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MOLECULAR ORBITAL STUDY OF BONDING AND CONFORMATIONS IN DINUCLEAR CYCLOPENTADIENYLDICARBONYL COMPLEXES OF MANGANESE AND CHROMIUM CONTAINING GERMANIUM, SULFIDE, DINITROGEN OR PHOSPHINIDENE BRIDGES

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Summary

We carried out nonempirical molecular orbital calculations on *syn*, *gauche* and *anti* conformations of four dinuclear complexes of Mn and Cr with various bridging ligands: $[CpM(CO)_2]_2(\mu_2\text{-}L)$ where M is Mn, L is C (as a model for Ge), N_2 or PPh; and M is Cr, L is S. Contrary to a recent claim, $[CpMn(CO)_2]_2Ge$ does not seem to contain Mn—Ge double bonds and is not analogous to allenes. The Mn—Ge bonds are partially triple so that internal rotation about the Mn—Ge—Mn axis is facile, in accord with the infrared spectra. Bonding in $[CpCr(CO)_2]_2S$ and in $[CpMn(CO)_2]_2N_2$ is very similar to that in the Ge-containing complex. We explain the observed nonrigidity of the Cr complex. Reported infrared data lead to mutually inconsistent conclusions about conformation of the N_2-containing complex in solution. On the basis of calculations, we suggest that these complex molecules are not centrosymmetric in solution. The N_2-bridged dinuclear molecules are better viewed as containing an N_2 molecule rather than two N atoms. The π-antibonding orbitals of N_2 are crucial for its bonding to metals; the filled π-bonding orbitals do not seem to donate electrons to the metal atoms. The calculations show substantial Mn—P π-bonding in $[CpMn(CO)_2]_2PPh$ and this molecule is best viewed as a three-center, four-electron system. We critically examine several other qualitative and intuitive explanations of bonding in these and similar complexes and discuss conclusions and predictions based on such explanations.

Introduction

Inorganic and organometallic complexes in which transition-metal atoms are bridged by ligands pose several kinds of questions that are not encountered in theoretical studies of complexes with terminal ligands only. To what extent do

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bridging ligands transmit electronic effects between the metal atoms? How does extended electron delocalization affect structure, reactivity and spectroscopic properties of the compound in which it occurs?

We shall address these questions in the study of the compounds $[CpMn(CO)_2]_2(\mu_2\text{-}L)$, where L is Ge, N_2 or PPh, and of $[CpCr(CO)_2]_2S$; Cp stands for $\eta^5\text{-}C_5H_5$ and Ph for C_6H_5. Although the four bridging ligands differ in size and in the nature of orbitals used for bonding with metals, the electronic structures of their complexes are sufficiently related to one another to make their comparison profitable. Because the existing descriptions of bonding in the germanium- and dinitrogen-containing complexes appear to contradict their structures and infrared spectra, we examined the electronic structures of these and other related complexes by molecular orbital calculations. This study is a part of our general investigation of multiple metal—ligand bonding [1,2] and of conformations of molecules that contain such bonds [3].

Details of the calculations

An approximation of the Hartree—Fock—Roothaan self-consistent field (SCF) technique, the Fenske—Hall method has been described elsewhere [4] and some of its applications have been reviewed [5,6]. The method is devoid of empirical or adjustable parameters so that results of a calculation (eigenvectors and eigenvalues) are completely determined by the geometry of the molecule and by the basis set.

We used interatomic distances and bond angles from the crystal structures of $[\eta^5\text{-}MeC_5H_4)Mn(CO)_2]_2Ge$ [7], $[CpCr(CO)_2]_2S$ [8], $[(\eta^5\text{-}MeC_5H_4)Mn(CO)_2]_2N_2$ [9] and $[CpMn(CO)_2]_2PPh$ [10]. To expedite calculations on the large molecules, we used C and Cp as models for Ge and MeC_5H_4, respectively. The basis functions were the same as in our previous work [1,2]. The basis set for S was taken from the literature [11].

Bonding abilities of the fragments

We partitioned each molecule into two closed-shell $CpM(CO)_2$ fragments (neutral when M is Mn and charged +1 when M is Cr) and the bridging ligand (C, S^{2-}, N_2 or PPh). After the SCF part of the calculation would converge in the atomic basis set, the molecular orbitals of the complex were transformed into a basis set of the fragment orbitals. This transformation and redistribution of charge among the fragments do not affect the results of the calculation but make them easier to interpret. The energies of the fragment orbitals in the molecular orbital diagrams are diagonal elements of the Fock matrices from the calculations on the complete molecules. These energies differ slightly from one compound to another and also from one conformation of the molecule to another because they reflect the influence of molecular environment upon fragments "ready for bonding". A fragment orbital is classified as σ or π in character according to its bonding ability with respect to another fragment.

Metal fragments

The electronic structures and bonding abilities of $CpMn(CO)_2$ and $CpCr(CO)_2$ are very similar and will be discussed together. Detailed descriptions of the manganese fragment can be found elsewhere [1,12] so only the salient features

Fig. 1.

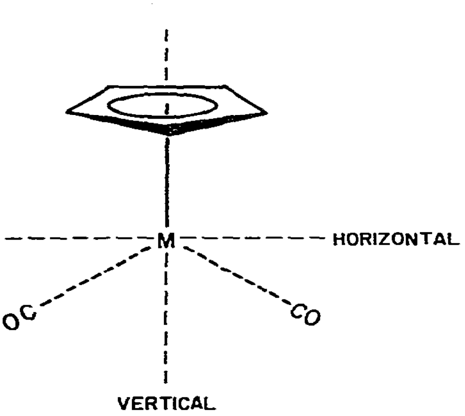

Fig. 2.

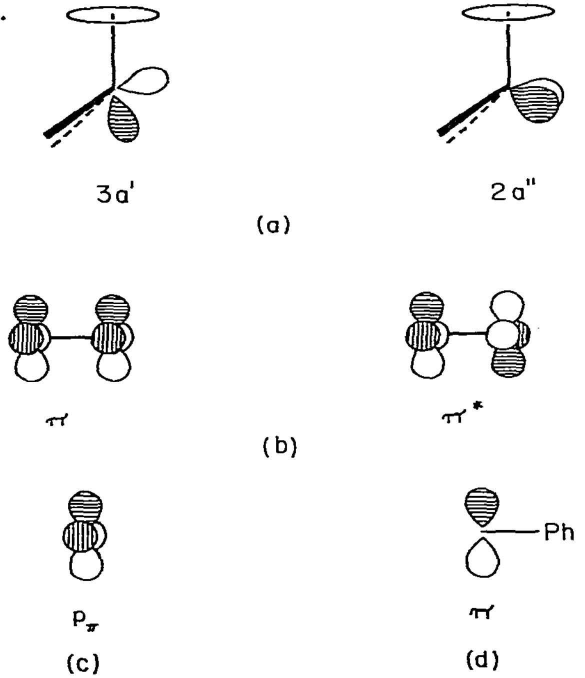

Fig. 1. Two reference planes of CpM(CO)$_2$ fragment.

Fig. 2. Crucial π-type molecular orbitals in: (a) CpM(CO)$_2$ fragment; (b) N$_2$; (c) C, Ge or S; and (d) PPh.

will be summarized here. The fragments have C_s symmetry, so their orbitals belong to symmetry species a' or a''. The six important orbitals of CpMn(CO)$_2$, in the order of increasing energies, are: $1a'$, $1a''$, $2a'$, $3a'$, $2a''$ (the HOMO) and $4a'$ (the LUMO). The π-type orbitals $1a'$ and $1a''$ are very close in energy and consist primarily of the doubly degenerate HOMO level e_1'' of the Cp ring. (In our previous paper [1] we designated orbitals $1a'$ and $1a''$ together as "Cp" and began symmetry-labeling from the next higher level, designated $2a'$ here.) The other four orbitals are largely localized on the Mn atom and composed mainly of its 3*d* orbitals; $2a'$ and $4a'$ have σ character, whereas $3a'$ and $2a''$ have π

TABLE 1

ENERGIES AND PERCENT COMPOSITIONS OF IMPORTANT ORBITALS OF CpCr(CO)$_2^+$

MO	*E* (eV)	Cr							Cp	(CO)$_2$
		d_{z^2}	$d_{x^2-y^2}$	d_{xy}	d_{xz}	d_{yz}	*s*	*p*	e_1''	2π
$4a'$	−12.62	45	2				13	19	8	10
$2a''$ (LUMO)	−15.38			5		67		8	7	12
$3a''$ (HOMO)	−15.78		10		64			4		20
$2a'$	−16.52	12	49		9			2		24
$1a'$	−19.86	14	6		1			4	70	
$1a''$	−19.88			9		11		5	70	

character. Orbital $2a'$ provides Mn—CO bonding within the fragment and is not important for bonding between the metal fragment and the bridging ligand. Orbitals $3a'$ and $2a''$, split by 0.3 eV, are particularly important for bonding in the complexes. Orbital $3a'$ can π-donate in the mirror plane (yz) of the metal fragment, which is called vertical, whereas the HOMO $2a''$ can π-donate in the xz plane, which is called horizontal. These two reference planes are shown in Fig. 1, and the two crucial orbitals are depicted in Fig. 2a.

A single minor difference between $CpMn(CO)_2$ and $CpCr(CO)_2^+$ is that in the Cr fragment $1a''$ is slightly below $1a'$, as Table 1 shows. The ability of these two metal fragments to form π bonds with the ligands in two perpendicular planes is very important for bonding in their complexes, including the bridged ones studied here.

Bridging ligands

In the analysis of bonding, the carbon atom is considered to have two filled orbitals (i.e., two *sp* hybrids) and two degenerate empty orbitals, designated p_π, orthogonal to each other. The valence orbitals of S^{2-} are analogous to those of C but are filled. The bonding ability of N_2 is rather similar to that of a carbon atom. The lone pairs make up the HOMO and two degenerate π-antibonding orbitals, marked π^*, make up the LUMO level. Less important for bonding with the metal are two degenerate π-bonding orbitals, which constitute a level designated π.

Phenylphosphinidene, PPh, can be viewed as containing a trigonally hybridized phosphorus atom with only six valence electrons. These electrons can be envisioned as providing two lone pairs and a P—Ph bond. The crucial orbital of the fragment is its LUMO, a pure *p* orbital of the phosphorus atom perpendicular to the trigonal plane; it is designated π. Important ligand orbitals are depicted in Fig. 2.

From the preceding discussion of the fragments it is clear how the bonds in the dinuclear bridged complexes are formed. The filled σ orbitals of the bridging ligands donate electron density to the LUMO's of the two metal fragments to form σ bonds. The π bonds are formed by back-donation chiefly from the $2a''$ or $3a'$ or both orbitals of the metal fragments into the π-accepting orbitals of the ligands, two in C and N_2 and one such orbital in PPh; in the chromium complex, π donation may be envisioned from S^{2-} to the metal fragments. In the discussions of bonding and conformations we shall emphasize the metal—ligand π interactions. The σ interactions are rather simple, not sensitive to rotation about the metal-bridging ligand axis, and therefore not included in the molecular orbital diagrams (figures) and tables.

Bonding in $[CpMn(CO)_2]_2Ge$ and its geometry

Before we examine the electronic structure and conformations of this interesting compound, it will be useful to summarize concisely the known facts about it and the explanations that have been offered for them. In a recent paper [7], Gäde and Weiss reported synthesis, crystal structure and spectra (infrared, NMR and mass) of $[(\eta^5\text{-}MeC_5H_4)Mn(CO)_2]_2Ge$. The molecule is centrosymmetric in the solid state, i.e., has *anti* structure shown in Fig. 3. On the basis of short Mn—Ge distances, the authors concluded that this compound is the first one to

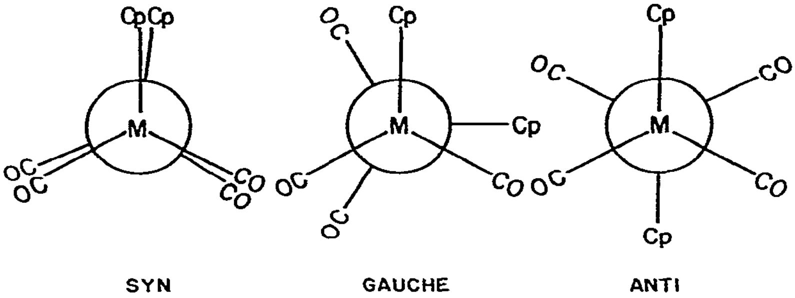

Fig. 3. Limiting conformations of molecules $[CpM(CO)_2]_2(\mu_2\text{-}L)$ that contain linear M—L—M units, viewed along this unit.

contain Mn—Ge double bonds. In an attempt to explain bonding, they decided that this molecule is analogous to a heteroallene and spoke about Mn—Ge π bonding. The hexane solution of the complex gave an infrared spectrum containing four CO-stretching bands instead of two, expected from a centrosymmetric structure. The authors suggested that this may be due to relatively free rotation about the Mn—Ge—Mn axis in solution, but did not investigate this phenomenon.

The infrared spectra alone rule out the analogy between this complex and allene and disprove the notion of Mn—Ge double bonds. As Fig. 4 shows, internal rotation in an allene-like molecule is hindered by full double bonds and would require about 70 kcal mol^{-1} or more to accomplish [13], whereas the infrared spectrum shows that the Ge-bridged complex exists as a mixture of conformers in solution. The centrosymmetric crystal structure also contradicts the allene-like description of bonding in the complex. If a $CpMn(CO)_2$ fragment were like a CR_2 group of an allene and had only one high-lying π orbital, the symmetry planes of two such fragments would have to be perpendicular (as in Fig. 4) in order to engage both p_π orbitals of Ge in the Mn—Ge bonding. It is very unlikely that one p_π orbital would be used for bonding with both metal fragments while the other such orbital remains unused and vacant. In other words, a planar structure is very unlikely for an allene. If both p_π orbitals of the bridging atom are to be engaged in bonding with the metal fragments in the centrosymmetric molecule, the metal fragment must have at least two orthogonal π orbitals energetically close to the p_π orbitals. As we pointed out in the discussion of fragments, this is indeed so and $CpMn(CO)_2$ is not analogous to CR_2 in its bonding ability.

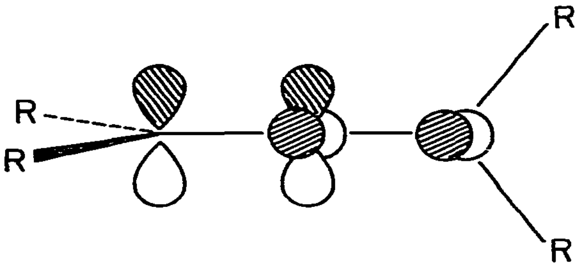

Fig. 4. Bonding in allenes. The two cumulated double bonds cause the two CR_2 planes to be perpendicular.

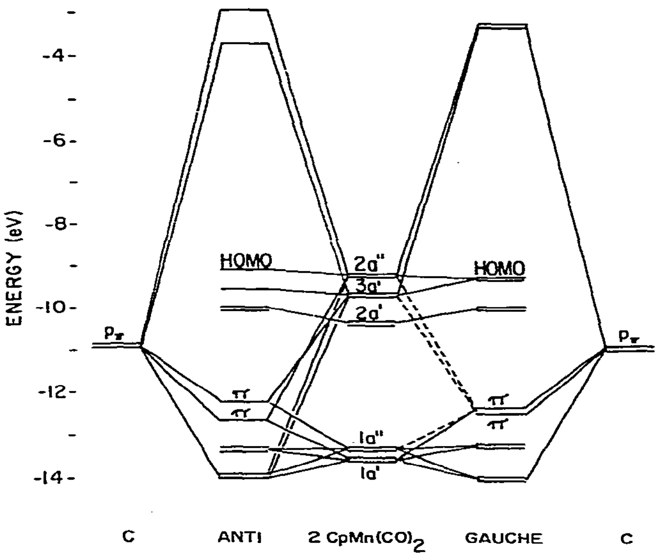

Fig. 5. Important molecular orbitals in *anti* and *gauche* conformations of $[CpMn(CO)_2]_2C$.

We carried out molecular orbital calculations on three rotamers of $[CpMn(CO)_2]_2C$, shown in Fig. 3. The results are shown in Fig. 5 and in Tables 2 and 3. The Mn—C—Mn π system in this molecule may be viewed as superposition of two three-orbital systems involving orbitals $2a''$, $3a'$ and p_π; they are shown schematically in Fig. 6. Orbitals $1a'$ and $1a''$, not included in Fig. 6, are of π type and can interact with p_π orbitals, but these interactions contribute little to the Mn—C bonding because $1a'$ and $1a''$ are localized mainly on the Cp rings. Thus, the molecule contains four three-orbital systems superimposed on one another. Each one of them gives rise to a familiar pattern of three molecu-

TABLE 2

ENERGIES AND PERCENT COMPOSITIONS OF IMPORTANT MOLECULAR ORBITALS OF *anti*-$[CpMn(CO)_2]_2C$

E (eV)	CpMn(CO)$_2$					C	CpMn(CO)$_2$				
	$1a'$	$1a''$	$2a'$	$3a'$	$2a''$	p_π	$2a''$	$3a'$	$2a'$	$1a''$	$1a'$
−2.96					25	45	25				
−3.69 (LUMO)				23		47		23			
−9.10 (HOMO)					50		50				
−9.57				49				49			
−9.97			44						44		
−10.11			47						47		
−12.19	22		2	13		14		13	2		22
−12.66		24			13	26	13			24	
−13.30		50								50	
−13.30	48										48
−13.90		26			11	26	11			26	
−14.01	16			12		34		12			16

TABLE 3

ENERGIES AND PERCENT COMPOSITIONS OF IMPORTANT MOLECULAR ORBITALS OF *gauche*-$[CpMn(CO)_2]_2C$

E (eV)	$CpMn(CO)_2$					C	$CpMn(CO)_2$				
	$1a'$	$1a''$	$2a'$	$3a'$	$2a''$	p_π	$2a''$	$3a'$	$2a'$	$1a''$	$1a'$
—3.30				10	14	46	14	10			
—3.37 (LUMO)				10	14	45	14	10			
—9.32 (HOMO)				26	23		23	25			
—9.35				26	24		23	26			
—10.00			42						45		
—10.11			49						46		
—12.35	18	5		6	6	17	6	6		5	19
—12.51	15	8		9	6	21	6	8		8	15
—13.19	12	32				3				34	11
—13.29	15	34								32	16
—13.94	9	12		6	6	30	6	6		12	9
—14.03	17	8		5	5	28	5	5		8	16

lar orbitals: bonding, nonbonding and antibonding. These patterns, with their inherent symmetry, are evident in Tables 2 and 3. Molecular orbitals designated π, which correspond to Mn—C π bonds, are common to the higher- and lower-lying sets of orbitals; in these molecular orbitals p_π's are mixed in-phase with

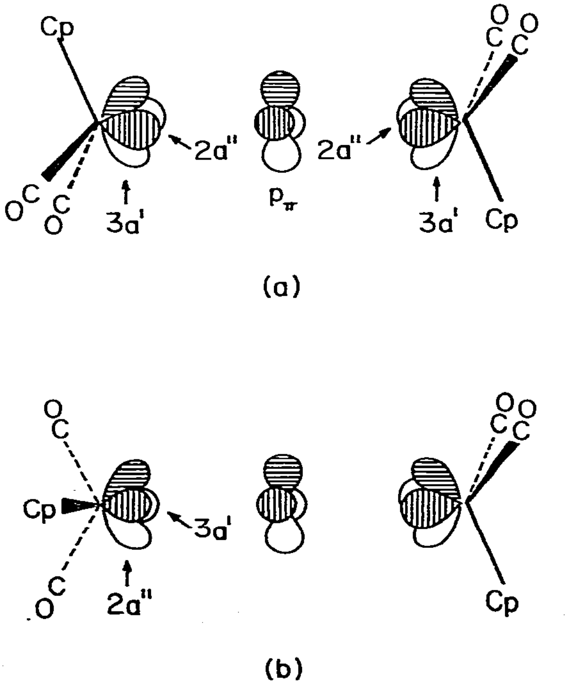

Fig. 6. The most important three-orbital π interactions in *anti* (a) and *gauche* (b) conformations of $[CpM(CO)_2]_2(\mu_2\text{-}L)$ that contains linear M—L—M unit. Depicted are the p_π orbitals of monoatomic bridging ligand L. When L is N_2, the orbital in the middle is π^* (an out-of-phase combination of two *p* orbitals), which is not shown.

$2a''$ and $3a'$ and out-of-phase with $1a'$ and $1a''$. Direct interactions between orbitals of the metal fragments are very weak because the Mn—Mn distance is 350 pm. Thus, the four uppermost filled molecular orbitals, nonbonding among the metals and the bridging atom, have almost the same energies as the corresponding fragment orbitals. The electronic structures of *syn* and *anti* conformations are very similar and the data are given only for the *anti* form. Figures 5 and 6 show that in the *anti* and *syn* conformers, which both have at least one mirror plane, one p_π orbital interacts with metal orbitals of a' symmetry while the other p_π orbital interacts with metal orbitals of a'' symmetry; the resulting molecular orbitals are orthogonal and do not mix. The *gauche* conformer has no overall symmetry at all (its point group is C_1) and the two three-orbital systems are mixed in every π-type molecular orbital. Labels a' and a'' for the fragment orbitals in the *gauche* conformer are not strictly valid but we use them because individual $CpMn(CO)_2$ fragments retain their local C_s symmetries and for the sake of clarity.

The structure, spectra and molecular orbital analysis all show that there are no Mn—Ge double bonds in $[(\eta^5\text{-}MeC_5H_4)Mn(CO)_2]_2Ge$ and that the electronic structure of this interesting molecule is not similar to that of an allene. When the two higher-lying three-orbital systems are considered, the Mn—Ge—Mn bonds can be viewed as partially triple.

The spectroscopic data of Gäde and Weiss can be easily explained by the notion of partial triple bonding. Since the metal-based orbitals $2a''$ and $3a'$ are energetically close and similarly localized on the Mn atoms, the Mn—Ge—Mn π-electron system is nearly cylindrical. Twists about this axis cause very little change in overlap and bonding, so that internal rotation in solution is facile. Any skewed rotamer would give rise to the observed four CO-stretching infrared bands.

This qualitative prediction of easy internal rotation is confirmed by quantitative analysis of the computed electronic structures of rotamers. We summed eigenvalues of the important occupied molecular orbitals in each rotamer. When the summation is over the six uppermost orbitals, those constituting the two upper three-orbital systems and the $2a'$ levels, the total orbital energies for *syn*, *gauche* and *anti* conformations are —63.84, —63.64 and —63.60 eV, respectively. When the summation is over ten molecular orbitals, and thus includes the two lower systems as well, the respective total orbital energies are —118.01, —118.09 and —118.11 eV. Both these sets of numbers show that there is practically no electronic preference for any rotamer. The crystal structure, calculated interatomic distances between the two rotating metal fragments and examination of molecular models all indicate that rotation about the Mn—Ge—Mn axis is not sterically hindered so that, in the absence of electronic preference, it should be facile. The reported ^1H NMR data [7] support this conclusion: one singlet for the Me groups in MeC_5H_4 and two triplets for the H atoms of the rings indicate that the two MeC_5H_4 ligands have identical average environments.

Bonding in $[CpCr(CO)_2]_2S$ and its nonrigidity

This molecule is isoelectronic with $[CpMn(CO)_2]_2Ge$ and bonding in these two complexes is essentially the same. Two three-orbital interactions, depicted in Fig. 6, give rise to two superimposed systems of orbitals. An additional sys-

TABLE 4

ENERGIES AND PERCENT COMPOSITIONS OF IMPORTANT MOLECULAR ORBITALS OF *anti*-$[CpCr(CO)_2]_2S$

E (eV)	$CpCr(CO)_2$					S	$CpCr(CO)_2$				
	$1a''$	$1a'$	$2a'$	$3a'$	$2a''$	p_π	$2a''$	$3a'$	$2a'$	$1a'$	$1a''$
−4.46					37	22	37				
−5.33 (LUMO)				34		23		34			
−8.08 (HOMO)					50		50				
−8.46				49				49			
−9.25			48	2				2	46		
−9.28			48						50		
−12.90		35		6		16		6		35	
−13.34	47				1	3	1				46
−13.39	49										50
−13.39		49								50	
−14.29	3				10	68	10				3
−14.61		14		7		55		7		14	

tem arises from the interaction among the metal $1a'$ and sulfur p_π orbitals. The electronic structures of *anti* and *gauche* conformations are summarized in Tables 4 and 5, respectively.

The electron cloud of the two partially triple Cr—S bonds within the linear Cr—S—Cr unit is nearly cylindrically symmetrical so that there is virtually no barrier to intramolecular rotation about this axis. The sum of eigenvalues (energies) of the occupied molecular orbitals included in Tables 4 and 5 is the same, −134.19 eV, for the *anti* and *gauche* conformations. This shows that there is no electronic barrier to the twisting. These theoretical conclusions are born out by the NMR and infrared spectroscopic evidence that the compound is stereochemically nonrigid in solution [8].

TABLE 5

ENERGIES AND PERCENT COMPOSITIONS OF IMPORTANT MOLECULAR ORBITALS OF *gauche*-$[CpCr(CO)_2]_2S$

E (eV)	$CpCr(CO)_2$					S	$CpCr(CO)_2$				
	$1a''$	$1a'$	$2a'$	$3a'$	$2a''$	p_π	$2a''$	$3a'$	$2a'$	$1a'$	$1a''$
−4.87				14	22	22	23	13			
−4.88 (LUMO)				13	23	22	22	14			
−8.30 (HOMO)				29	21		20	29			
−8.32				30	20		20	29			
−9.27			36						60		
−9.28			60						36		
−13.10		36		2	2	12	2	2		40	
−13.11		39		2	2	13	2	2		34	
−13.39	32	3								2	63
−13.39	62	2								3	32
−14.47		9		4	4	59	4	4		10	
−14.47		10		4	4	58	4	4		9	

Bonding in $[CpMn(CO)_2]_2N_2$*, its geometry and infrared spectra*

Transition-metal complexes containing N_2 ligand have been studied because of their possible use for catalytic reduction of nitrogen [14—22]. In all known dinuclear complexes that contain bridging N_2 ligand, it is bonded end-on to both metal atoms. Bonding in such complexes has been discussed qualitatively in several articles [23—29], but only one molecular orbital calculation (using extended Hückel method) has been done on one such compound [30].

We carried out calculations on three conformations of $[CpMn(CO)_2]_2N_2$ shown in Fig. 3. The Mn—N distances in this molecule (187.5 pm) are much longer than the N—N distance (111.8 pm). The latter is only slightly longer than the bond length in free N_2 (109.76 pm) [31], which means that the N—N bond strength is little affected by coordination of N_2 to the metal fragments. This is true about all but two or three compounds with terminal end-on or bridging N_2 ligands [16,28]. This fact is consistent with our calculated orbital overlaps. The overlap of the p_π orbitals within the N_2 ligand is 0.33, whereas the overlap of the antibonding π^* orbitals of N_2 with the π-donating orbitals $2a''$ and $3a'$ of the $CpMn(CO)_2$ fragments is only about 0.10. So both crystallographic and theoretical results indicate that this complex is best viewed as consisting of two metal fragments and a dinitrogen molecule rather than two nitrogen atoms. We partitioned the complex molecule accordingly for the basis set transformation.

The most important results of our calculations on *anti* and *gauche* conformations of this molecule are presented in Tables 6 and 7, respectively. The bonding is qualitatively similar to that in the corresponding rotamers of $[CpMn(CO)_2]_2Ge$. The main difference between these two compounds is that π^* orbitals of the N_2 ligand are much higher in energy (—2.78 eV) than p_π orbitals of the less electronegative Group IV atom (p_π orbitals of C in the model complex are at —10.39 eV). Because of the large energy difference, orbitals $1a'$ and $1a''$ practically do not interact with the π^* orbitals, so that the four levels between —12.84 and

TABLE 6

ENERGIES AND PERCENT COMPOSITIONS OF IMPORTANT MOLECULAR ORBITALS OF *anti*-$[CpMn(CO)_2]_2N_2$

E (eV)	$CpMn(CO)_2$					N_2	$CpMn(CO)_2$				
	$1a'$	$1a''$	$2a'$	$3a'$	$2a''$	π^*	$2a''$	$3a'$	$2a'$	$1a''$	$1a'$
—0.48					5	41	5				
—0.86 (LUMO)				6		54		6			
—8.07 (HOMO)					49		49				
—8.53				49				49			
—9.47			47						47		
—9.51			49						49		
—9.90					41	18	41				
—10.01				41		13		41			
—12.85		50								50	
—12.87	49										49
—12.88		50								50	
—13.01	47										47

TABLE 7

ENERGIES AND PERCENT COMPOSITIONS OF IMPORTANT MOLECULAR ORBITALS OF *gauche*-$[CpMn(CO)_2]_2N_2$

E (eV)	$CpMn(CO)_2$					N_2	$CpMn(CO)_2$				
	1*a*′	1*a*″	2*a*′	3*a*′	2*a*″	π^*	2*a*″	3*a*′	2*a*′	1*a*″	1*a*′
—0.67				2	3	49	3	2			
—0.75 (LUMO)				2	3	45	3	2			
—8.30 (HOMO)				22	26		30	20			
—8.31				20	30		26	22			
—9.49			47						47		
—9.52			48						48		
—9.97				26	15	15	17	24			
—9.98				24	17	15	16	26			
—12.84	11	35								43	10
—12.85	4	50								41	5
—12.93	36	11								11	37
—12.98	45										43

—13.01 eV in both conformations are bonding and antibonding combinations of pure 1*a*′ and 1*a*″ orbitals. There are only two superimposed three-orbital systems in the N_2-containing dimer and each of them consists essentially of three molecular orbitals, as before. The orbitals between —9.90 and —10.01 eV in both conformations represent Mn—N_2 π bonds, whereas the higher-lying filled orbitals are nonbonding among the metal fragments and dinitrogen. According to our calculations, filled π-bonding orbitals of N_2 (designated π) do not interact with the vacant orbitals in the metal fragments; in other words, N_2 does not act as a π donor. This is logical because the π-type vacant orbitals of $CpMn(CO)_2$ are about 23 eV above the filled π level of N_2. The interactions of the filled π level of N_2 with low-lying, filled orbitals of the metal fragments do not result in transfer of electron density among them. Our findings are consistent with the photoelectron spectra and molecular orbital calculations on the mononuclear complex $CpMn(CO)_2N_2$ [32]. The total electronic energy of the molecule practically does not change with rotation about the Mn—N—N—Mn axis; the sums of the eigenvalues of the uppermost filled molecular orbitals are —107.14, —107.17 and —107.10 eV for *syn*, *gauche* and *anti* conformations, respectively. Since the Mn atoms are almost 500 pm apart, the steric interactions between the metal fragments are certainly negligible and the molecules in solution should be easily twisted, as was the case with two complexes discussed above.

We believe that the analysis of these theoretical calculations enables us to evaluate qualitative bonding schemes for N_2-bridged dinuclear complexes that have been proposed before and to examine some published spectroscopic data for $[CpMn(CO)_2]_2N_2$. Our results are essentially consistent with the bonding scheme of Gray and his coworkers, who emphasized the importance of donation from the metal *d* orbitals into dinitrogen π^* orbitals [23]. However, we disagree with the bonding model proposed by Chatt and his coworkers [18,21, 24]. They treat M—N_2—M as a four-center unit, M—N—N—M, and arrange its π-type molecular orbitals in the order of increasing number of nodal surfaces:

0, 1, 2 and 3. In this simplified treatment, the molecular orbitals involving π^* level of N_2 are predicted to lie below the molecular orbitals involving much more stable π level of N_2. Such a reasoning is appropriate for a molecule like butadiene, in which the four atoms are identical or very similar and the bond lengths are nearly equal. But in M—N—N—M system a nodal surface between the strongly bound N atoms causes much greater destabilization of the orbital in which it occurs than do nodal surfaces between the distant $CpMn(CO)_2$ and N_2 units.

The fact that $[CpMn(CO)_2]_2N_2$ has a center of symmetry in the solid state was interpreted as if the π-donating orbitals of both metal-containing units were competing for the same π-accepting π^* orbital of N_2; it was concluded that back-bonding to N_2 is not significant in this complex [33]. The calculations show, however, that both $2a''$ and $3a'$ π-donating orbitals of the metal fragments interact with the π^* orbitals of N_2 and that the back-bonding is substantial; each π^* orbital accepts 0.35 electrons. The interactions are analogous to those shown in Fig. 6 for monoatomic L. This theoretical finding agrees with large decrease in the N_2-stretching frequency from free N_2, via the mononuclear complex, to the dinuclear complex discussed here [9].

It was reported [9] that $[CpMn(CO)_2]_2N_2$ and its analog with η^5-MeC_5H_4 display only two CO-stretching bands in their infrared spectra, which would mean that the molecules are centrosymmetric in solution. At the same time, a moderately strong N_2-stretching band was reported for each complex under identical conditions. The N_2-stretching vibration of a centrosymmetric molecule (A_1 species in C_{2h} point group) is not infrared-active but is Raman-active. Therefore we think that the infrared data from different spectral regions for the same molecule are not consistent with each other. As we pointed out above, internal rotation in this molecule should be facile. We believe that the N_2-stretching band, expected for a twisted structure, was correctly assigned. The wavenumber of that band is logical in comparison with those of free N_2 and $CpMn(CO)_2N_2$ [9]. The assignment would be quite convincing if supported by infrared spectra of ^{15}N-enriched complexes and by Raman spectra. The reported two very strong CO-stretching bands may in fact be more than two but overlapped bands even though their reported wavenumbers differ by as much as 45 cm^{-1} in both compounds. Such infrared spectra would be fully consistent with the presence of twisted molecules in solution.

Bonding in $[CpMn(CO)_2]_2PPh$ and its nonrigidity

Phosphinidene, unlike other bridging ligands discussed so far, has only one π-accepting orbital (which we designate π) for interactions with the π-donating orbitals of two $CpMn(CO)_2$ fragments. In that respect PPh resembles carbene ligands. We carried out calculations on two conformations of this molecule, which are shown in Fig. 7. The results are summarized in Tables 8 and 9. In the *anti* conformation, orbital π of PPh interacts only with $2a''$ orbitals of the metal fragments. In the *gauche* conformation, π interacts with $2a''$ of one metal fragment and $3a'$ of another. Since orbitals $2a''$ and $3a'$ are energetically and spatially similar, the twisting does not affect the bonding significantly. The electronic energies of the *anti* and *gauche* rotamers are practically the same; the summed eigenvalues of the eleven uppermost filled molecular orbitals are

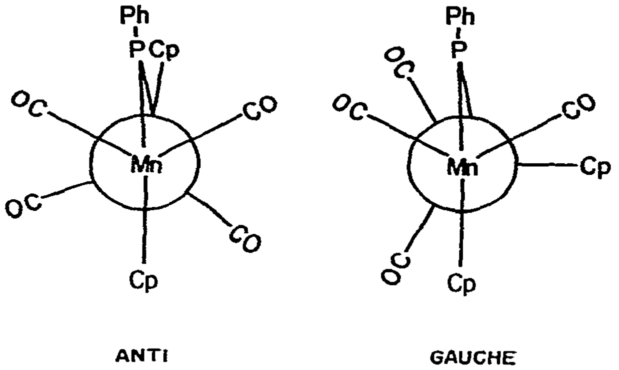

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Fig. 7. Conformations of $[CpMn(CO)_2]_2PPh$, which contains bent Mn—P—Mn unit, viewed in the Mn—Mn direction.

—124.10 and —124.02 eV, respectively. This is consistent with the presence of many CO-stretching bands in the infrared spectrum of dissolved complex and supports the conclusion that rotamers are present in solution [10]. Thus, our analysis corroborates the qualitative conclusion by Huttner and his coworkers that this molecule is a three-center system with four π electrons [10]. It was suggested that the structure of this complex is consistent with pure σ bonding between the Mn and P atoms [33]. A phosphorus atom that makes three σ bonds would not be coplanar with the atoms attached to it; the structure would most likely be pyramidal. In addition to this elementary reasoning, the calculations reveal π back-donation of 0.33 electrons from the metal fragments to PPh; all this charge remains localized on the P atom. The overlaps of π with $2a''$ and $3a'$ are 0.152 and 0.124, respectively and mixing of these orbitals is substantial, as Tables 8 and 9 show. Synthetic results also indicate that the phosphinidene-bridged dinuclear complexes are best viewed as three-center, four-electron π

TABLE 8

ENERGIES AND PERCENT COMPOSITIONS OF IMPORTANT MOLECULAR ORBITALS OF *anti*-$[CpMn(CO)_2]_2PPh$

E (eV)	$CpMn(CO)_2$					PPh	$CpMn(CO)_2$				
	$1a'$	$1a''$	$2a'$	$3a'$	$2a''$	π	$2a''$	$3a'$	$2a'$	$1a''$	$1a'$
—5.71 (LUMO)					31	33	33				
—8.76 (HOMO)					51		49				
—8.78				50				40			
—9.05				42				52			
—9.66			22	2				2	70		
—9.73			72						24		
—12.45					17	61	17				
—12.46	14								2		34
—13.07										96	
—13.15	48										43
—13.18		96									

TABLE 9

ENERGIES AND PERCENT COMPOSITIONS OF IMPORTANT MOLECULAR ORBITALS OF *gauche*-$[CpMn(CO)_2]_2PPh$

E (eV)	$CpMn(CO)_2$					PPh	$CpMn(CO)_2$				
	$1a'$	$1a''$	$2a'$	$3a'$	$2a''$	π	$2a''$	$3a'$	$2a'$	$1a''$	$1a'$
−5.94 (LUMO)					34	35		27			
−8.28 (HOMO)				4			89				
−8.96				4	40			53			
−9.16				75	3			3	9		
−9.51				12					83		
−9.91			95								
−11.90					16	31		11			31
−12.79	4					2				84	
−12.84	28				2	9		3		16	
−13.31	2	93									4
−13.45	18	6			3	17		2			51

systems: $CpMn(CO)_2$—PPh—$Fe(CO)_4$ unit, isoelectronic with the compound under discussion, acts as an allyl-like ligand in the complex with $Fe(CO)_3$ [34].

Concluding remarks

This study demonstrates, we believe, how unrealistic it may be to envision localized bonds in molecules where electrons are in fact delocalized and to discuss bonding in transition-metal complexes by comparing them with seemingly analogous compounds of main-group elements. To properly describe bonding in a complex molecule it is essential to know the bonding abilities of its fragments in some detail.

It has very recently been predicted that, since the pyramidal fragment $CpMn(CO)_2$ has a metal-based lone pair, it should be able to form adducts with various σ-accepting Lewis acids and to dimerize into $[CpMn(CO)_2]_2$, which would contain a metal—metal double bond [33]. As we showed above, the HOMO and the next occupied orbital of $CpMn(CO)_2$ can indeed be termed metal-based lone pairs, but these orbitals have π character with respect to the missing ligand. The LUMO, on the other hand, has σ character. It is not likely that, without drastic changes in its bonding ability, the manganese fragment would form Lewis adducts with σ acceptors. Likewise, the manganese fragments should not easily dimerize even if their tilting with respect to each other causes some mixing of the σ- and π-type orbitals. Indeed, our calculations on the fictitious dimer $[CpMn(CO)_2]_2$ show its frontier orbitals to be in-phase and out-of-phase combinations of the corresponding fragment orbitals. Since both bonding and antibonding molecular orbitals resulting from each interaction are filled, there seems to be no net metal—metal bond in the dimer.

The explanations of bonding put forth in this study may be applicable to other bridged dinuclear complexes as well. Compounds with arsinidene [35] and stibandiyl [36] bridging ligands have structures and infrared spectra similar to those of the phosphinidene complexes examined here. Infrared spectra of compounds $[CpMn(CO)_2]_2L$ in which L is S [37], S_2 [38], Se [38] or Se_2 [38] indicate to us that rotamers are present in solutions. Epimerization of the compound in which L is $As_2H_2Ph_2$ proceeds by intramolecular twisting about the As—As axis in the bridging ligand [39]. Unlike its congeners, the compound in which L is P_2Me_4O was reported to give rise to only two CO-stretching infrared bands [40] and thus seems to be centrosymmetric in solution as well as in the solid state. This rigidity may have steric origin.

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