text{RCOMn}(\text{CO})_4(\text{S})$ , followed by  $\text{RCOMn}(\text{CO})_4(\text{S}) + 2\text{a} \rightarrow \text{RCHO}$ . (3) In benzene: **1c**  $\rightarrow$   $\text{R}\cdot + \cdot\text{Mn}(\text{CO})_4\text{P}$ , followed by  $\text{R}\cdot + 2\text{c} \rightarrow \text{RH}$ . (4) In benzene: **1c** +  $\text{CO} \rightarrow \text{RCOMn}(\text{CO})_4\text{P}$ , followed by  $\text{RCOMn}(\text{CO})_4\text{P} + 2\text{c} \rightarrow \text{RCHO}$ . The kinetics of the reactions are described and the factors influencing the choice of reaction pathway discussed.

Binuclear reductive elimination reactions between transition-metal alkyls and transition-metal hydrides constitute important steps in a variety of stoichiometric and catalytic processes, for example, the product-forming steps in certain hydrogenation and hydroformylation reactions. However, only recently have such reactions received direct attention.<sup>1</sup> Several studies have revealed diverse reactivity patterns and led to disparate mechanistic conclusions; only in a few cases has an actual binuclear reductive elimination step been directly identified. Norton<sup>1a</sup> has reported that the thermal decomposition of  $\text{OsH}(\text{CH}_3)(\text{CO})_4$  is an intermolecular process and suggested that methane is formed by reductive elimination from a binuclear acyl hydride intermediate. He also reported similar reactivity patterns for reactions of iridium and rhodium acyls with osmium hydrides. More commonly, reductive elimination reactions between metal acyl and metal hydride complexes yield aldehydes. Recently, it has been suggested that the aldehyde-producing step in hydroformylation involves such a binuclear reductive elim-

ination reaction between  $\text{RCOCo}(\text{CO})_4$  and  $\text{HCo}(\text{CO})_4$ .<sup>2</sup> Inhibition of the reaction by CO suggests that this step involves a vacant coordination site.<sup>3</sup> Bergman<sup>4</sup> has reported that reaction between a molybdenum alkyl  $\text{CpMo}(\text{CH}_3)(\text{CO})_3$  and the corresponding hydride  $\text{CpMoH}(\text{CO})_3$  produces acetaldehyde through binuclear reductive elimination, following alkyl migration to generate a coordinatively unsaturated acyl complex. For the corresponding benzylmolybdenum complex, Mo-C bond homolysis apparently is competitive with alkyl migration and mixtures of aldehyde and toluene are formed.<sup>4</sup> Gladysz<sup>5</sup> has reported that  $\text{C}_6\text{H}_5\text{Mn}(\text{CO})_5$  reacts rapidly with

(1) For recent reviews see: (a) Norton, J. R. *Acc. Chem. Res.* **1979**, *12*, 139. (b) Bergman, R. G. *Acc. Chem. Res.* **1980**, *13*, 113. (c) Halpern, J. *Inorg. Chim. Acta* **1982**, *62*, 31.

(2) Alemdaraglu, N. H.; Penninger, J. C. M.; Otlay, E. *Monatsh. Chem.* **1976**, *107*, 1153.

(3) Heck, R. F.; Breslow, D. S. *Chem. Ind. (London)* **1960**, 467. Heck, R. F. *Adv. Organomet. Chem.* **1966**, *4*, 243. Heck, R. F. "Organotransition Metal Chemistry"; Academic Press: New York, 1975; p 217.

(4) Jones, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 5447.

(5) Tam, W.; Wong, W.-K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 1589.

<sup>†</sup> Dedicated to the memory of Earl L. Muetterties.