tem the solute does not obey Henry's law so the solvent could not be expected to obey Raoult's law.

However, as presented elsewhere in detail,[6,16-20] the authors, on the basis of reasoning from molecules, are not surprised when they find the activity of the solvent obeying an equation of the form $a_1 = 1 - k_1N_2$ with $k_1 \neq 1$.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
STATE UNIVERSITY OF NEW YORK AT BUFFALO, BUFFALO, NEW YORK 14214

Application of Extended Hückel Theory to the Calculation of the Potential Energy Curve of Diatomic Copper

BY C. R. HARE, T. P. SLEIGHT, W. COOPER, AND G. A. CLARKE

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Extended Hückel theory molecular orbital calculations using the Cusachs approximation of the exchange or resonance integrals have been carried out on the Cu_2 molecule. The agreement with the reported experimental internuclear distance, dissociation energy, and vibrational stretching frequency, which define the potential energy curve, is good. The results are also in accord with the ionization potential and the energy of the first spectral transition. Other approximations to the off-diagonal matrix elements are shown to be less satisfactory.

Introduction

The extended Hückel molecular orbital theory[1,2] has proved to be a simple but useful approach for the description of many molecular properties. The theory requires only the appropriate choice of the Coulomb integrals or orbital energies (H_{ii}), the orbital exponents (single Slater or double ζ), and a physically reasonable method of approximating the exchange or resonance (H_{ij}) integrals. This approach has been applied, with some success, to the calculation of a limited number of properties of simple molecules such as H_2 and H_2O[3,4] and to the more complicated transition metal complexes[2] or metalloporphyrins.[5] However, if the extended Hückel theory is to be considered of general utility, it should be capable of reproducing many of the physical observables of simple molecules. In this connection, Allen and Russell[6] have recently carried out bond angle calculations on a number of small molecules using the extended Hückel method. Their results have shown that the extended Hückel theory is capable of reproducing both the *ab initio* Hartree–Fock solutions and the known shapes of small molecules. They also provided the theoretical justification which allows the sum of one-electron energies to represent the total molecular energy in determining molecular geometry. However, extensive semiempirical calculations have not[7] as yet established general criteria for the determination of the equilibrium bond distances of widely differing molecules. It is therefore only a convenience that most semiempirical calculations employ experimentally determined molecular geometries.

It seemed desirable to initiate related semiempirical calculations with a systematic examination of the consequences of some parameter choices and approximations to the off-diagonal terms for the homonuclear diatomic molecules of the transition metals. Calculations on these molecules are further simplified by the absence of charge separation which precludes the need for corrections to the energy such as the Madelung term and iterations to self-consistent charge. Recently, information on some of the physical properties of the homonuclear diatomic molecules of the transition metals has become available.[8-12] Of these molecules, gaseous diatomic copper has been the most extensively studied, information being available for the dissociation energy, equilibrium internuclear distance, vibrational frequency, ionization potential and energy of the first transition ($^1\Sigma_g{}^+ \rightarrow {}^1\Sigma_u{}^+$). Enough information is therefore available to allow a meaningful investigation and test of the semiempirical extended Hückel theory on the Cu_2 molecule.

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Methods and Results

The LCAO–extended Hückel theory calculations carried out on Cu_2 in this work have included only the 3d, 4s, and 4p Slater-type atomic orbitals on copper. The other filled orbitals may be considered to be core and therefore ignored since they are not expected to exert major bonding effects over most regions of interest. Initially all four of the common approximations to the off-diagonal elements of the Hamiltonian matrix were used. These included the Mulliken[13] formula, which relates the off-diagonal elements to overlap integrals (S_{ij})

$$H_{ij} = KS_{ij} \tag{1}$$

The Wolfsberg–Helmholz[14] and Ballhausen–Gray[15] modifications of the Mulliken approximation assume the H_{ij} term to be proportional to the overlap and to either the arithmetic mean of the corresponding diagonal elements

$$H_{ij} = {}^1/_2KS_{ij}(H_{ii} + H_{jj}) \tag{2}$$

or the geometric mean of the diagonal elements

$$H_{ij} = KS_{ij}(H_{ii}H_{jj})^{1/2} \tag{3}$$

respectively. These approximations are inherently incapable of introducing a minimum in the potential energy curve for H_2 or any other related two-electron problem (with each atom having a single *n*s valence electron in a Slater-type orbital). Therefore, the Cusachs[3] approximation for H_{ij} was also used. This formulation introduces the desirable feature of an

$$H_{ij} = {}^1/_2S_{ij}(K - |S_{ij}|)(H_{ii} + H_{jj}) \tag{4}$$

S_{ij}^2 dependence which parallels the limiting behavior of off-diagonal kinetic energy integrals (T_{ij}). The most appropriate of these forms for diatomic copper can then be determined by comparison of several of the calculated properties with the corresponding experimental quantities. The splitting parameter K in eq 1–4 was initially assumed to be equal to 2.0.

Further, the Clementi–Raimondi orbital exponents[16] were used for the overlap integral calculations, and the Hartree–Fock orbital energies, obtained from Clementi's "Table of Atomic Functions,"[17] were used to approximate the Coulomb integrals (H_{ii}). These Coulomb integrals were −13.5, −6.45, and −2.94 ev, respectively, while the orbital exponents were 4.40, 1.46, and 1.46, respectively, for the 3d, 4s, and 4p orbitals. Calculations were carried out for interatomic distances, *r*, varying from 1.0 to 20 Å. The calculated physical properties and the observed experimental results are given in Table I. The calculated ionization potential is given here as the negative of the energy of the highest filled molecular orbital in accordance with Koopmans' theorem.[18] The energy difference, Δ, between the highest filled σ molecular orbital and the next highest unoccupied σ^* orbital corresponds to the $^1\Sigma_g^+ \rightarrow {}^1\Sigma_u^+$ spectral transition. The potential energy variations with internuclear distance are given in Figure 1.

TABLE I

COMPARISON OF CALCULATED PROPERTIES OF Cu_2 WITH VARIOUS APPROXIMATIONS TO THE RESONANCE INTEGRALS (H_{ij})[a]

Property	Mulliken eq 1	Wolfsberg–Helmholz eq 2	Ballhausen–Gray eq 3	Cusachs eq 4
r_e, Å	~2.0	<1.46	<1.46	2.50
D_e, ev	>250	>5.30	>5.30	2.21
IP, ev	13.45	12.91	9.17	7.56
Δ, ev	~6.75	>4.80	>5.01	2.72

[a] The Coulomb integrals (H_{ij}) are −13.50, −6.45, and −2.94 ev with orbital exponents 4.40, 1.46, and 1.46 for the 3d, 4s, and 4p orbitals, respectively, having $K = 2.0$.

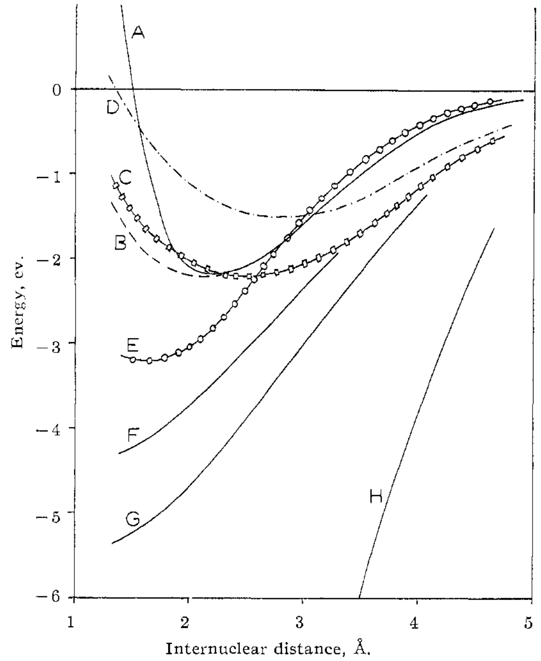

Figure 1.—Dependence of the calculated potential energy curve of Cu_2 upon the extended Hückel theory parameters. Exponents are as follows. Curve A (eq 4): K, 2.0; 3d, 3.16; 4s, 1.75; 4p, 1.75. Curve B (eq 4): K, 2.0; 3d, . . .; 4s, 1.75; 4p, ... Curve C (eq 4): K, 2.0; 3d, 4.40; 4s, 1.46; 4p, 1.46. Curve D (eq 4): K, 1.8; 3d, 4.40; 4s, 1.46; 4p, 1.46. Curve E (eq 3): K, 1.8; 3d, 3.16; 4s, 1.75; 4p, 1.75. Curve F (eq 3): K, 1.8; 3d, 4.40; 4s, 1.46; 4p, 1.46. Curve G (eq 3): K, 2.0; 3d, 4.40; 4s, 1.46, 4p, 1.46. Curve H (eq 1): K, 2.0; 3d, 4.40; 4s, 1.46; 4p, 1.46. The Coulomb integrals are −13.50 −6.45, and −3.94 ev for the 3d, 4s, and 4p orbitals, respectively.

The superiority of the Cusachs H_{ij} approximation with the given parameter set is evident from Table I and a comparison of curves C, G, and H of Figure 1. That is, the best agreement with the experimental values is obtained with calculations carried out assuming eq 4. An even better fit of the experimental quantities can be obtained by using eq 4 and Clementi–Hartree–Fock orbital energies and orbital exponents.[17] For the latter each orbital exponent is chosen from the predominant component of the Hartree–Fock orbitals,

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the values being 3.16, 1.75, and 1.75 for the 3d, 4s, and 4p orbitals, respectively. The Coulomb integrals were those previously cited. Some of these results are summarized in Table II and Figure 1 (curve A). This latter curve is compared in Figure 2 with a Morse curve calculated from the experimental data of Travis and Barrow[8] with $D_e = 1.85$ ev. It can be seen that the two curves closely parallel one another; however, if one were to use the upper limit of the dissociation energy[10] (2.21 ev) to construct the Morse curve, then the curves would be nearly identical. The value of ω_e cited in Table II is obtained by using the calculated D_e and the Morse equation so as best to fit the potential well in the harmonic region. The semiempirical method used here is therefore fully capable of reproducing the potential energy curve of Cu_2.

TABLE II

COMPARISON OF THE PROPERTIES OF Cu_2 CALCULATED BY THE CUSACHS APPROXIMATION WITH THE EXPERIMENTAL VALUES[a]

Property	Calcd value	Lit. value
r_e, Å	2.19	2.22[8]
ω_e, cm^{-1}	200	264.5[8]
D_e, ev	2.19	1.99,[9] 2.21,[10] 1.85[8]
IP, ev	7.53	~6.7[11]
Δ, ev	2.63	2.70[8]

[a] The Coulomb integrals (H_{ij}) are −13.50, −6.45, and −2.94 ev with orbital exponents 3.16, 1.75, and 1.75 for the 3d, 4s, and 4p orbitals, respectively, having $K = 2.0$.

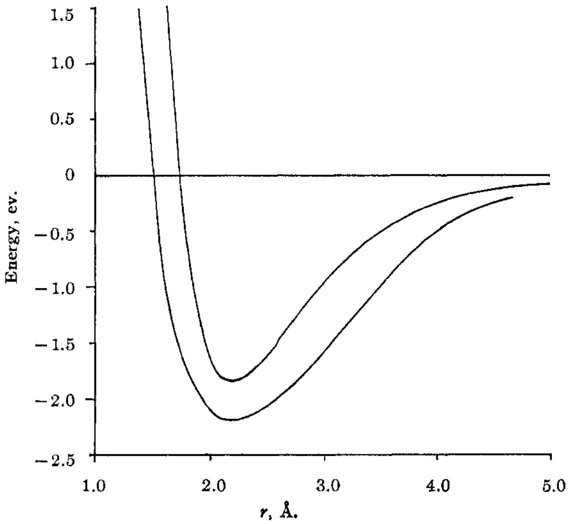

Figure 2.—Computed potential energy curve (lower) and calculated Morse curve (upper) for Cu_2.

To investigate the stability of the results with respect to a change in K, calculations were carried out using the previous approximations with $K = 1.8$, thereby reducing the off-diagonal elements. The former values for the Coulomb integrals were retained in all cases. Because of the similarity of the results in the Wolfsberg–Helmholz[14] approximation with those in the Ballhausen–Gray[15] approximation only the latter are given in Figure 1. The Mulliken[13] approximation was not considered further because of the unreasonable results obtained with $K = 2.0$ (see Table I).

The decrease in the absolute values of the off-diagonal matrix elements is manifested by a broadening of the potential curve and hence a decrease in the stretching frequency. The dissociation energy, ionization potential, and the spectral transition, Δ, are also decreased by the reduction in K. The only quantity improved by the change in K in the Cusachs approximation is the ionization potential for either set of orbital exponents. The potential energy curve using the Clementi–Raimondi exponents and $K = 1.8$ is given as curve D in Figure 1. A somewhat better fit of the calculated and experimental properties is achieved by both the Ballhausen–Gray and the Wolfsberg–Helmholz approximations with $K = 1.8$ rather than 2.0. (See Table III.) These results are considerably improved when the Clementi exponents (3d, 3.16; 4s, 1.75; 4p, 1.75) are utilized in the overlap integral calculations (Figure 1, curves E and F). However, the Cusachs approximation, measured in terms of being able to provide the more consistent set of results, appears to be the most appropriate one for the description of the molecular properties with the parameters investigated. Subsequent discussions will therefore be confined to the results obtained with this approximation and $K = 2.0$.

TABLE III

CALCULATIONS OF Cu_2 WITH THE SPLITTING FACTOR $K = 1.8$[a]

Property	Ballhausen–Gray[b]	Ballhausen–Gray[c]	Cusachs[b]	Cusachs[c]
r_e, Å	<1.46	<1.80	2.75	2.30
D_e, ev	>4.27	>3.16	1.53	1.49
IP, ev	~8.6	~8.2	7.19	7.19
Δ, ev	>4.60	>3.87	2.17	2.11

[a] The Coulomb integrals are −13.50, −6.45, and −2.94 ev for the 3d, 4s, and 4p orbitals in each case. [b] The orbital exponents are 4.40, 1.46, and 1.46 for the 3d, 4s, and 4p orbitals, respectively. [c] The orbital exponents are 3.16, 1.75, and 1.75 for the 3d, 4s, and 4p orbitals, respectively.

The effect of truncating the basis set to only 4s orbitals, or to 4s and 4p orbitals, is strikingly illustrated by curve B of Figure 1. In the attractive region beyond 2.2 Å the potential energy curve, obtained from calculations using only the 4s atomic orbitals with an orbital exponent of 1.75 and a Coulomb integral of −6.45 ev, closely follows the curve obtained with the larger basis set of 3d, 4s, and 4p orbitals (curve A). However, in the repulsive region, the rise of the potential energy curve associated with the truncated basis set is much less sharp in nature, indicating a considerable loss in the atom–atom repulsion can be achieved by excluding the 3d electrons. A similar pattern is observed with the basis set containing the 4s and 4p atomic orbitals. These latter results are identical with curve B. This clearly illustrates the repulsive character of the closed shell at relatively short distances. The stretching frequency is, therefore, particularly sensitive to the basis set chosen.

An examination of the eigenvectors at the internuclear distance of 2.19 Å indicates that the highest filled σ molecular orbital essentially arises from the 4s orbitals on the separate atoms since it is 91% s, 7%

d_{z^2}, and 2% p_z in nature. Thus the bond in Cu_2 is predominantly a σ bond arising from the overlap of the 4s orbitals. Figure 3 shows how the energy of the molecular orbitals varies as the internuclear distance is changed. At internuclear distances of less than 1.5 Å, a crossover of the σ* (3d) orbitals with the π* (3d) and δ* (3d) orbitals occurs. This apparent anomaly is concomitant with extremium conditions on the overlaps associated with the d_{z^2} orbitals. For example, the 4s–$3d_{z^2}$ overlap is nearly constant at 0.05 through the bonding region, then it approaches zero at 1.4 Å, and decreases to −0.05 at 1.0 Å. The $3d_{z^2}$–$3d_{z^2}$ overlap, however, uniformly increases to 0.15 at 1.4 Å and then decreases to 0.11 at 1.0 Å. This is a manifestation of a net canceling in the axial overlaps associated with the penetration of a positive lobe on one center with the negative lobe on the other center. This condition should have no important effect on the equilibrium properties since it occurs at rather short internuclear distances. The energy level diagram for diatomic copper at the equilibrium internuclear distance is shown in Figure 4. As can be seen, the molecular orbitals derived from the 3d atomic orbitals are very low in energy and therefore do not mix appreciably with the 4s or 4p orbitals, nor do they effectively contribute to the bond energy at r_e. On the other hand, the 4s and 4p orbitals are close in energy, and appreciable mixing can occur. This is indicated in Figure 4 by the dashed lines.

The success of the calculations for Cu_2 encouraged us to extend them to related polyatomic systems (Cu_n). Unfortunately, no quantitative information is available for these higher order species. However, it is known that Cu_3 exists.[19] It is therefore of some interest to speculate on the existence of some of these systems. We therefore carried out stability calculations for Cu_3 (linear and triangular), Cu_4 (square planar), and Cu_6 (octahedral) with the best parameter set at fixed internuclear separations. The results are listed in Table IV. In each case the molecules are predicted to exist; furthermore, it would appear that the linear Cu_3 molecule is more stable than the triangular isomer.

Discussion

The calculations reported here indicate that the Hartree–Fock atomic orbital energies of a Cu atom in the ground state are directly applicable to the description of the molecular properties of Cu_2. In general, this is not always the case; the orbital parameters can frequently be critical to the problem since the atomic parameters do not necessarily reflect the molecular environment appropriate to the semiempirical procedure. The choice of orbital exponents for the Slater-type orbitals used in extended Hückel theory therefore plays the role of refining the results to a full description of the molecular properties. The important selection here is that of the 4s orbital. As in the case of other s electron systems (*e.g.*, H_2^+ or H_2) the orbital was contracted from a "hydrogenic-type" value. We found the best value to be that of the predominant term of the Hartree–Fock orbitals given by Clementi.[17] The 4p orbital was assigned the same exponent as the 4s orbital and the 3d value was also taken as the predominant Hartree–Fock term. The more extensive 4s exponent values, given by

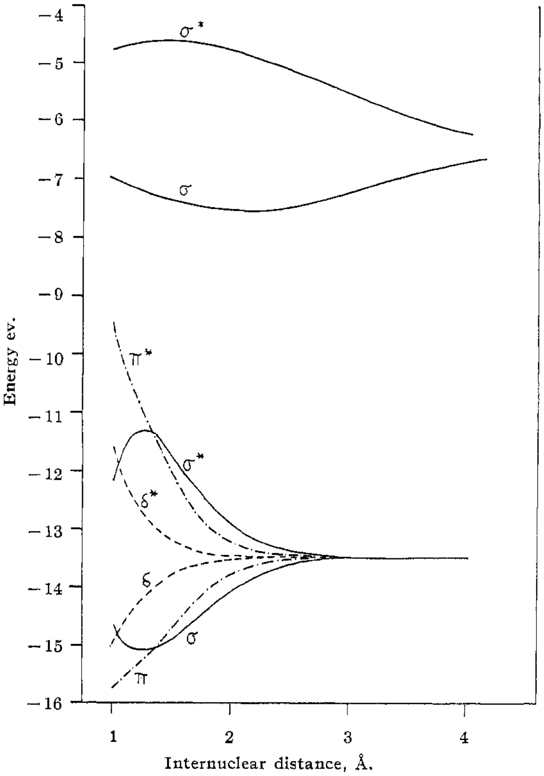

Figure 3.—Energy variation of the molecular orbitals with internuclear distance.

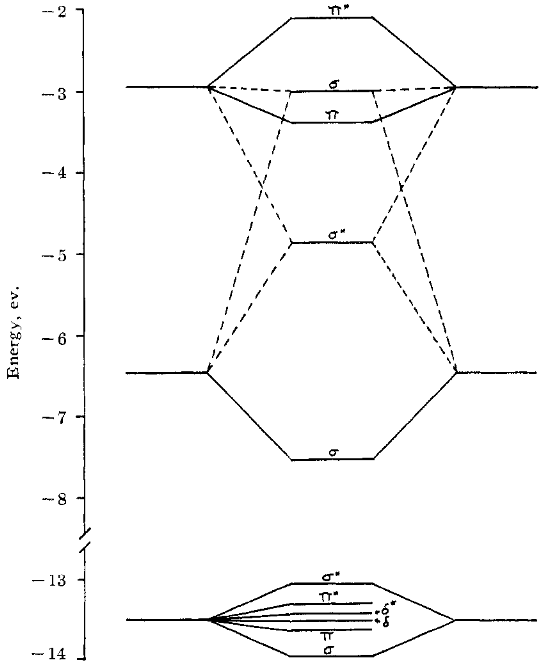

Figure 4.—Molecular orbital energy level diagram for Cu_2 at the equilibrium internuclear distance.

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TABLE IV

CALCULATED DISSOCIATION ENERGIES FOR SEVERAL Cu$_n$ MOLECULES

Molecule	Internuclear dist, Å	D_e, ev
Cu$_3$ (linear)	2.3	2.84
Cu$_3$ (triangular)	2.3	2.24
Cu$_4$ (square planar)	2.3 (adjacent atoms)	3.11
Cu$_6$ (octahedral)	2.4 (from center of inversion)	3.6

Clementi and Raimondi[16] or by Slater's[20] rules, were found to be inadequate.[21]

The traditional transition metal basis set of 3d, 4s, and 4p orbitals proved to be optimum for the description of the Cu$_2$ molecule. The lowest filled molecular orbitals, which are largely 3d in character, were important in accounting for the core repulsions at short distances and were extremely important for the calculation of the stretching frequency, ω_e. The inclusion of the higher lying 4p orbitals in the basis set was important for the calculation of the spectral transition, Δ, since the 4s–4p$_z$ mixing effectively lowers the energy of the σ^* orbital. The 4s orbitals were the most important ones since all molecular properties of Cu$_2$ are largely dependent upon them.

The energy and core repulsion in the Cusachs approximation varies as $S^2/(1 + S)$ at short internuclear distances. This dependence approximates the core repulsions of Cu$_2$ and gives the best reproduction of the potential energy curves in the bonding and repulsive regions. The solutions obtained by using other approximations are substantially poorer and a variation of parameters (H_{ii}, K, and orbital exponent), within reasonable limits, will not substantially improve the results.

The calculations of D_e, r_e, ω_e, Δ, and the ionization potential comprise all of the bonding parameters for Cu$_2$. These results are good and illustrate that the semiempirical extended Hückel theory may be used with adequate choice of parameters and basis set to calculate other such molecular properties. Unfortunately such data do not always exist for most problems of interest to inorganic chemists, but it should be required that calculations of this nature faithfully reproduce other properties in addition to the spectrum. Presently, calculations are in progress on other homonuclear diatomic molecules of the transition metals. It is hoped that the parameters which best describe these molecules can be extended to heteronuclear diatomic molecules and complexes of the transition metals.

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(21) We have found that calculations using double ζ valence orbital basis sets yield results that are nearly identical with those using single orbital exponents; hence, only the latter were used here.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY
FLORIDA STATE UNIVERSITY, TALLAHASSEE, FLORIDA 32306

Metal Carbonyl–Phosphorus Trifluoride Systems. V. Decacarbonyldimanganese

BY R. J. CLARK, J. P. HARGADEN, H. HAAS,[1] AND R. K. SHELINE

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Decacarbonyldimanganese reacts with phosphorus trifluoride to yield a variety of substitution products. These products are formed either by thermal reaction or ultraviolet irradiation under several sets of conditions. The product of the ultraviolet reaction is usually a mixture of four major species having mono-, di-, and triphosphine substitution plus trace amounts of other minor species. The species from this uv reaction have both axial and equatorial substitution. They can be isolated by gas–liquid partition chromatography and identified by a variety of means. The thermal reaction gives a different product distribution from the ultraviolet reaction in that substitution here is almost exclusively on the axial positions. The Mn$_2$(PF$_3$)$_x$(CO)$_{10-x}$ species are yellow solids melting below 100°. They are moderately stable in air and some solvents, but react rapidly with solvents like alcohols yielding solvolysis products such as Mn$_2$(CO)$_9$[P(OCH$_3$)$_3$].

Introduction

Dimanganese decacarbonyl contrasts strongly with most other metal carbonyls in that only a limited number of simple substitution derivatives have been prepared. By way of comparison, the group VI carbonyls form literally hundreds of simple substitution products.[2] The tendency of the parent carbonyl to undergo valence disproportionation instead of substitution and the intractability of substitution products once formed are among the most important factors in the sparsity of substitution products of dimanganese decacarbonyl.[3] Some simple substitution products do occur, particularly with ligands capable of some degree of π bonding.

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(1) Part of this research is included in the dissertation of H. Haas submitted to the Graduate School of Florida State University.

(2) G. R. Dobson, I. W. Stolz, and R. K. Sheline, *Advan. Inorg. Chem. Radiochem.*, **8**, 1 (1966).

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