

- Soc., **99**, 6793 (1977). I thank these authors for providing me with a copy of the manuscript prior to publication.
- (3) (a) R. D. Harcourt, *Theor. Chim. Acta*, **2**, 437 (1964); **4**, 202 (1966); (b) *ibid.*, **6**, 131 (1966); (c) *J. Chem. Educ.*, **45**, 779 (1968); **46**, 856 (1969); (d) *J. Mol. Struct.*, **9**, 221 (1971). In the latter sections of ref 3b the adjective "apparent" was omitted because continuous use of it seemed unnecessary. The reasons for apparent octet violation that are described by Halgren et al.² correspond to those that have also been advanced in some of these references; see in particular ref 3a, pp 439, 440, and 437.
- (4) This effect, namely, that "as a result of the Pauli exclusion principle, self cancellations occur when the LCAO expansions for fractional localized (YA and AB) molecular orbitals are inserted into the determinantal wave functions and multiplied out",² is discussed in both ref 2 and by us: *Aust. J. Chem.*, **22**, 279 (1969).
- (5) The y , a , ψ_{ab} , and b orbitals that we use here and in the earlier papers^{1,3} correspond to the l , c , π_{cr} , and r orbitals of ref 2. We have ignored all overlap integrals in any normalization constant, and in the orthogonality relationship for the AB molecular orbitals. The same simplifications have been made by Halgren et al.² for the calculation of their bond indices. It is to be understood that YA-type overlap integrals need to be included if the YA binding energy for either 1 or 3 were to be calculated from eq 2 and 1.
- (6) Halgren et al.² comment that the Heitler-London wave function for 1 should be formulated as $\psi(\text{IVHL}) = |(y\bar{a} + a\bar{y})\psi_{ab}b| + |(y\bar{a} - a\bar{y})b\psi_{ab}|$. This wave function may be expressed as $\psi(\text{IVHL}) = |y\bar{a}ab| + |a\bar{y}b\bar{a}| + 2k(|y\bar{a}bb| + |a\bar{y}bb|)$, which is equivalent to eq 2 (with k replacing $2k$) when the latter is expanded to give eq 5.
- (7) R. D. Harcourt and J. F. Sillitoe, *Aust. J. Chem.*, **27**, 691 (1974). If the order of spatial orbitals for the four π and four π' electrons is $y, a, \psi_{ab}, b, y', a', \psi'_{ab}$, and b' within a Slater determinant, then the $S = 0 \pi + \pi'$ wave function for 2 is $|\alpha\beta\alpha\beta\alpha\beta\alpha\beta| + |\beta\alpha\beta\alpha\beta\alpha\beta\alpha| - |\alpha\beta\alpha\beta\beta\alpha\beta\alpha| - |\beta\alpha\beta\alpha\alpha\beta\alpha\beta|$. These four Slater determinants generate the spin distributions of 8a-d.
- (8) The arguments that have been advanced against this proposition by Halgren et al.² are easily refuted. Firstly, Halgren et al.² claim that only two electrons (those occupying \bar{a} and ψ_{ab} or a and ψ_{ab}) are involved in bonding to atom A in eq 2. Therefore, two A-atom spin orbitals participate in bonding. For eq 1 for valence-bond structure 3, only one A atom spin orbital (a or \bar{a}) participates in bonding. Therefore, qualitatively at least, the A atom may increase its valence when 1 is generated from 3 by delocalizing a non-bonding B electron into the AB orbital. Further, if the atomic spin orbitals a or \bar{a} of eq 2 are involved in bonding, they need to overlap with another atomic spin orbital. Spin requirements indicate that the latter orbitals can only be the \bar{y} or y orbitals of eq 2. Halgren et al. seem to reject this possibility early in their footnote, but concede it later by referring to the partial YA bonding of "increased-valence" structure 1.
- (9) D. R. Armstrong, P. G. Perkins, and J. J. P. Stewart, *J. Chem. Soc., Dalton Trans.*, 838 (1973); eq 7 of ref 2. The formula $V_{AB} = 2k^2/(1 + k^2)^2$ for a one-electron bond may also be derived using either of the following procedures: (a) For the one-electron structures (A B), (A-B), and (A B) with wave functions $a, (a + b)/2, 1/2$ and b , the A atom valencies (V_{AB}) and atomic orbital charges (P_{aa}) are 0, $1/2$, and 0, and 0, $1/2$, and 0, respectively, in which we have assumed that the A-atom valence is $1/2$ for the "homopolar" one-electron bond (A-B). The V_{AB} is related to the P_{aa} through the expression $V_{AB} = 2P_{aa}(1 - P_{aa}) \equiv 2k^2/(1 + k^2)^2$ when $\psi_{ab} = (a + kb)/(1 + k^2)^{1/2}$ for the one-electron bond. Because the bond order P_{ab} is $k/(1 + k^2)$, the identity $P_{aa}(1 - P_{aa}) = P_{ab}^2$ pertains. (b) A similar approach for the three-electron structures (A B), (A-B), and (A B) gives the relationship $V_{AB} = -2(2 - P_{aa})(1 - P_{aa}) \equiv 2k^2/(1 + k^2)^2$ when $\psi_{ab} = (a + kb)/(1 + k^2)^{1/2}$ and $\psi'_{ab} = (ka - b)/(1 + k^2)^{1/2}$. The identity $(P_{aa} - 2)(1 - P_{aa}) = P_{ab}^2$ follows. See also K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968).
- (10) (a) R. D. Harcourt, ref 3c; (b) *J. Mol. Struct.*, **8**, 11 (1971); (c) *Int. J. Quantum Chem.*, **5**, 479 (1971).
- (11) (a) Reference 1a and ref 4-19 therein and ref 7; (b) P. C. Hiberty and C. Leforestier, *J. Am. Chem. Soc.*, **100**, 2012 (1978); (c) R. D. Harcourt and G. E. Martin, *J. Chem. Soc., Faraday Trans. 2*, **73**, 1 (1977).

Ab Initio Studies on the Electronic Structure of ONF (Nitrosyl Fluoride) and NOF (Nitrogen Hypofluorite)

L. J. Lawlor, K. Vasudevan, and F. Grein*

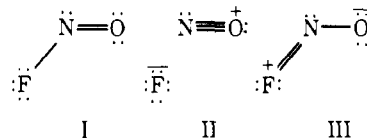
Contribution from the Department of Chemistry, University of New Brunswick, P. O. Box 4400, Fredericton, New Brunswick E3B 5A3, Canada. Received March 17, 1978

Abstract: Using ab initio Gaussian self-consistent field (SCF) and configuration-interaction (CI) methods, the geometry, binding energy, and dipole moment are obtained for ONF and NOF. It is found that only CI methods lead to agreement with the experimental NF bond distance of ONF. The optimized geometry for NOF is 1.07 Å for the N-O and 1.76 Å for the O-F bond distance, with a bond angle of 112.3°. Basis sets with polarization functions are required to obtain a positive atomization energy for ONF. Population analysis data show both molecules to be of polar structure. The molecular orbital and natural orbital contributions to the N-F bond of ONF (and O-F bond of NOF) are studied.

Introduction

The chemical bonding in nitrosyl fluoride (ONF) has been a matter of considerable interest. In Table I experimental bond distances, bond dissociation energies, infrared data, and dipole moments are given for N-O, N-F, and O-F bonded molecules.¹⁻⁴⁵ It is seen that the N-O bond distance of ONF (1.136 Å) is smaller than that of NO (1.15 Å), indicating a slight positive charge in the N-O region (compare the NO⁺ distance of 1.06 Å). The N-O stretching frequency is the same as in NO. No other molecules, with the possible exception of ONF₂⁺ and NOF, have such a short N-O bond distance or high N-O stretching frequency. Similarly, comparing ONF with other N-F bonded molecules, one finds from Table I that the N-F bond distance of ONF is much longer (1.512 Å) than for other N-F bonded molecules, and that the N-F stretching frequency is unusually low. The dipole moment is rather large.

Pauling⁴⁶ explained the bonding in ONF by utilizing three contributing resonance structures with weights of 25, 50, and 25%, respectively. Owing to the high proportion of structure II, the NF distance is explained to be very long and the N-O



distance shorter than for the NO molecule. Pauling concluded that the nitrosyl group is less electronegative than either nitrogen or oxygen, owing to the high stability of the N≡O triple bond (79 kcal/mol). Linnett⁴⁷ considered the N-F bond in ONF to be a one-electron bond, thereby accounting for its unusual bond distance. In his scheme, the atoms assume formal charges of $1/2$ for O and $-1/2$ for F.

Spratley and Pimentel⁴⁸ used a molecular orbital approach to describe the bonding and some physical properties of a series of molecules XNO (X = H, F, Cl, Br, Li, etc.). In this scheme, the X-N bonding is due to the overlap of the lone p electron of X (s for H, Li, etc.) with the singly occupied π^* orbital of NO. Changes in the N-O bond length, stretching frequency, and force constant are attributed to the electronegativity of the X group. Strongly electronegative X groups should withdraw

Table I. Experimental Data on N-O, N-F, and O-F Bonded Molecules

A. N-O					
molecule	$R_{\text{NO}}, \text{\AA}$	$\nu_{\text{N-O}}, \text{cm}^{-1}$	$K_{\text{NO}}, \text{mdyn/\AA}$	av $D(\text{N-O}), \text{kcal/mol}$	μ, D
NO ⁺	1.062 ¹	2300-2350 ²			
NOF	(1.10) ^b	1903.9 ^{3a}			(4.242) ^b
ONF ₂ ⁺	(1.13) ⁴	1858 ⁵			
ONF	1.136 ⁶	1876.8 ⁷	15.93 ⁷	135.3 ⁵	1.81 ⁸
NO	1.15 ⁹	1876 ¹⁰	15.5 ¹⁰	163 ¹¹	0.158 ^{12,13}
ONF ₃	1.159 ¹⁴	1691 ¹⁵			0.039 ¹⁶
FNO ₂	1.179 ¹⁷	1550 ¹⁸	9.83 ¹⁸	102.3 ^{5,18}	0.466 ¹⁸
NO ₂	1.197 ¹⁹	1470 ²⁰	8.43 ²¹	111 ²²	
ON(CH ₃) ₃	1.36 ²³	937 ²⁴	3.8-4.8 ²⁴		
B N F					
molecule	$R_{\text{NF}}, \text{\AA}$	$\nu_{\text{N-F}}, \text{cm}^{-1}$	K_{NF}^c	av $D(\text{N-F}), \text{kcal/mol}$	μ, D
ONF ₂ ⁺	(1.33) ⁴	1030 ⁵			
NF ₃	1.37 ²⁵	949 ²⁶		66 ²⁷	0.234 ²⁸
ONF ₃	1.432 ¹⁴	836 ¹⁵			0.039 ¹⁶
FNO ₂	1.467 ¹⁷	822.4 ¹⁸		52.7 ¹⁸	0.466 ¹⁷
ONF	1.512 ⁶	522.9 ⁷		55.4 ⁸	1.81 ⁸
C. O-F					
molecule	$R_{\text{OF}}, \text{\AA}$	$\nu_{\text{O-F}}, \text{cm}^{-1}$	$K_{\text{OF}}, \text{mdyn/\AA}$	av $D(\text{O-F}), \text{kcal/mol}$	μ, D
OF ₂	1.405 ²⁹	928 ³⁰	4.78 ²⁹	37 ³¹	0.297 ³²
NO ₃ F	1.42 ³³	928 ³⁴	3.10 ³⁵	32.9 ^{5,35}	
CF ₃ OF	1.421 ^{36a}	883 ^{36b}		43.5 ³⁷	
HOF	1.442 ³⁸	886 ³⁹	4.37 ⁴⁰	54 ⁴⁰	2.23 ⁴¹
O ₂ F ₂	1.58 ⁴²	621 ⁴³	1.50 ⁴³	18.4 ⁴⁴	1.44 ⁴²
NOF	(1.76) ^b	483.3 ^{3a}			(4.24) ^b
D. ONF-NOF					
molecule	bond angle, deg		$\delta_{\text{ABC}}, \text{cm}^{-1}$		
ONF	110.0 ⁶		775.5 ⁷		
NOF	(112.3) ^b		725.3 ^{3a}		

^a Values calculated using Lehmann's rule.⁴⁵ For a species AB_x, $\nu_{\text{AB}} = (1/x)(\nu_{\text{sym}} + (x-1)\nu_{\text{asym}})$. ^b Values in parentheses have been calculated. ^c The force constants for the NF bonds have not been included since they are very dependent on the particular function used in their calculation.

electrons from the π^* orbital, thus strengthening the N-O bond. The opposite is true for weakly electronegative X groups. From their quoted N-O stretching frequency of 1844 cm^{-1} (vs. 1876 cm^{-1} for NO) the authors conclude that F releases a small amount of charge into the N-O bond. However, recent data indicate a value of 1876 cm^{-1} for $\nu_{\text{N-O}}$, identical with that of NO. Spratley and Pimentel argue that F and NO have similar electronegativities, so that F can be replaced by NO, and the N-F bond of ONF is similar to the weak bond in the (ON)₂ dimer. However, the observed dipole moment of ONF, 1.81 D, speaks in favor of an (ON)⁺F⁻ charge distribution in ONF. (The observed dipole moment of NO is small, 0.158 D,^{12,13} and calculated to be of N⁻O⁺ polarity.⁴⁹) As will be seen later, the highest occupied molecular orbital of ONF, 10a', involves the overlap of a 2p orbital on F with the π^* orbital on NO, and is thus representative of the Spratley-Pimentel bonding scheme. Its role will be studied in more detail.

Recently the isolation of the very unstable nitrogen hypofluorite (NOF) in an inert gas matrix has been reported.^{3a-c} The infrared frequencies of NOF are also reported in Table I. It is seen that the N-O stretching frequency is higher than in ONF, and that the O-F stretching frequency is lower than the N-F stretching frequency of ONF. These observations indicate NOF to have even more polar character than ONF, in the sense (NO)⁺F⁻.

A number of ab initio calculations on ONF,⁵⁰⁻⁵⁶ and one on NOF,⁵² have been reported. The results of these calculations are summarized in Table II. For ONF very few calculations have achieved binding relative to the separated atoms. The

larger basis set calculation of Snyder and Basch⁵⁴ yielded the lowest energy for a single-determinant wave function but gave no binding energy. Only in a few cases has a full geometry optimization been carried out. The optimization by Peslak et al.⁵² for ONF gives R_{NO} too long and R_{NF} about right. The 4-31G basis set gives a good value for R_{NO} , but R_{NF} is short by about 0.04 \AA .⁵³ The calculated bond angles agree well with the experimental value.

The only geometry optimization on NOF, for which experimental values are not known, performed by Peslak et al.,⁵² gives R_{NO} longer than in ONF, contrary to the conclusion one draws from the observed higher vibrational N-O frequency of NOF (Table I).

Since the published theoretical studies are unsatisfactory in describing the experimentally observed properties of ONF and NOF, a new investigation, with improved theoretical methods, was found to be necessary. The present study has been undertaken with the following objectives: (1) to improve the quality of the ONF wave function such that it reproduces the experimental geometry of ONF, thereby answering the question why wave functions usually considered to be good fail to give a good NF bond distance; (2) to optimize the geometry of its isomer NOF; (3) to establish a binding energy for ONF, and hopefully also for NOF; (4) to qualitatively discuss the bonding in ONF and NOF, with particular reference to the Spratley-Pimentel bonding scheme.

Theoretical Methods and Results

In order to achieve the above objectives, it was clear from

Table II. Summary of Previous ab Initio Calculations on ONF and NOF

authors	basis set ^a primitive	contracted	energy, ^b hartrees	binding energy, ^c hartrees	comments
Scrocco, Tomasi, Petrongolo ⁵⁰	S(2s,1p)		-227.7084		equilibrium geometry ^d only exponents from Slater's rules
Peyerimhoff and Buenker ⁵¹	S(2s,1p) (9s,5p)	(3s,1p)	-227.7061 -228.3800	-0.1820	exponents are best-atom ζ 's fixed $R_{NO} = 1.13 \text{ \AA}$ and calculated $R_{NF} = 1.52 \text{ \AA}$, bond angle = 111.1°
Peslak, Klett, David ⁵²	O,N(5s,2p) F(7s,2p)		-227.6236	+0.0537	geometry optimization $R_{NO} = 1.24 \text{ \AA}$, $R_{NF} = 1.50 \text{ \AA}$, bond angle = 109°
Pople, Del Bene, Ditchfield ⁵³	(8s,4p)	(2s,1p)	-227.1388	+0.0037	geometry optimization $R_{NO} = 1.222 \text{ \AA}$, $R_{NF} = 1.380 \text{ \AA}$, bond angle = 108.2°
	(8s,4p)	(3s,2p)	-228.2823	-0.0165	geometry optimization $R_{NO} = 1.137 \text{ \AA}$, $R_{NF} = 1.468 \text{ \AA}$, bond angle = 110.20°
Snyder and Basch ⁵⁴	(10s,5p)	(4s,2p)	-228.5521	-0.0170	equilibrium geometry
Pulay and Sawodny ⁵⁵	(7s,3p/1) (5s3p/1) (5s3p)		-228.1921 -226.4128 -226.2227		several points about equilibrium geometry—not a full-optimization s and p π functions used on NO bond and s functions used on NF bond.
McWilliams, Herring, Chong ⁵⁶	S(3s,2p) third order perturbation correction to the above		-228.4162 -228.7499		equilibrium geometry
NOF					
Peslak, Klett, David ⁵²	O,N(5s,2p) F(7s,3p)		-227.5491	-0.0208	geometry optimization $R_{NO} = 1.27 \text{ \AA}$, $R_{OF} = 1.55 \text{ \AA}$, bond angle = 113°

^a "S" indicates a Slater basis set; all other calculations employ a Gaussian basis set. ^b Minimum energy reported. ^c A negative value denotes lack of binding. ^d Experimental geometry⁶ of ONF: $R_{NO} = 1.136 \text{ \AA}$, $R_{NF} = 1.512 \text{ \AA}$, bond angle = 110.0°

Table III. Basis Set Description and Ground State SCF Energies for ONF and NOF

basis set	brief description	ref	ONF		NOF	
			total energy, hartrees	binding energy, ^a kcal/mol	total energy, hartrees	binding energy, kcal/mol
I	4-31G; (8s4p/3s2p)	58	-228.2822	-10.4	-228.1927	-66.6
II	6-31G; (10s4p/3s2p)	59	-228.5104	-10.5	-228.4209	-66.6
III	Csizmadia; (8s4p/4s3p)	60	-228.4635	-10.6		
IV	Whitten; (10s5p/4s2p)	61	-228.5479	-21.3		
V	Dunning; (9s5p/4s2p)	62	-228.5705	-10.0	-228.4836	-64.6
VI	Dunning; (10s6p/5s3p)	63	-228.6039	-3.1	-228.5155	-58.8
VII	V+ diffuse functions	64	-228.5732			
VIII ^b	I+ bond functions (s,p)	65	-228.3826	52.7		
IX ^b	V+ bond functions (s,p)	65	-228.6594	45.8	-228.5671	-12.2
X	V+ d-type functions	66	-228.6792	58.4	-228.5813	-3.1

^a A negative value denotes lack of binding. ^b The bond functions, located at the center of mass of each bond, have exponents of 1.20 for the N-O and 1.10 for the N-F bond.

the outset that ab initio calculations at the Gaussian 70 level⁵⁷⁻⁵⁹ are insufficient for a proper description of ONF and NOF. Therefore, two types of extensions were foreseen. First, better basis sets are to be used. This involves the inclusion of polarization and diffuse orbitals. Secondly, the possibility of a configuration-interaction (CI) treatment was envisaged in order to allow for mixing of other configurations with the single-determinant self-consistent field (SCF) wave function.

At the SCF level, various basis sets were used in order to optimize the geometry of ONF and NOF, and to obtain a positive binding energy for ONF and NOF. In Table III, the basis sets are briefly described, and the total energies and binding energies are given. Basis sets I-VI are of double- ζ type.⁵⁸⁻⁶³ In basis set VII, diffuse functions⁶⁴ were added, in basis sets VIII and IX bond functions,⁶⁵ and in basis set X d orbitals.⁶⁶ The geometries corresponding to the given energy values are shown in Table IV for ONF and in Table V for NOF. Table III indicates that only basis sets IX and X, both using polarization functions, resulted in positive binding energies (atomization energies), up to 58 kcal/mol for ONF. For NOF, at the best -3 kcal/mol was obtained, corresponding to an unstable NOF molecule.

The results of partial geometry optimizations, performed with the basis sets previously described, are shown in Table IV. As mentioned before, the 4-31G and 6-31G basis sets underestimate the NF bond distance. None of the better basis sets improves this situation. Since our basis sets are all of good quality, and lead usually to excellent geometry verifications, we concluded that a CI treatment is necessary for obtaining an accurate NF bond distance.

For this purpose, two sets of CI calculations were performed, one with basis set IX (bond functions) and one with X (d orbitals). A systematic selection of configurations was carried out,⁶⁷ using energy criteria with threshold values of 0.5, 1.0, 1.5, etc., μ hartree. As reference configurations (found by a preliminary CI treatment) we used the ground-state configuration and its double excitations $1a''^2 \rightarrow 3a''^2$, $10a''^2 \rightarrow 11a''^2$, and $1a''2a'' \rightarrow 3a''^2$, and three other less significant double excitations. The core orbitals $1a'$ to $3a'$, corresponding to the 1s orbitals on the three atoms, were frozen. Only the six lowest virtual orbitals were allowed to participate in the excitations. All single and double excitations with respect to the reference configurations were generated. The number of configurations generated was 18 551; the number selected for the final CI was 1600-1700, depending on the NF distance. All energies (given

Table IV. Geometry Optimization Results and Calculated Dipole Moment for ONF^b

basis set	R_{NO} , Å	R_{NF} , Å	ONF, deg	μ , D
SCF Results				
I	1.13	1.47	110	1.39
II	1.14	1.47	110	1.39
III	1.14	1.48	(110)	1.47
V	1.15	1.46	(110)	1.42
VI	(1.13)	(1.47)	(110)	
VII	1.15	1.48	(110)	1.52
VIII	1.13	1.38	(110)	0.78
IX	1.13	1.39	(110)	0.93
X	(1.13)	1.39	(110)	
CI Results ^a				
IX	(1.13)	1.52	(110)	
X	(1.13)	1.52	(110)	

^a The CI energies corresponding to the given geometries are -228.7768 hartrees for IX and -228.7954 hartrees for X. ^b Parameters in parentheses were not optimized.

Table V. Geometry Optimization Results and Calculated Dipole Moments for NOF^b

basis set	R_{NO} , Å	R_{OF} , Å	NOF, deg	μ , D
SCF Results				
I	1.10	1.72	111.5	4.05
II	1.10	1.73	111.5	4.24
V	1.10	1.78	110.9	5.31
VI	(1.10)	(1.72)	(111.5)	
IX	1.07	1.81	112.3	5.64
X	(1.10)	(1.72)	(111.5)	
CI Results ^a				
IX	(1.07)	1.76	(112.3)	

^a The CI energy corresponding to the given geometry is -228.7073 hartrees. ^b Parameters in parentheses were not optimized.

in Table IV) were extrapolated to a zero threshold value.⁶⁸ Table IV indicates that the CI wave functions give a satisfactory NF bond distance of 1.52 Å, the same for the two basis sets.

In the case of the isomer NOF, the experimental geometry is unknown. The results of geometry optimizations at the SCF level, using 4-31G, 6-31G, and other basis sets, are given in Table V. CI optimizations were performed on the OF distance using basis set IX (with bond functions) and methods very similar to those employed for ONF. Eight reference configurations were used, with respect to which 19 010 configurations were generated and 1400-1500 selected. Table V shows that the CI-optimized OF distance is slightly shorter than the SCF-optimized one (for the same basis set).

Discussion

In the following, the results obtained for ONF and NOF will be discussed with particular consideration of binding energies, geometries, and electronic structure.

Using double- ζ basis sets with polarization functions, the calculated binding energy for ONF, at the best 58 kcal/mol, is unsatisfactory in comparison with the estimated value of 200 kcal/mol. For hydrocarbons about 50-75% of the binding energy is calculated using double- ζ basis sets.⁵⁸ Electron correlation plays a more significant role in obtaining the correct binding energy for ONF (and NOF) than for most other molecules.

The experimental ONF geometry, in particular the NF bond distance, could only be verified by a CI treatment. At the SCF level the NF distance was found to be short by about 0.04 Å,

Table VI. ONF Molecular Orbital Characteristics with Respect to NF Dissociation^a

MO	R_e	$R_{N-F} = \infty$
9a'	2p _{zF}	2p _{zF}
10a'	($\pi_{xNO}^* + 2p_{xF}$)	2p _{xF}
11a'	($\pi_{xNO}^* - 2p_{xF}$)	π_{xNO}^*
1a''	($\pi_{yNO} + 2p_{yF}$)	π_{yNO}
2a''	($\pi_{yNO} - 2p_{yF}$)	2p _{yF}
3a''	($\pi_{yNO}^* - 2p_{yF}$)	π_{yNO}^*

^a The molecule lies in the $x-z$ plane, with ON along the z axis.

and even shorter when polarization functions were used. It is of interest to consider the configurations which mixed most strongly with the SCF configuration, thereby contributing to the lengthening of the NF bond. Such are 1a''² → 3a''² and 10a''² → 11a''², which are two of the seven added reference configurations as described earlier. Their CI expansion coefficients are -0.11 at the NF bond distance of 1.50 Å. Usually, the significance of added configurations is explained by their contributions toward a proper dissociation. In Table VI we show the main composition of several molecular orbitals at equilibrium and their dissociation characteristics for N-F dissociation. The contributions are expressed in terms of NO and F orbitals. In this analysis, the SCF configuration (C_s symmetry group)

$$1a'^2 2a'^2 3a'^2 4a'^2 5a'^2 6a'^2 7a'^2 8a'^2 1a''^2 2a''^2 10a''^2$$

is seen to be... $\pi_{NO}^4(\pi_{NO}^* 2p_{xF})^2 2p_{yF}^2 2p_{zF}^2$ at equilibrium, and to dissociate to $NO^+(\pi^4)$ and $F^-(2p^6)$.

The common feature of the added configurations is that they are NF antibonding, where the doubly occupied NF-bonding orbitals 1a'' and 10a'' are replaced by the NF-antibonding orbitals 3a'' and 11a''. This implies that the HF configuration, by its attempt to lower the total electronic energy as much as possible, overemphasizes the bonding aspect in the NF region, and that the most important corrections are the addition of NF-antibonding configurations. Furthermore, 1a''² → 3a''² changes π_{NO}^4 to $\pi_{NO}^2 \pi_{NO}^{*2}$, making the NO bond weaker, and probably lengthening it somewhat (the change is not expected to be significant). None of the added configurations dissociates to $NO(\pi^4 \pi^*) + F(2p^5)$. Proper dissociation is not an important issue at the equilibrium NF distance, and will only show at larger separations.

In the following, we use orbital density plots (Figure 1) and Mulliken population analysis data (Table VII) to study the bonds in ONF, especially the NF bond. As seen from Table VII, the total NF overlap population is very small, and has positive contributions from 4a', 5a', 7a', 8a', and 1a''. The overlap population due to the 10a'' molecular orbital (MO) is negative. From MO electron density plots, calculated for basis set VI, and shown partly in Figure 1, it is concluded that the NF bond has its strongest contribution from the 7a'' MO, and weak contributions from other orbitals, including 10a''. Since such conclusions are drawn from a visual interpretation of orbital diagrams, they have to be taken with some caution. In any case, the role of the 10a'' molecular orbital can only be small. Of all occupied molecular orbitals, only 10a'' is of π^* character in the NO region. As was mentioned earlier, Spratley and Pimentel explain the ON-X bond by an overlap of the π^* orbital of NO with the partially occupied valence orbital of X. Therefore, according to their scheme, the 10a'' orbital should be responsible for the ON-F bond, which is not confirmed by the present MO calculations.

According to their MO coefficients, Peyerimhoff and Buenker^{51,69} classify all molecular orbitals either as predominantly ON or F orbitals. Only 10a'' is considered to be an ONF orbital, with contributions from all three atoms. From this they

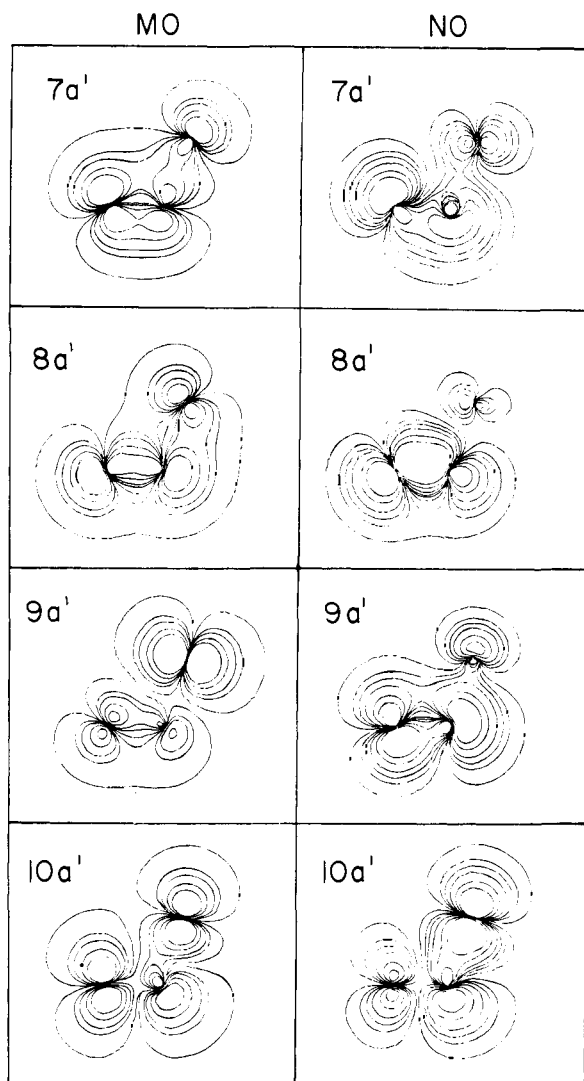


Figure 1. Orbital density contour plots of molecular and natural orbitals of ONF (contour values used for MOs are 0.10, 0.050, 0.020, 0.010, and 0.0010 and those used for NOs are 0.10, 0.050, 0.020, 0.010, 0.0050, and 0.0010).

concluded that $10a'$ is the molecular orbital responsible for the ON-F bond. Their published $10a'$ plot resembles closely our $10a'$ plot. Although their conclusions are in line with the simple bonding scheme of Spratley and Pimentel, we have reservations about their arguments. First, some orbitals characterized as ON or F orbitals have a relatively strong component also for the other group. Second, the orbital plot of $10a'$ is not compared with other orbital plots. Such a comparison would show that other orbitals are more strongly NF bonding than $10a'$.

A total electron density plot of ONF looks very similar to that given by Peslak et al.⁵² and Peyerimhoff and Buenker,⁵¹ and hence is not shown here. From these plots, it has been suggested that the molecule can be considered as a fluorine atom and a nitric oxide group, retaining their individual identities. This may, however, be misleading since it would be difficult to distinguish visually between the above description and a description involving a large F^- and NO^+ contribution.

In Figure 1 we also show the natural orbital (NO) density plots, obtained from a CI wave function with basis set V. They are shown besides the molecular orbital which contributes most to the natural orbital. Table VIII gives the expansion coefficients of the NOs relative to the MOs. Expansion coefficients with respect to the virtual orbitals are not given. It is to be noted that the NOs are not necessarily ordered according to de-

Table VII. Mulliken Population Analysis for ONF and NOF (6-31G Basis Set)

A. Overlap Population					
orbital	ONF		orbital	NOF	
	ON	NF		ON	OF
1a'	0.0000	0.0007	1a'	0.0000	0.0002
2a'	0.0035	0.0000	2a'	0.0036	0.0001
3a'	0.0008	0.0001	3a'	-0.0001	0.0000
4a'	0.4999	0.0837	4a'	0.5486	0.0123
5a'	0.0622	0.0408	5a'	0.0142	0.0564
6a'	-0.7086	-0.0204	6a'	-0.6113	-0.0182
7a'	0.2702	0.0516	7a'	0.3489	-0.0115
8a'	0.0418	0.1113	1a''	0.3553	0.0142
1a''	0.2933	0.1217	8a''	-0.2405	0.0044
9a'	-0.0339	-0.0125	9a''	0.0037	-0.0124
2a''	0.1086	-0.0843	2a''	0.0075	-0.0121
10a'	-0.3335	-0.2320	10a''	-0.1802	-0.0203

B. Total Overlap Population				
ONF		NOF		
ON	NF	ON	OF	
0.2043	0.0607	0.2497	0.0131	

ONF		NOF	
N: +0.56		N: +0.40	
O: -0.19		O: +0.08	
F: -0.37		F: -0.48	

Table VIII. Natural Orbitals in Terms of Ground-State Molecular Orbitals^a

MO	7a' (1.979)	8a' (1.982)	9a' (1.992)	10a' (1.950)
4a'	-0.0238	0.3915	0.0651	0.0538
5a'	0.0866	-0.1678	0.0286	0.1614
6a'	0.5209	0.2732	0.1621	0.1130
7a'	0.6636	0.1626	-0.3573	0.3877
8a'	-0.3327	0.7330	-0.4644	-0.1095
9a'	0.0372	0.4244	0.7869	-0.0101
10a'	-0.4093	-0.0038	0.0777	0.8921

MO	NO	
	1a'' (1.944)	2a'' (1.986)
1a''	0.7920	0.6100
2a''	-0.6104	0.7918

^a The occupation numbers are given in parentheses.

creasing occupation numbers but according to their highest MO component. The interesting change is that the $10a'$ natural orbital, while retaining the π^* antibonding character in the ON region, assumes the role of the $7a'$ MO in the NF bond region. Thereby, the $10a'$ natural orbital becomes the strongest NF bonding natural orbital, with weaker contributions from other natural orbitals. This implies that in a natural orbital basis, $10a'$ has the properties required by the Spratley-Pimentel bonding scheme. However, it is to be remembered that the natural orbitals result from a correlated treatment of the molecule, and that the $10a'$ molecular orbital makes only a weak contribution to the NF bond.

Considering the difficulties encountered in calculating a reasonable binding energy for ONF, it is understandable that no binding energy was calculated for the less stable isomer NOF. As seen from Table V, the calculated NO bond distance in NOF is shorter than in ONF, in agreement with the ob-

served higher N-O stretching frequency (Table I). The calculated O-F bond distance is much larger than OF bond distances in other molecules. A long O-F bond has been expected, since the O-F stretching frequency of NOF is considerably smaller than O-F stretching frequencies of other O-F bonded molecules listed in Table I. Comparing the OF stretching frequency of NOF with that of O_2F_2 , one predicts an O-F bond distance in excess of 1.58 Å.

The calculated OF distances change in unexpected ways on the addition of polarization functions and on application of CI methods. Usually, optimized bond distances shorten when polarization functions are introduced, reflecting the fact that electronic charge is moved into the bond region. For NOF, however, the OF distance slightly increases (from 1.78 to 1.81 Å). A similar observation was made for H_2O_2 ,⁷⁰ where the inclusion of bond functions in the O-O region led to a slight increase in the O-O distance. CI optimization of NOF leads to a decrease of the OF distance (from 1.81 to 1.76 Å), again contrary to the ONF result. Then, the lengthening of the NF bond was explained by the replacement of NF bonding orbitals by NF antibonding orbitals in the participating configurations. For NOF, on the other hand, the highest occupied orbital is OF antibonding, and its replacement by another OF antibonding orbital should affect the OF bond distance only weakly, in an unpredictable direction. The most significant added configurations are $10a'^2 \rightarrow 11a'^2$, $10a' \rightarrow 11a'$, and $7a' 1a'' \rightarrow 11a' 3a''$. The orbitals $10a'$, $11a'$, and $3a''$ are OF antibonding, whereas $7a'$ and $1a''$ are weakly OF bonding.

In line with the long O-F bond distance, the calculated dipole moment of NOF is unusually large. Such a dipole moment corresponds to a separation of about $1/2$ electron charge by 1.73 Å. Overlap population data (Table VII) and orbital density plots (Figure 2) for NOF (obtained from basis set VI) confirm that the OF bond is weak, with contributions from the $4a'$, $5a'$, $8a'$ (population analysis), and the $7a'$ (density plot) molecular orbitals. $10a'$ is slightly OF antibonding. The NO overlap population in NOF exceeds that in ONF, in agreement with the observed stretching frequencies.

Summary and Conclusion

It was found necessary for ONF to use CI methods in order to obtain the experimental NF bond distance. It is argued that satisfactory results for binding energy and dipole moment also require the use of CI wave functions. In the added configurations, molecular orbitals which are antibonding in the NF region replace the NF bonding orbitals $1a''$ and $10a'$ ($10a'$ is weakly bonding), thereby effecting a lengthening of the NF bond. As a qualitative argument it is suggested that for molecules containing strong and weak bonds, such as ONF, the limitations inherent in a single configuration are expected to favor the strong bond. The description of the weak bond depends on the molecular orbitals present in the SCF configuration. For ONF, the highest occupied molecular orbital is weakly bonding, and the NF bond strength is overestimated. On the other hand, for NOF, the highest occupied molecular orbital is OF antibonding, and the low-lying virtual orbitals are also antibonding. The OF bond distance is slightly reduced by the CI treatment.

Mulliken population analysis data indicate that a considerable amount of polarization occurs in ONF, with F negatively and NO positively charged. The corresponding situation also applies to NOF. The total charge density plots show two almost separate molecular fragments, and are consistent with the $NO^+ - F^-$ polarization model.

The $10a'$ molecular orbital of ONF, which is of π^* type in the NO region and overlapping with 2p on F, and the prime representative of the Spratley-Pimentel bonding scheme, is only weakly bonding. Other molecular orbitals, especially $7a'$, contribute more significantly to the NF bond. Similar con-

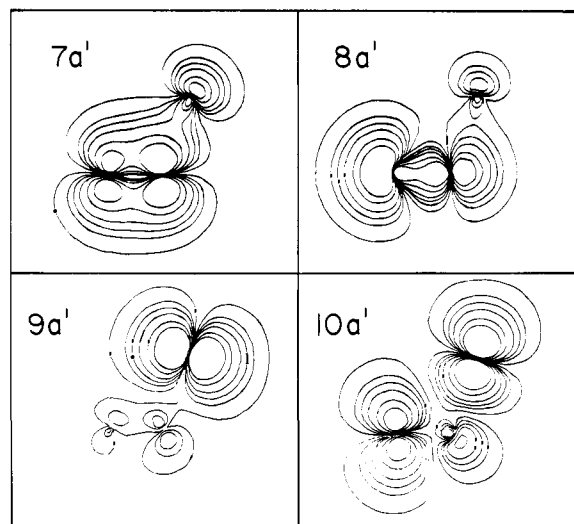


Figure 2. Molecular orbital density contour plots of NOF (contour values used are 0.10, 0.050, 0.020, 0.010, 0.0050, and 0.0010).

clusions are obtained for NOF. The $10a'$ natural orbital, however, satisfies all requirements of this bonding scheme.

Theoretical difficulties in obtaining good binding energies for fluorine compounds are well documented.^{71,72} Fluorine compounds often require the use of a correlated wave function for a satisfactory binding energy, owing to the small size of the fluorine atom and the resulting high electron density. In this paper, it is suggested that electron correlation is also necessary for the description of weak bonds in molecules which contain both strong and weak bonds, owing to the limitations imposed on the single-determinant SCF wave function, and the preferential treatment such a wave function gives to the strong bonds in the molecule.

Acknowledgments. The National Research Council of Canada supported this research via operating grants and a postgraduate scholarship to one of us (L.J.L.). We acknowledge with gratitude the facilities made available by the University of New Brunswick's Computing Center. We are much indebted to Dr. J. Passmore for his suggestions and continuous interest, and to Dr. R. C. Raffanetti for permission to use his BIGGMOLI computer program.

References and Notes

- (1) "Interatomic Distances", The Chemical Society, London, 1958.
- (2) J. E. Griffiths and W. A. Sunder, *J. Fluorine Chem.*, **8**, 533 (1975).
- (3) (a) R. R. Smardzewski and W. B. Fox, *J. Chem. Phys.*, **60**, 2104 (1974); (b) *J. Am. Chem. Soc.*, **96**, 304 (1974); (c) *J. Chem. Soc., Chem. Commun.*, 241 (1974).
- (4) L. J. Lawlor, 4-31G geometry optimization, unpublished results.
- (5) K. O. Christe and W. Maya, *Inorg. Chem.*, **8**, 1253 (1969).
- (6) D. J. Millen, K. S. Buckton, and A. C. Legon, *Trans. Faraday Soc.*, **65**, 1975 (1969).
- (7) L. H. Jones, "Inorganic Vibrational Spectroscopy", Vol. 1, Marcel Dekker, New York, N.Y., 1971.
- (8) D. W. Magnuson, *J. Chem. Phys.*, **19**, 1071 (1951).
- (9) J. H. Shaw, *J. Chem. Phys.*, **24**, 399 (1956).
- (10) G. Herzberg, "Molecular Spectra and Molecular Structure I: Spectra of Diatomic Molecules", Van Nostrand, Princeton, N.J., 1950.
- (11) M. C. Ball and A. H. Norbury, "Physical Data for Inorganic Chemists", Longman, London, 1974.
- (12) C. A. Bunus and J. O. Graybeal, *Phys. Rev.*, **109**, 1553 (1958).
- (13) R. M. Neumann, *Astrophys. J.*, **161**, 779 (1970).
- (14) V. Plato, W. O. Hartford, and K. Hedberg, *J. Chem. Phys.*, **53**, 3488 (1970).
- (15) K. O. Christe, E. C. Curtiss, and C. J. Shack, *Spectrochim. Acta, Part A*, **31**, 1035 (1975).
- (16) W. H. Kirckhoff and D. R. Lidl Jr., *J. Chem. Phys.*, **51**, 467 (1969).
- (17) A. C. Legon and D. J. Millen, *J. Chem. Soc. A*, 1736 (1968).
- (18) O. L. Bernitt, R. H. Miller, and I. C. Hiatsune, *Spectrochim. Acta, Part A*, **23**, 237 (1967).
- (19) G. R. Bird, *J. Chem. Phys.*, **25**, 1040 (1956).
- (20) "Comprehensive Inorganic Chemistry", Vol. 2, Pergamon Press, Elmsford, N.Y., 1973.

- (21) J. P. Devlin and I. C. Hiatsune, *Spectrochim. Acta*, **17**, 206 (1961).
 (22) T. L. Cottrell, "The Strength of the Chemical Bond", 2nd ed., Butterworths, London, 1958.
 (23) M. Lister and L. E. Sutton, *Trans. Faraday Soc.*, **35**, 495 (1939).
 (24) P. A. Giguere and D. Chin, *Can. J. Chem.*, **39**, 1216 (1961).
 (25) J. Sheridan and W. Gordy, *Phys. Rev.*, **79**, 513 (1950).
 (26) F. W. Levine and S. Abramowitz, *J. Chem. Phys.*, **48**, 2562 (1966).
 (27) C. B. Colburn and A. Kennedy, *J. Chem. Phys.*, **35**, 1892 (1961).
 (28) M. L. Unland, J. H. Lucher, and J. R. Van Wazer, *J. Chem. Phys.*, **50**, 3214 (1969).
 (29) Y. Morino and S. Saito, *J. Mol. Spectrosc.*, **19**, 435 (1966).
 (30) J. W. Nebgen, F. I. Metz, and W. B. Rose, *J. Mol. Spectrosc.*, **21**, 99 (1966).
 (31) J. Troe, H. Wagner, and G. Weden, *Z. Phys. Chem. (Frankfurt am Main)*, **56**, 238 (1967).
 (32) L. Pierce, R. Jackson, and N. DiCanni, *J. Chem. Phys.*, **35**, 2240 (1961).
 (33) L. Pauling and L. O. Brockway, *J. Am. Chem. Soc.*, **59**, 13 (1937).
 (34) J. Shamir, D. Yell'in, and H. Claassen, *Isr. J. Chem.*, **12**, 1015 (1974).
 (35) R. H. Miller, D. L. Bernitt, and I. C. Hiatsune, *Spectrochim. Acta, Part A*, **23**, 223 (1967).
 (36) (a) F. P. Deodati and L. S. Bartell, *J. Mol. Struct.*, **8**, 395 (1971); (b) R. R. Smardzewski and W. B. Fox, *J. Fluorine Chem.*, **6**, 417 (1975).
 (37) J. Czarnowski, E. Costellano, and H. J. Schumacher, *Chem. Commun.*, 1255 (1968).
 (38) H. Kim, E. F. Pearson, and E. H. Appelman, *J. Chem. Phys.*, **56**, 1 (1972).
 (39) J. A. Goleb, H. H. Claassen, H. M. Studier, and E. H. Appelman, *Spectrochim. Acta, Part A*, **28**, 65 (1972).
 (40) P. N. Nobel and G. C. Pimentel, *Spectrochim. Acta, Part A*, **24**, 797 (1968).
 (41) S. L. Rock, E. F. Pearson, E. H. Appelman, C. L. Norris, and H. W. Flygare, *J. Chem. Phys.*, **59**, 3940 (1973).
 (42) E. W. Lawless and I. C. Smith, "Inorganic High Energy Oxidizers", Marcel Dekker, New York, N.Y., 1968.
 (43) K. R. Loos, G. T. Gaetschel, and V. A. Camponile, *J. Chem. Phys.*, **52**, 4418 (1970).
 (44) J. T. Malone and H. A. McGee, Jr., *J. Phys. Chem.*, **69**, 4338 (1965).
 (45) N. J. Lehmann, *J. Mol. Spectrosc.*, **7**, 261 (1961).
 (46) L. Pauling, "The Nature of the Chemical Bond", 3rd ed., Cornell University Press, Ithaca, N.Y., 1960.
 (47) J. W. Linnett, *J. Am. Chem. Soc.*, **83**, 2643 (1961).
 (48) R. D. Spratley and G. C. Pimentel, *J. Am. Chem. Soc.*, **88**, 2394 (1966).
 (49) F. P. Billingsley II, *J. Chem. Phys.*, **62**, 864 (1975).
 (50) C. Petrongolo, E. Scrocco, and J. Tomasi, *J. Chem. Phys.*, **48**, 407 (1968).
 (51) S. D. Peyerimhoff and R. J. Buenker, *Theor. Chim. Acta*, **9**, 103 (1967).
 (52) J. Peslak Jr., D. S. Klett, and C. W. David, *J. Am. Chem. Soc.*, **93**, 5001 (1971).
 (53) R. Ditchfield, J. Del Bene, and J. A. Pople, *J. Am. Chem. Soc.*, **94**, 4806 (1972).
 (54) L. C. Snyder and H. Basch, "Molecular Wavefunctions and Properties", Wiley, New York, N.Y., 1972.
 (55) W. Sawodny and P. Pulay, *J. Mol. Spectrosc.*, **51**, 135 (1974).
 (56) D. P. Chong, F. G. Herring, and D. McWilliams, *J. Electron Spectrosc. Relat. Phenom.*, **7**, 445 (1975).
 (57) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969); W. J. Hehre, W. A. Lathan, D. Ditchfield, M. D. Newton, J. A. Pople, *QCPE No. 10*, 1973, p 236.
 (58) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971).
 (59) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **56**, 2257 (1972).
 (60) P. G. Mezey and I. G. Csizmadia, *Can. J. Chem.*, **55**, 1181 (1977).
 (61) J. L. Whitten, *J. Chem. Phys.*, **44**, 359 (1966).
 (62) T. H. Dunning, Jr., *J. Chem. Phys.*, **53**, 2823 (1970).
 (63) T. H. Dunning, Jr., *J. Chem. Phys.*, **55**, 716 (1971).
 (64) T. H. Dunning, Jr., and P. J. Hay in "Modern Theoretical Chemistry". Vol. 3, H. F. Schaefer III, Ed., Plenum Press, New York, N.Y., 1977.
 (65) L. J. Lawlor, K. Vasudevan, and F. Grein, to be published.
 (66) P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, **28**, 213 (1973).
 (67) R. J. Buenker and S. D. Peyerimhoff, *Theor. Chim. Acta*, **35**, 33 (1974).
 (68) R. J. Buenker and S. D. Peyerimhoff, *Theor. Chim. Acta*, **39**, 217 (1975).
 (69) R. J. Buenker and S. D. Peyerimhoff, *Chem. Rev.*, **74**, 127 (1974).
 (70) P. G. Burton and B. R. Markey, *Aust. J. Chem.*, **30**, 231 (1977).
 (71) J. Berkowitz and A. C. Wahl, *Adv. Fluorine Chem.*, **7** (1973).
 (72) S. Rothenberg and H. F. Schaefer III, *J. Am. Chem. Soc.*, **95**, 2095 (1973).

Paramagnetic Organometallic Compounds of the Early Transition Metals Stabilized by Chelating Benzyl and Phenyl Ligands

Leo E. Manzer

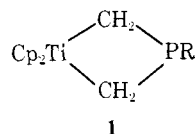
Contribution No. 2566 from the Central Research & Development Department, E. I. du Pont de Nemours and Company, Experimental Station, Wilmington, Delaware 19898. Received April 17, 1978

Abstract: The reactions of $\text{LiCH}_2\text{C}_6\text{H}_4\text{-}o\text{-NMe}_2$ and $\text{LiC}_6\text{H}_4\text{-}o\text{-CH}_2\text{NMe}_2$ with Cp_2MCl ($\text{M} = \text{Ti, V, Sc}$; $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$), CpTiCl_2 , CrCl_3 , and ScCl_3 led to the isolation of thermally stable, air-sensitive organometallic complexes whose stability is attributed to chelation. The reaction of $\text{CpTi}(\text{C}_6\text{H}_4\text{-}o\text{-CH}_2\text{NMe}_2)_2$ with CO_2 leads to elimination of 1 equiv of *N,N*-dimethylbenzylamine and incorporation of CO_2 into the aromatic ring. The reaction of $\text{Cr}(\text{CH}_2\text{C}_6\text{H}_4\text{-}o\text{-NMe}_2)_3$ with CO_2 gives a paramagnetic complex in which CO_2 has inserted into only one Cr-C bond and with diketones to give (diketonate) $\text{Cr}(\text{CH}_2\text{C}_6\text{H}_4\text{-}o\text{-NMe}_2)_2$. The factors which contribute to the stabilization of paramagnetic organometallic compounds are discussed.

Introduction

The vast majority of organometallic compounds are diamagnetic.^{1,2} Little effort has been directed toward the synthesis of paramagnetic organometallic compounds because of the reactivity and instability of these compounds. The use of bulky alkyl substituents³⁻⁷ such as $-\text{CH}_2\text{SiMe}_3$, $-\text{CH}(\text{SiMe}_3)_2$, and $-\text{CMe}_3$ has yielded some very interesting and stable complexes. Recent work in our laboratory⁸⁻¹¹ as well as in others¹¹⁻¹² has shown that considerable stabilization can be achieved by the use of chelating organic ligands. For example, Brintzinger¹³ studied the reactions of alkyl Grignard reagents with Cp_2TiCl and found that the resulting paramagnetic compounds, $\text{Cp}_2\text{TiR}_2^-$, were very reactive and unstable at room temperature. In contrast, we found¹⁴ that the chelating lithium reagents

$\text{Li}(\text{CH}_2)_2\text{PR}_2$ reacted with Cp_2TiCl ,¹⁵ at room temperature, to give **1** as thermally stable, paramagnetic, crystalline solids.



Similar compounds were isolated for vanadium and scandium. The stability of these complexes prompted us to examine, in greater detail, the stabilizing effect of chelating organic ligands. The work described in this paper is concerned with the preparation of compounds of the general types **2** and **3** (where $\text{M} = \text{Sc, Ti, V, and Cr}$; $\text{L} = \text{Cp, diketone}$; $x = 0, 1, 2$; $y = 1-3$).