

## Electronic Structure and Bonding in Manganese Pentacarbonyl Halides and Hydride

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The electronic structure and bonding of  $\text{Mn}(\text{CO})_5\text{L}$  ( $\text{L} = \text{Cl}, \text{Br}, \text{I}, \text{H}$ ) are investigated in the LCAO approach using a non-parameterized calculation. The highest occupied molecular orbital for the halogen compounds is found to be predominantly halogen, in agreement with the interpretation of recently obtained photoelectron spectra. The  $\pi$ -acceptor ability of the carbonyl ligand both *cis* and *trans* to group L is examined and related to simplified carbon-oxygen force constants. It is found that a ligand-ligand interaction bringing about an electron-donor effect from ligand L to *cis* carbonyl may be important. The interaction between the metal and halogen  $\pi$  orbitals results in no  $\pi$  donation from the halogen to the metal with the result that a large charge asymmetry about the halogen atom is predicted.

### Introduction

In recent years, the preparation of transition metal complexes of the type  $\text{M}(\text{CO})_5\text{L}$ , where L is a ligand system ranging from a single hydrogen atom to a polyatomic group, has sparked investigations and vigorous discussions<sup>2-10</sup> of the effects of these ligands upon the bonding characteristics of the carbonyl groups. Attempts have been made to classify<sup>11</sup> the ligands according to their  $\sigma$ - and  $\pi$ -bonding properties (either as electron donors, electron acceptors, or mixtures thereof) and their ability to influence the chemical and physical properties of the *trans* carbonyl group to a different degree or in a different manner than the carbonyl groups *cis* to the ligand L.

These experimental studies coincided with interest in our laboratory to expand the applications of our recent method for molecular orbital calculations<sup>12</sup> to systems whose symmetry was lower than  $\text{O}_h$  yet still involved six-coordination to the metal atom. We chose the systems  $\text{Mn}(\text{CO})_5\text{L}$  where  $\text{L} = \text{Cl}, \text{Br}, \text{I},$  and  $\text{H}$  for several reasons. First of all, the contrast between the pure interaction of the hydrogen atom compared to the (traditional)  $\pi$ -electron donor properties of the halogens should prove informative. Secondly, since our calculational method is completely specified by the choice of basis functions (which in turn are chosen by conformity to calculated atomic charges), the compounds pose a challenge to the reliability of the procedure. In particular, values of the halogen and carbonyl diagonal energy matrix elements relative to each other and to the metal terms

will have dramatic effects on the form of the resultant molecular orbitals. The uppermost orbitals must be in accord with recent information available from photoelectron spectroscopic measurements.<sup>13</sup> Thirdly, the ligand L will affect the bonding abilities of the *trans* carbonyl group to a different extent than the *cis* carbonyl group, an effect which should also be evident in the molecular orbitals.

### Calculation Procedure

The computational technique used in this work is essentially the same as that previously described in our studies on the hexacarbonyls of vanadium, chromium, and manganese.<sup>12</sup> Two calculational simplifications have been incorporated. In ref 12, two methods for evaluation of the two-center off-diagonal matrix element,  $F_{ab}$ , were employed. Equation 4 of ref 12 was used for metal-ligand terms while eq 2 was used for ligand-ligand and intraligand interactions. In the present work, eq 4 was used throughout, namely

$$\langle \phi^a | F | \chi^b \rangle = S(\phi^a, \chi^b) [\epsilon_a + \epsilon_b] - (\phi^a | -(\nabla^2/2) | \chi^b \rangle + \sum_{v \neq a, b} (\phi^a | (q_v/r_v) | \chi^b \rangle) \quad (1)$$

In the earlier work the three-center nuclear attraction integrals involved in the last quantity in the expression above were evaluated exactly. Following the suggestion of Hillier,<sup>14</sup> we now estimate these integrals *via* a simplified Mulliken approximation

$$\langle \phi^a | 1/r_2 | \chi^b \rangle = S(\phi^a, \chi^b) [(1/r_{av}) + (1/r_{bv})]/2 \quad (2)$$

The one-center off-diagonal matrix elements are set to zero in this approximation since the overlap integral is zero.

Prior to the acceptance of these approximations, we carried out extensive sets of comparative calculations by both procedures. The effects on both the eigenvalues and the eigenvectors are small, particularly when following trends within a series of interrelated species as the pentacarbonyls under discussion here. Space limitations do not permit presentation of the

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(3) F. A. Cotton and R. M. Wing, *J. Organometal. Chem. (Amsterdam)*, **9**, 511 (1967).

(4) H. B. Gray, E. Billig, A. Wojcicki, and M. Faron, *Can. J. Chem.*, **41**, 1281 (1963).

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(11) W. A. G. Graham, *ibid.*, **7**, 315 (1968).

(12) K. G. Caulton and R. F. Fenske, *ibid.*, **7**, 1273 (1968).

(13) S. Evans, J. C. Green, M. L. H. Green, A. F. Orchard, and D. W. Turner, *Discussions Faraday Soc.*, No. 47 (1969).

(14) I. H. Hillier, *J. Chem. Soc., A*, 878 (1969).

comparative sets although they are given in the thesis work available through Dissertation Abstracts.<sup>1</sup>

**Basis Functions.**—Although for purposes of discussion the carbonyl ligand basis functions will be represented in terms of the free carbonyl molecular orbitals, the calculations were carried out in the atomic orbital basis set and then transformed to the ligand MO basis after self-consistency was achieved. For the carbon and oxygen 2s and 2p functions Clementi's<sup>15</sup> double- $\zeta$  best-atom functions for the neutral atoms were employed. The 2s functions were curve-fit to single- $\zeta$  form using a maximum overlap criterion.<sup>16</sup> For the halogen orbitals, single- $\zeta$  best-atom functions for the neutral atoms were used.<sup>17,18</sup> The valence s and p orbitals formed the basis set for the halogens. These functions were Schmidt orthogonalized so that all one-center overlaps with the core functions are zero. A single- $\zeta$  exponent of 1.0 was used for the 1s hydrogen in  $\text{Mn}(\text{CO})_5\text{H}$ . A second calculation with  $\zeta = 1.2$  was also carried out, but the variations were so negligible that these results will not be presented.

For the manganese basis functions, the 1s–3d atomic orbitals given by Richardson, *et al.*,<sup>19</sup> for  $\text{Mn}^+$  were used. The 4s, 4p, and 4d orbitals were constructed invoking the maximum-overlap criterion<sup>16,20</sup> with the ligand atom nearest the metal. Since the systems presented here offer three possibilities, the halogen, the *trans* carbonyl carbon, or one of the *cis* carbonyl carbons, a choice had to be made. For reasons of computational simplicity, the orbital exponents were maximized with respect to the *cis* carbonyls and held constant for all of the calculations. A further advantage of this approach is that any changes seen in electron distributions could be attributed to changes in the L ligand rather than variations due to alterations in the metal basis set. The metal 4s, 4p, and 4d wave functions are filed with the ADI<sup>21</sup> along with the other basis functions employed in this work.

**Bond Distances and Angles.**—Wherever possible, the bond distances were taken from experimental data. The values are summarized in Table I. The C–O distance was kept constant at 1.128 Å, the distance observed in free CO.<sup>22</sup> This simplification, in accord<sup>23</sup> with the insensitivity of the carbon–oxygen bond length for the bond order range of 2–3, was made to facilitate the interpretation of the bonding in terms of a single set of ligand basis functions expressed as carbonyl molecular orbitals. Since the manganese–carbon dis-

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(21) Materials supplementary to this article has been deposited as Document No. NAPS-00918 with the ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 3rd Ave., New York, N. Y. 10022. A copy may be secured by citing the document number and by remitting \$1.00 for microfiche or \$3.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS-NAPS.

(22) G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., Princeton, N. J., 1950.

(23) F. A. Cotton and R. M. Wing, *Inorg. Chem.*, **4**, 314 (1965).

TABLE I

BOND DISTANCES (Å) FOR  $\text{Mn}(\text{CO})_5\text{L}$ 

Compound	Mn–C <sub>ax</sub>	Mn–C <sub>eq</sub>	Mn–L
$\text{Mn}(\text{CO})_5\text{H}^a$	1.822	1.853	1.601
$\text{Mn}(\text{CO})_5\text{Cl}^b$	1.792	1.887	2.37
$\text{Mn}(\text{CO})_5\text{Br}$	1.792	1.887	2.50 <sup>c</sup>
$\text{Mn}(\text{CO})_5\text{I}$	1.792	1.887	2.71 <sup>d</sup>

<sup>a</sup> Reference 25. <sup>b</sup> Reference 24. <sup>c</sup> R. F. Bryan, personal communication, The University of Virginia, Charlottesville, Va. <sup>d</sup> For the covalent radius of  $\text{Mn}^+$  see M. J. Bennett and R. Mason, *Nature*, **205**, 760 (1965); for the covalent radius of I see L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 225.

tances in  $\text{Mn}(\text{CO})_5\text{Br}$  and  $\text{Mn}(\text{CO})_5\text{I}$  are unknown, the experimental values for  $\text{Mn}(\text{CO})_5\text{Cl}$  were used for all of the halogen complexes. The Mn–I distance was taken as the sum of the covalent radii of these atoms, a procedure which is also applicable to the known Mn–H, Mn–Cl, and Mn–Br distances.

In the work reported here, all C<sub>ax</sub>–Mn–C<sub>eq</sub> and L–Mn–C<sub>eq</sub> bond angles were taken as 90°. The known experimental values for  $\text{Mn}(\text{CO})_5\text{Cl}$  are within 2° of this value.<sup>24</sup> For  $\text{Mn}(\text{CO})_5\text{H}$  neutron diffraction has determined the average C<sub>ax</sub>–Mn–C<sub>eq</sub> angle to be 96.5°. <sup>25</sup> As a check, we have carried out a calculation with these positions. Each occupied molecular orbital differed by less than 0.3 eV from those at 90° with only minor alterations in the eigenvectors.

### Carbon Monoxide Molecular Orbitals

So that comparisons between CO bonding in the complexes could be made with free carbon monoxide, the eigenvectors and eigenvalues for the isolated ligand were calculated by means of our approximate approach. The resultant values, together with the Mulliken overlap populations for the molecular orbitals, are given in Table II. The eigenvalues in Table II are generally

TABLE II

EIGENVECTORS, ORBITAL ENERGIES, AND OVERLAP POPULATIONS FOR CO

	2s	2p <sup>o</sup>	2s <sup>o</sup>	2p <sup>o</sup>	E, eV	Overlap pop.
3 $\sigma$	0.2868	-0.2340	0.6920	0.1049	-42.104	0.746
4 $\sigma$	0.4356	0.0919	-0.4339	0.7193	-22.460	0.192
5 $\sigma$	-0.6451	-0.6817	-0.1518	0.4736	-13.806	-0.256
6 $\sigma$	-1.0993	1.1421	1.2390	0.8668	126.070	0.000
1 $\pi$		0.4626		0.7462	-20.990	0.917
2 $\pi$		-0.9538		0.7530	0.366	0.000

lower in energy than the values obtained in our previous calculations in which the Slater basis set was employed.<sup>12</sup> This stabilization of the orbital energies by the use of an expanded basis set is analogous to the results of rigorous SCF calculations. Using a Slater basis, Ransil<sup>26</sup> obtained orbital energies of -40.78, -19.92, -13.08, and -15.86 eV for the occupied 3 $\sigma$ , 4 $\sigma$ , 5 $\sigma$ , and 1 $\pi$  orbital energies. Nesbet,<sup>27</sup> using an expanded basis set, obtained -42.16, -22.45,

(24) R. F. Bryan, P. T. Greene, and A. R. Manning, Abstracts of American Crystallographic Association, Seattle, Wash., March 1969, No. M6.

(25) S. J. La Placa, W. C. Hamilton, J. A. Ibers, and A. Davison, *Inorg. Chem.*, **8**, 1928 (1969).

(26) B. J. Ransil, *Rev. Mod. Phys.*, **32**, 245 (1960).

(27) R. K. Nesbet, *J. Chem. Phys.*, **43**, 4403 (1965).

−15.52, and −17.77 eV, respectively. It is of interest to note that the orbital energies associated with the simpler basis set achieve a better correspondence to the experimental ionization potentials obtained from photoelectron spectroscopy.<sup>28</sup> Since the basis set employed in this work results in eigenvalues which more closely approximate those of Nesbet than Ransil, it will not be surprising to observe a similar deviation between calculated and spectroscopic energy levels in the metal complexes when the orbitals are essentially localized on the carbonyl groups.

As seen from the form of the eigenvectors,  $5\sigma$  is primarily an sp-hybrid orbital located on the carbon atom. This, then, is the orbital which will be involved in  $\sigma$  bonding to the metal atom. It is important to note that the overlap population of  $5\sigma$  is negative which has the effect of decreasing the  $\sigma$ -electron density between the carbon and oxygen atoms. That is, it is an *antibonding* orbital. Donation of the electrons from this orbital to the metal atom will have the effect of increasing the  $\sigma$ -bond strength.

The  $2\pi$  orbital of CO is unoccupied in the free ligand. It also is located primarily on the carbon atom and will be involved in  $\pi$  interactions with the occupied  $d_\pi$  metal orbitals. Insofar as electrons are "transferred" to the  $2\pi$  orbital, the  $\pi$  bonds between the carbon and oxygen atoms will be weakened. This is the familiar "back-bonding" effect. It will be of interest to examine the  $5\sigma$  and  $2\pi$  occupations in the carbonyl groups that are *cis* and *trans* to the hydrogen and halogen atoms and note the changes and differences as a function of the L ligand. It is these two orbitals with which we will be most concerned since  $5\sigma$  is the highest occupied and  $2\pi$  the lowest unoccupied molecular orbital of free carbon monoxide. Therefore, these orbitals will interact the most with the metal 3d orbitals because they are energetically available.

### Results and Discussion

Since a complete tabulation of the eigenvectors and eigenvalues for the four compounds would require an excessive amount of space, these have been placed on file with the ADI.<sup>21</sup> Particular eigenvalues and information such as orbital occupations which are obtainable from the eigenvectors will be presented as needed. Occasional comparisons will be made with  $\text{Mn}(\text{CO})_6^+$ ; therefore the corresponding values for this compound have been included. Although  $\text{Mn}(\text{CO})_6^+$  is an octahedral compound, the molecular orbital results are presented in a  $C_{4v}$  basis to facilitate comparison with the manganese pentacarbonyl derivatives.

**$\text{HMn}(\text{CO})_5$ .**—In a hexacarbonyl complex such as  $\text{Mn}(\text{CO})_6^+$ , the uppermost occupied molecular orbitals are the fully occupied  $2t_{2g}$  orbitals. Our previous calculations<sup>12</sup> have indicated that these orbitals are principally metal  $3d_\pi$  in character, and, as expected from qualitative considerations,<sup>29</sup> the  $2t_{2g}$  eigenvalue

(28) D. W. Turner and D. P. May, *J. Chem. Phys.*, **45**, 471 (1966).

(29) F. A. Cotton and G. W. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience Publishers, New York, N. Y., 1966, p 707.

is stabilized relative to the  $3d_\pi$  diagonal energy matrix element as a consequence of interaction with the antibonding  $2\pi$  orbitals of the carbonyl groups. We can relate  $\text{HMn}(\text{CO})_5$  to the hexacarbonyl by envisioning the replacement of one of the carbonyl groups by the hydride ion,  $\text{H}^-$ . Such an alteration should not only cause some changes in the  $\sigma$ -electron framework but should be particularly noticeable in the  $\pi$  interactions. Since, to a very good approximation, the hydrogen has little or no  $\pi$ -acceptor ability, a redistribution of electronic charge within the  $\pi$  system must result. The degeneracy of the  $t_{2g}$  orbitals is reduced in the  $C_{4v}$  symmetry of the molecule to a doubly degenerate e representation and a  $b_2$  representation. In our basis set, the  $2t_{2g}$  MO of  $\text{Mn}(\text{CO})_6^+$  splits up into the  $7e$  and  $2b_2$  MO's in  $\text{HMn}(\text{CO})_5$ . The metal d orbital ( $d_{xy}$ ) which is a basis function for the  $b_2$  representation interacts simultaneously with the four *cis* carbonyl groups while each of the other two  $\pi$ -bonding d orbitals ( $d_{xz}$  and  $d_{yz}$ ) interact with the axial carbonyl and two of the planar carbonyl groups. For some time, it has been held that the absence of a  $\pi$ -acceptor ligand along one chosen axis should enhance the  $\pi$ -acceptor ability of the group *trans* to it to a greater extent than those *cis*.<sup>30</sup> Possible experimental evidence for such an effect is the shortening of the Mn–C distance *trans* to ligand L compared to the Mn–C distance for the *cis* carbonyl ligand. (See Table I.)

Despite the resultant increase in  $3d$ -*trans*  $2\pi$  carbonyl interaction (and the corresponding increase of the  $3d$ -*trans*  $2\pi$  overlap integral), our calculations indicate that the  $7e$  orbital energy is higher (less negative) than that of the  $2b_2$  orbital. The calculated value is −9.80 eV for  $7e$  and −10.36 eV for  $2b_2$ . Thus the splitting of the  $t_{2g}$  degeneracy can be viewed as a consequence of destabilization of the  $7e$  orbitals because of the absence of  $\pi$ -acceptor ability of the hydrogen ligand. The validity of the  $7e$ - $2b_2$  ordering is affirmed by recent photoelectron spectroscopic studies on  $\text{HMn}(\text{CO})_5$  which clearly show, on the basis of the intensities of the first two ionization bands, that ionization first occurs from the  $7e$  orbital. The photoelectron results indicate a band of relative intensity 2 at 9.00 eV and a second band of relative intensity 1 at 10.60 eV.<sup>18</sup> The agreement between the calculated orbital energies quoted above (−9.80 and −10.36 eV) is gratifying, since we are operating within the confines of Koopmans' theorem.<sup>31</sup>

**Electronic Distribution.**—Various mathematical relationships can be used as a measure of changes in electronic distributions between molecular systems. These include density mappings, charge distributions based upon Mulliken<sup>32</sup> or Löwdin<sup>33</sup> population analyses, bond orders, overlap populations, and orbital occupa-

(30) F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962).

(31) T. Koopmans, *Physica*, **1**, 104 (1933).

(32) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841 (1955).

(33) (a) P.-O. Löwdin, *ibid.*, **18**, 365 (1950); (b) E. R. Davidson, *ibid.*, **46**, 3320 (1967).

tions. All are attempts to systematize the relative changes occurring in the eigenvectors. With the exception of density mappings, our investigations have examined each of the aforementioned techniques and we find the most easily envisioned choice is that of orbital occupation. Upon completion of the calculations, the resultant eigenvectors were reexpressed in terms of the carbon monoxide molecular orbitals and the electrons in the occupied metal complex molecular orbitals were "distributed" *via* a Mulliken population analysis.

In all of the complexes, the orbital occupations of the carbonyl  $3\sigma$ ,  $4\sigma$ ,  $1\pi_x$ , and  $1\pi_y$  orbitals remain nearly fully occupied as in free CO. The occupations of the other orbitals are given in Table III. For

TABLE III  
ORBITAL OCCUPATIONS FOR  $\text{Mn}(\text{CO})_5\text{L}$

	$\text{Mn}(\text{CO})_6^+$	$\text{HMn}(\text{CO})_5$	$\text{Mn}(\text{CO})_5\text{Cl}$	$\text{Mn}(\text{CO})_5\text{Br}$	$\text{Mn}(\text{CO})_5\text{I}$
$L_\sigma$	1.335	1.188	1.420	1.310	1.217
$L_\pi$	...	...	4.000	4.000	4.000
$5\sigma_{\text{eq}}$	1.335	1.363	1.382	1.381	1.381
$5\sigma_{\text{ax}}$	1.335	1.358	1.352	1.349	1.345
$2\pi_{\text{eq}}^y$	0.186	0.230	0.203	0.212	0.224
$2\pi_{\text{eq}}^z$	0.186	0.207	0.194	0.194	0.195
$2\pi_{\text{ax}}^z$	0.186	0.248	0.263	0.263	0.264
$2\pi_{\text{ax}}^y$	0.186	0.248	0.263	0.263	0.264
$d_{z^2}$	0.805	0.847	0.757	0.803	0.847
$d_{x^2-y^2}$	0.805	0.776	0.746	0.742	0.737
$d_{xy}$	1.370	1.286	1.324	1.320	1.315
$d_{xz}$	1.370	1.400	1.430	1.429	1.424
$d_{yz}$	1.370	1.400	1.430	1.429	1.424
Total 3d	5.720	5.709	5.687	5.723	5.747
4s	0.335	0.337	0.353	0.361	0.365
Total 4p	1.383	1.374	1.272	1.301	1.312

the moment, we shall only be interested in the results presented for  $\text{Mn}(\text{CO})_6^+$  and  $\text{HMn}(\text{CO})_5$ . A striking feature of the values is their overall similarity from one complex to another. However, the trends that are observable are precisely what one would expect from the known experimental evidence of the systems. For example, the total  $2\pi$  occupation of the carbonyl groups *cis* (0.437) and *trans* (0.496) to the hydrogen in  $\text{HMn}(\text{CO})_5$  is increased rather substantially from their values in the hexacarbonyl complex (0.372). This is in accord with the changes observed in the calculated<sup>34</sup> C–O force constants for  $\text{HMn}(\text{CO})_5$  of 16.46 mdyne/Å for  $\text{CO}_{\text{ax}}$  and 16.88 mdyne/Å for  $\text{CO}_{\text{eq}}$ . Also, the C–O force constant in  $\text{Mn}(\text{CO})_6^+$  has been calculated to be 18.33 mdyne/Å,<sup>35,36</sup> indicating a lesser amount of  $2\pi$  CO occupation in the hexacarbonyl as compared to the hydride compound. Aside from the semiquantitative force constants given above, all of the C–O stretching modes except  $A_1$  (radial) are less for the  $\text{HMn}(\text{CO})_5$  than for  $\text{Mn}(\text{CO})_6^+$ . The simplified force constants and  $2\pi$  CO occupations both

indicate that the *trans* carbonyl ligand obtains a weaker covalent bond than the *cis* ligand.

It is of interest to note that the occupations of the  $5\sigma$  carbonyl orbitals, both *cis* and *trans*, change only slightly in any of the complexes. An increased occupation of this orbital would denote a weakening of the  $\sigma$ -bond strength between the carbon and oxygen since the orbital is slightly antibonding. Whether a change from 1.335 to 1.363, hexacarbonyl to hydride, constitutes a significant weakening is difficult to assess. It is clear, however, that changes in the  $2\pi$  occupation are more important not only because of their greater magnitude but because they are more antibonding in character than the  $5\sigma$  orbitals. This is in accord with the frequent assumption that the changes in  $\pi$  bonding are principally responsible for observed changes in physical and chemical properties of the carbonyl groups.<sup>30</sup>

One somewhat unexpected result is the essential constancy of the total 3d orbital occupations. Notice that while changes on the order of 0.05 electron can occur in the occupation of individual d orbitals, the total change from  $\text{Mn}(\text{CO})_6^+$  to  $\text{HMn}(\text{CO})_5$  is 0.011 electron despite the alterations involved in going from a positive ion to a neutral molecule. It appears that the d orbitals act primarily as transmitters of electron density from one part of the ligand framework to another. However, in this adaptation a considerable degree of charge asymmetry develops about the manganese atom.

**Pentacarbonyl Halides.**—The class of compounds  $\text{Mn}(\text{CO})_5\text{X}$ , where X = Cl, Br, or I, presents a unique opportunity to investigate the effects of combining a set of  $\pi$  acceptors, the carbonyls, with simple  $\pi$ -donor species, the halides. In most of the calculations<sup>20, 37–40</sup> on halide-transition metal complexes the halogen atomic orbital energy levels have been shown to be substantially below the 3d metal orbitals so that the higher occupied molecular orbitals are mainly metal in character. This effect is also evident experimentally in the interpretation of ligand→metal charge-transfer bands<sup>41</sup> and electron spin resonance results<sup>42</sup> for species such as  $\text{MnCl}_6^{4-}$  in which it has been shown that the orbitals containing the unpaired electrons are primarily metal in character. A qualitative energy level diagram based upon the transference of this concept to the pentacarbonyl halide systems is given in Figure 1a. Note that the expected ordering of the orbitals would be  $8e > 2b_2 > 7e$ , with the latter orbital energy well separated from the first two. Two days before we had completed the preliminary integral calculations for the halides, we were informed of the results from photoelectron spectroscopy by Evans, *et al.*,<sup>13</sup> on these species. Their values definitely indicated that the sequence of levels must be  $8e > 7e > 2b_2$  with the uppermost occupied

(34) P. S. Braterman, R. W. Harrill, and H. D. Kaesz, *J. Am. Chem. Soc.*, **89**, 2851 (1967).

(35) This C–O force constant was obtained *via* the method of ref 30, with  $\nu_{\text{CO}}$  equal to 2101  $\text{cm}^{-1}$  from ref 36 and an interaction constant of 0.25 mdyne/Å.

(36) R. J. H. Clark, *J. Organometal. Chem.* (Amsterdam), **6**, 167 (1966).

(37) K. D. Carlson and C. Moser, *J. Chem. Phys.*, **46**, 35 (1967).

(38) P. O. Offenhardt, *ibid.*, **47**, 2951 (1967).

(39) H. Basch, A. Viste, and H. B. Gray, *ibid.*, **44**, 10 (1966).

(40) J. W. Richardson, D. M. Vaught, T. F. Soules, and R. R. Powell, *ibid.*, **50**, 3633 (1969).

(41) C. K. Jørgenson, *Struct. Bonding* (Berlin), **1**, 3 (1966).

(42) F.-D. Tsay and L. Helmholz, *J. Chem. Phys.*, **50**, 2642 (1969).

orbital, 8e, primarily halogen in character. Such a sequence could be obtained only if the halogen  $\pi$  levels were at nearly the same energy or less stable than the metal  $3d_{\pi}$  energies. Since our calculational technique does not permit the arbitrary placement of the starting levels, it was with some trepidation that we programmed the final input for the computation of the eigenvalues and eigenvectors. The results, presented in Table IV,

TABLE IV  
CALCULATED AND OBSERVED ORBITAL ENERGIES (eV)  
FOR 8e, 7e, AND  $2b_2$  ORBITALS

Orbital	—Mn(CO) <sub>5</sub> Cl—		—Mn(CO) <sub>5</sub> Br—		—Mn(CO) <sub>5</sub> I—	
	Calcd	Exptl	Calcd	Exptl	Calcd	Exptl
8e	8.61	8.80	7.92	8.76	7.46	8.35–8.65
7e	10.40	10.43	10.15	10.04	9.95	9.57
$2b_2$	10.65	11.00	10.47	10.80	10.29	10.37

were very satisfying. Not only was the sequence  $8e > 7e > 2b_2$  obtained for the three halide complexes but the eigenvalues were in good accord with those expected from the photoelectron results on the basis of Koopmans' theorem.

The eigenvectors associated with the 8e and 7e orbitals are in agreement with the conclusions of Evans, *et al.* The per cent character of these molecular orbitals are given in Table V. Not only is each 8e orbital

TABLE V  
PER CENT CHARACTER OF 8e, 7e, AND  $2b_2$  ORBITALS

Orbital		%		
		Mn(CO) <sub>5</sub> Cl	Mn(CO) <sub>5</sub> Br	Mn(CO) <sub>5</sub> I
8e	$3d_{zz}$	10.52	5.23	2.92
	$X_{pz}$	86.28	93.75	96.98
7e	$3d_{zz}$	59.25	64.53	66.66
	$X_{pz}$	13.81	6.54	3.47
$2b_2$	$3d_{xy}$	64.46	64.33	64.13
	$2\pi$ CO <sub>eq</sub> <sup>a</sup>	31.65	31.80	32.02

<sup>a</sup> Total per cent for the four equatorial carbonyl ligands.

primarily halogen but the increasing halogen character is in keeping with the decreasing electronegativity of the halogens from chlorine to iodine. The splitting of the 8e ionization band in Mn(CO)<sub>5</sub>I is in accord with this increasing halogen character and the stronger spin-orbit coupling in iodine, as has been explained by Evans and coworkers.

A simplified version of the energy level diagram for Mn(CO)<sub>5</sub>X is given in Figure 1b. The location of the halogen  $\pi$  diagonal matrix element relative to the metal  $3d_{\pi}$  is in striking contrast to that obtained in several transition metal halides. The explanation obviously lies in the presence of the carbonyl groups. First of all, we note from Table III that the  $p_{\pi}$  orbital occupancy of the halide ligands remains at 4.00, *i.e.*, completely filled. The combined participation of the halogen  $\pi$  orbitals in the 7e and 8e orbitals, see Table V, does not result in any net transfer of charge from the halogens to either the metal or the carbonyl groups. Analogous to the hydride complex, all the electron donation from the halogen occurs through the  $\sigma$  system. Whether this  $\sigma$  donation is through the metal orbitals to the  $2\pi$  carbonyl orbitals or directly to the  $2\pi$  carbonyl

orbitals, as will be discussed later, the carbonyl groups act as "electron sinks," drawing charge from the metal with the result that the 3d and halogen levels become close in energy and actually reverse themselves for the bromide and iodide as compared to the order found in several transition metal halide systems. Indeed, pentacarbonyl *halide* is a misnomer in the sense that the charges on the halogens are much nearer the neutral atom than the negative ion.

The charge-removal effect caused by the  $2\pi$  CO orbitals interacting with the  $3d_{\pi}$  Mn orbitals tends to lower the 3d energy levels so that they are nearly degenerate with or below the halogen  $p_{\pi}$  levels. Aside from this effect, there is the off-diagonal term  $F(3d_{\pi}, 2\pi$  CO) in the energy matrix which results in a stabilization of the molecular orbital which is predominantly metal below the starting 3d energy. This effect is amply illustrated in Figure 1b for the 7e molecular orbital and is exactly analogous to the effect observed for the  $2t_{2g}$  molecular orbital in the hexacarbonyls of vanadium, chromium, and manganese.<sup>12</sup> The fact that the 8e molecular orbital must be orthogonal to 7e results in the 8e orbital energy being considerably less stable than that observed for most halogen  $p_{\pi}$  ionization potentials.<sup>13</sup>

Close inspection of our calculated eigenvalues and comparison with the photoelectron spectrum for the compounds indicates two shortcomings in our calculations. The  $9a_1$  orbital energy is calculated to be at  $-10.75$  eV for Mn(CO)<sub>5</sub>Cl,  $-10.08$  eV for Mn(CO)<sub>5</sub>Br, and  $-9.46$  eV for Mn(CO)<sub>5</sub>I. Comparison of these values with the calculated orbital energies given in Table IV for 8e, 7e, and  $2b_2$  indicates that the  $9a_1$  orbital lies slightly below the  $2b_2$  orbital for Mn(CO)<sub>5</sub>Cl and actually lies above the 7e orbital for Mn(CO)<sub>5</sub>Br and Mn(CO)<sub>5</sub>I. The per cent character of this orbital for all three compounds is greater than 70%  $p_{\sigma}$  halogen. There is no evidence in any of the photoelectron spectra to indicate that this orbital should lie so high in energy. There are two possible causes for this placement of the  $9a_1$  orbital. Both are understandable in the context of the approximations employed in the calculations.

Because of the point-charge approximation for interactions with electron densities of nearest neighbors, the method appears to underestimate the separation of the  $p_{\sigma}$  and  $p_{\pi}$  diagonal terms. With the diffuse functions associated with the halogens, exchange integrals such as  $\langle d_{\sigma}p_{\sigma} | d_{\sigma}p_{\sigma} \rangle$  become large and important. Our calculation fails to take adequate account of the resultant stabilization of the halogen  $p_{\sigma}$  diagonal matrix element. Similar effects would also apply to the off-diagonal element between the metal and  $p_{\sigma}$  orbitals. Both effects, if treated more accurately, could result in sufficient stabilization of the eigenvalues to permit a clear separation of the  $9a_1$  from the 8e, 7e, and  $2b_2$  orbitals. These latter orbitals, being  $\pi$  in character, are less affected by the point-charge approximation. Thus, we conclude that the placement of the  $9a_1$  orbital energy by our calculations is inadequate.

A second discrepancy lies in the absolute values of

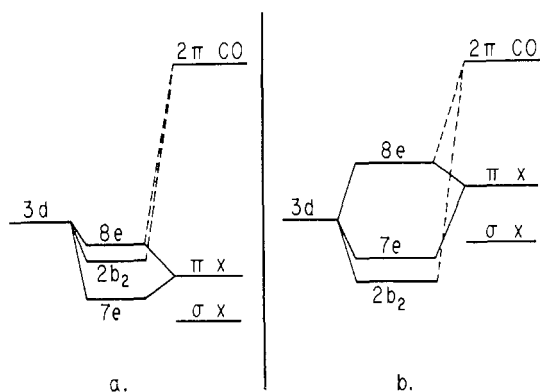


Figure 1.—Energy level alternatives for upper levels of  $\text{Mn}(\text{CO})_5\text{X}$ .

the ionization energies of the electrons in orbitals that are essentially carbonyl  $5\sigma$ ,  $4\sigma$ , and  $1\pi$  in character. We have already mentioned the dependence of these levels on the choice of basis orbitals in the SCF calculations, as well as ours, on the free ligand. The same effect is evident in the complexes. Our eigenvalues for these carbonyl-type orbitals are more stable than the values suggested from the photoelectron results. The photoelectron spectra for  $\text{Mn}(\text{CO})_5\text{L}$  exhibit ionization of the predominantly carbonyl electrons in the region 13–20 eV. The corresponding calculated eigenvalues for  $\text{Mn}(\text{CO})_5\text{L}$  are in the region 18–25 eV. It appears from the above discussion that a constant shift of about 5 eV would be sufficient to bring about a good correlation between the experimental and computed results for these orbitals. However, it should be mentioned that the eigenvectors are in complete accord with the interpretations of the characters of the orbitals involved in the photoelectron spectra. Investigations show that adjustment in the form of the basis functions or arbitrary increases in the halogen  $p_\sigma$  and  $p_\pi$  separation could correct the eigenvalues without substantial distortion of the eigenvectors but such techniques are outside the restrictions we have imposed upon the method. Furthermore, the deviations cause no ambiguity in the interpretation of the experimental results obtained by Evans and coworkers.

**Orbital Occupations and Vibrational Spectra in the Carbonyl Region.**—The vibrational spectra of the manganese pentacarbonyl halides have been studied in detail in terms of both the observed frequencies and intensities. The infrared spectra of the halides are available from 70 to  $4300\text{ cm}^{-1}$  which includes the regions of metal–ligand, overtone, and combination bands. The Raman spectra from 60 to  $2200\text{ cm}^{-1}$  are also known.

The carbonyl stretching frequencies occur in the region from  $1900$  to  $2200\text{ cm}^{-1}$ . For the halides the next lower frequencies are below  $700\text{ cm}^{-1}$ . This separation of frequencies has led to factorization of the force field for these compounds, particularly within the framework of the Cotton–Kraihanzel (CK) model which assumes that changes in carbonyl stretching frequencies are due to changes in  $\pi$  bonding for the M–C–O unit through the  $d_\pi$ – $2\pi$  interaction.<sup>30</sup> While the CK force-field method

has been criticized,<sup>5,43</sup> Jones<sup>44</sup> has suggested that trends in the C–O force constants in a series of similar compounds are meaningful. Obviously, a degree of caution is desirable in the interpretations. With such precautions in mind, it is of interest to compare the trends in orbital occupation with the calculated force constants ( $k$ ) for the three halides. The key quantities are summarized in Table VI.

TABLE VI  
FORCE CONSTANTS AND ORBITAL OCCUPANCIES OF THE  
CO GROUPS IN THE PENTACARBONYL HALIDES

	$5\sigma$	$2\pi_y$	$2\pi_x$	$2\pi$ total	$k$
<i>cis</i> CO					
Cl	1.382	0.203	0.194	0.397	17.50
Br	1.381	0.212	0.194	0.406	17.41
I	1.381	0.224	0.195	0.419	17.28
<i>trans</i> CO					
Cl	1.352	0.263	0.263	0.526	16.22
Br	1.349	0.263	0.263	0.526	16.26
I	1.345	0.264	0.264	0.528	16.30

We note, first of all, that the gross differences in *cis* and *trans*  $k$  values are readily assignable to the differences in total  $2\pi$  occupation. However, the much smaller trends within the  $k$  values are less clear-cut. For the *trans* CO group, it is uncertain whether a variation of  $0.08\text{ mdyn/\AA}$  from chloride to iodide is real since the values lie within the possible errors of the force constant calculations. On the other hand, since structural data were unavailable, the internuclear distances of the metal to *trans* CO groups were kept constant in the three compounds. Minor variations could possibly lead to the small trend required to bring the  $2\pi$  occupation in accord with the *trans*  $k$  values. One also notices a minor trend in  $5\sigma$  occupation in this set which could possibly be magnified by distance changes.

A more significant insight into the factors which influence  $2\pi$  occupation is given by the trends in the *cis* group. Throughout the series, the *cis*  $2\pi_y$  orbital is the only one to undergo substantial change, a change which correlates with the trend in *cis*  $k$  values. This led us to seek out the reason for this trend. The answer resides in what can be called “direct ligand to ligand donation.” The set of  $2\pi_y$  orbitals of the *cis* carbonyl groups participate in the  $a_1$  representation. In this representation it can interact directly with the  $\pi$ -bonding orbital of the halogen ligand as illustrated in Figure 2. As the halogen functions become more diffuse, the degree of interaction should increase and more of the halogen charge can be transferred directly to the  $2\pi_y$  orbitals rather than *via* the indirect transmission through the metal  $d_\pi$  orbitals. Thus, in the occupied  $9a_1$  orbital, the per cent  $2\pi_y\text{ CO}_{\text{eq}}$  character increases in the order: Cl (5.3%), Br (6.9%), I (8.8%). This transfer is responsible for the increasing  $2\pi$  occupation for the series. The possibility of this direct donation from the L ligand to the *cis* carbonyl has been neglected in most of the considerations given to the effects caused

(43) L. M. Bower and M. H. B. Stiddard, *Inorg. Chim. Acta*, **1**, 231 (1967).

(44) L. H. Jones, *Inorg. Chem.*, **6**, 1269 (1967).

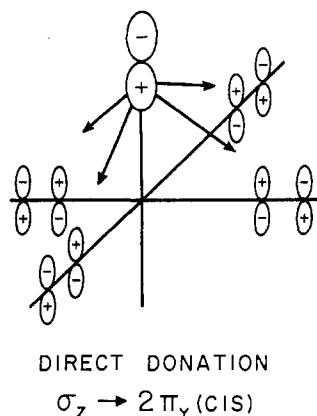


Figure 2.—Orbitals involved in halide to carbonyl electron transfer.

by variation of the L ligand. Variations in direct donation ability of the various L ligands may be partially responsible for infrared intensity changes observed for series of  $\text{Mn}(\text{CO})_5\text{L}$  complexes.<sup>45</sup>

**The Metal-Ligand Bonds.**—We will discuss the M-CO bonds first and then the M-L bonds. The most comprehensive study of the low-frequency spectra for the halide compounds is the ir and Raman work of Clark and Crosse.<sup>46</sup> The ir spectrum of  $\text{Mn}(\text{CO})_5\text{H}$  has also been investigated thoroughly.<sup>47</sup> From a calculational viewpoint we estimate the metal-ligand covalent bond strengths in terms of the  $\sigma$  and  $\pi$  Mulliken overlap populations of the metal functions with the carbon functions of the carbonyl ligand. Contributions from the metal  $4d_\pi$  and  $4p_\pi$  functions are omitted as these terms are small and often negative. The  $4p$  orbital is found to be predominantly involved in the  $\sigma$  bonding framework, in accord with recent studies on metal hexacarbonyls.<sup>48,49</sup>

For the four substituted compounds studied here, the  $\text{M}-\text{CO}_{ax}$   $\sigma$  overlap populations are  $0.569 \pm 0.004$ , while the corresponding quantity for  $\text{M}-\text{CO}_{eq}$  is  $0.587 \pm 0.003$ . Thus, there is little difference in the  $\sigma$ -bonding ability of the *cis* vs. the *trans* carbonyl ligands. This effect is also evident in the  $5\sigma$  CO populations in Table III. That is, the values for the *cis* and *trans* carbonyl ligands differ only slightly.

However, more substantial differences are apparent in the  $3d_\pi-\text{C}_\pi$  overlap populations for *cis* and *trans* groups. For example, the  $3d_\pi-\text{C}_\pi$  (*trans*) population in  $\text{Mn}(\text{CO})_5\text{Cl}$  is 0.215 compared to 0.153 for the  $3d_\pi-\text{C}_\pi$  (*cis*) ligands which suggests a stronger bond between the metal and *trans* carbonyl ligand. Analogous values are obtained for the hydride and the other halides. Indeed, within the halide sequence essentially no change is observed. Since the axial and equatorial Mn-C bond distances were not varied in going from Cl to Br to I, it is not completely justified to assert that the Mn-C bond strengths are the same in the three species, although

(45) S. F. A. Kettle and I. Paul, personal communication, The University, Sheffield, England.

(46) R. J. H. Clark and B. C. Crosse, *J. Chem. Soc., A*, 224 (1969).

(47) W. F. Edgell, J. W. Fisher, G. Asato, and W. M. Risen, Jr., *Inorg. Chem.*, **8**, 1103 (1969).

(48) K. G. Caulton, Ph.D. Thesis, The University of Wisconsin, 1968.

(49) A. F. Schreiner and T. L. Brown, *J. Am. Chem. Soc.*, **90**, 3366 (1968).

such a conclusion is given some support by the work of Edgell, *et al.*,<sup>47</sup> in their study of the stretching frequencies of the Mn-CO groups.

The Mn-X (X = halogen) stretching frequencies occur below  $300\text{ cm}^{-1}$ . Of course, for increasing atomic number of the halogen, the Mn-X stretching frequency is expected to drop from mass considerations. The observed ir frequencies are  $295\text{ cm}^{-1}$  for Mn-Cl,  $218\text{ cm}^{-1}$  for Mn-Br, and  $187\text{ cm}^{-1}$  for Mn-I.<sup>46</sup> Valenti, *et al.*,<sup>50</sup> indicate that the Mn-X stretch is fairly localized from other motions in the below  $300\text{ cm}^{-1}$  region of the spectrum. Clark and Crosse<sup>46</sup> have calculated simplified Mn-X force constants and found Mn-Cl > Mn-Br > Mn-I when treating the system as a diatomic Mn-X. On the other hand, if the carbonyl groups are included in the effective mass of the metal (*i.e.*,  $M + 140$ ), higher force constants are obtained and they are nearly equal for the three compounds.

As in the case of the metal-carbonyl bond we relate the metal-halogen overlap population to the covalent bond strength. The Mn-X  $\sigma$  overlap population for the three halogen compounds is  $0.39 \pm 0.01$  while the  $\pi$  overlap population is  $-0.031 \pm 0.002$ . Thus, we conclude that the halogen atom is bound to the metal by the  $\sigma$  bonds and that the covalent bond strength is nearly constant. The small and negative  $\pi$  overlap populations indicate that there is no transfer of charge to the metal from the halogen atom in the  $\pi$  orbitals (Table III). The invariance of the Mn-X overlap populations among the halogens is in agreement with the constancy of the metal-halogen force constant calculation mentioned above which included the mass of the carbonyl ligands.

**Quadrupole Coupling Constants.**—As indicated by the orbital occupations in Table III, the halogen  $p_x$  and  $p_y$  orbitals are completely filled and all charge donation from the halides to the  $\text{Mn}(\text{CO})_5$  moiety occurs *via* the  $p_z$  orbital. The resultant charge asymmetry about the halogens should be reflected in large halogen quadrupole coupling constants. At this time, the experimental values are unknown.

Invariably, semiempirical calculations have concentrated on the *correlation* of the results with known experimental values. The temptation to *predict* the coupling constants in this case is too strong to resist. Conservatively, one can confidently say that the experimental values of the nqr frequencies should be substantially greater than those found in  $\text{TiCl}_4$ ,  $\text{FeCl}_6^{3-}$ , and similar halide complexes.<sup>20</sup> A step further is to take advantage of the Cotton-Harris relationship which connects the orbital occupations with the nqr frequencies.<sup>51</sup> Our predicted values for the nqr frequencies are 31.82 Mcps for  $\text{Mn}(\text{CO})_5\text{Cl}$ , 265.57 Mcps for  $\text{Mn}(\text{CO})_5\text{Br}$ , and 268.25 Mcps for  $\text{Mn}(\text{CO})_5\text{I}$ .<sup>52</sup>

It should be kept in mind that the Cotton-Harris

(50) V. Valenti, F. Cariati, C. Forese, and G. Zerbi, *Inorg. Nucl. Chem. Letters*, **3**, 237 (1967).

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(52) Atomic values for <sup>35</sup>Cl, <sup>79</sup>Br, and <sup>127</sup>I are those used by J. M. Sichel and M. A. Whitehead, *Theoret. Chim. Acta*, **11**, 263 (1968).

model does not include Sternheimer corrections.<sup>53</sup> Furthermore, the asymmetry values assume that the Mulliken population analysis is appropriate for the interaction of the rather diffuse metal 4p wave function with the halogen. Nevertheless, we present these

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values in the hope of encouraging nqr studies on these species.

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## The Synthesis of Novel Chlorosilyl and Chlorogermyl Mercurials with Some of Their Chemical Reactions<sup>1a</sup>

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When a mercury alkyl is irradiated in the presence of trichlorosilane, bis(trichlorosilyl)mercury, a white crystalline solid, and the alkane are formed. In a similar reaction with methyldichlorosilane, bis(methyldichlorosilyl)mercury is a product. With trichlorogermane as a reactant a similar light-induced reaction produces bis(trichlorogermyl)mercury. These novel mercurials react with compounds possessing a silicon-hydrogen bond to form disilanes. Preparations are described for methylpentachlorodisilane, 1,1-dimethyltetrachlorodisilane, 1,2-dimethyltetrachlorodisilane, 1,1,1-trimethyltrichlorodisilane, 1,1,2-trimethyltrichlorodisilane, 1,1,1,2-tetramethyltrichlorodisilane, 1,1,2-tetramethyldichlorodisilane, 1,1,2-tetramethylchlorodisilane, trichlorosilyltrichlorogermane, and trimethylsilylmethyltrichlorogermane using various modifications of this reaction. Syntheses have been devised for the mercurials, bis(trichlorosilyl)mercury, bis(methyldichlorosilyl)mercury, bis(trichlorogermyl)mercury, and (trimethylsilylmethyl)trichlorogermylmercury. Bis(dimethylchlorosilyl)mercury is formed at low temperatures but decomposes at temperatures above  $-79^{\circ}$ . Bis(trichlorosilyl)mercury also reacts with dimanganese decacarbonyl to form trichlorosilylmanganese pentacarbonyl.

### Introduction

Since Wiberg and his coworkers first reported the preparation and characterization of bis(trimethylsilyl)mercury,<sup>2</sup> there has been a steady increase in the attention devoted to the chemistry of this most interesting compound. The photolysis and pyrolysis yield reactions readily interpreted as reactions of the trimethylsilyl radical.<sup>3-5</sup> Other reactions more readily can be described as four-center reactions.<sup>6,7</sup> The reaction of bis(trimethylsilyl)mercury with dichlorobromomethyl mercurial results in the formation of the most interesting bis(trimethylsilyldichloromethyl)mercury,<sup>8</sup> presumably as a consequence of the insertion of dichlorocarbene into the Hg-Si bond in bis(trimethylsilyl)mercury.

Bis(trialkylgermyl)mercury compounds first were

(1) (a) Most of the work herein reported was presented at the IVth International Symposium on Organometallic Chemistry, July 27-Aug 1, 1969, Bristol, England. (b) To whom inquiries concerning this publication should be addressed at the Department of Chemistry, Tufts University, Medford, Mass. 02155.

(2) E. Wiberg, O. Stecher, H. J. Andrascheck, L. Kreuzbichler, and E. Staude, *Angew. Chem., Int. Ed. Engl.*, **2**, 507 (1963).

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(5) E. J. Louis and G. Urry, *Tetrahedron Lett.*, 3295 (1968).

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(7) R. Fields, R. N. Haszeldine, and R. E. Hutton, *ibid.*, C, 2559 (1967).

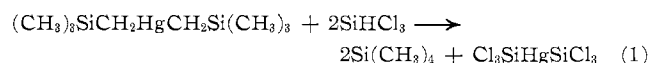
(8) D. Seyferth, R. J. Cross, and B. Prokai, *J. Organometal. Chem.*, **7**, 20 (1967).

reported by Vyazankin,<sup>9</sup> who with his several colleagues has reported the preparation and several chemical reactions of these germyl mercury compounds. Also various different trialkylsilyl mercury compounds have been examined.<sup>10</sup>

Until the present work no chlorosilyl or chlorogermyl mercurials have been reported.

### Results and Discussion

When bis(trimethylsilylmethyl)mercury is irradiated in the presence of the approximate stoichiometric amount of trichlorosilane, a reaction occurs as described in eq 1.



The reaction shown is essentially quantitative and it is possible to obtain highly pure bis(trichlorosilyl)mercury from the product mixture by removing the very volatile tetramethylsilane and extracting the grayish white crystalline solid residue with dry methylene chloride. Removal of the solvent from the extracted material leaves beautiful white platelike crystals of the mercurial. The new compound, bis-

(9) N. S. Vyazankin, G. A. Razuvaev, and E. N. Gladyshev, *Dokl. Akad. Nauk SSSR*, **151**, 1326 (1963).

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