butene on the basis that Z-crotyl anion (I) is more stable than E-crotyl anion (II).² Although considerable spectral evidence has been accumulated that Z is more stable than E in related anions,³ the only study in which a relative stability assignment was made for crotyl anion itself led to the conclusion that the E form (II) predominated.4 We wish to report that crotyllithium, previously prepared by a laborious route,⁵ is readily available by metalating 1-butene or Z- or E-2-butene, that at 35° in tetramethylethylenediamine (TMEDA) it is ionic, with the Z form (I) predominating over the E

$$J = 10.2 \text{ Hz} \qquad \begin{array}{c} & \delta & 6.0 \\ H & J &= 10.2 \text{ Hz} \\ H & \alpha & \beta \\ & \gamma & H & \delta & 2.9 \\ \delta & 1.2 & \Theta \\ H & CH_3 & \delta & 1.4 \\ & I \\ \end{array} \qquad \begin{array}{c} & CH_3 \\ & \Theta \\ & \delta \\ & I \\ \end{array}$$

form (II) by $\sim 85:15$, and that on alkylation with *n*-butyl bromide, it gives a 6:1 ratio of Z- to E-2-octene.

Crotyllithium is readily prepared by slowly adding TMEDA (5 ml) at -10° to a solution of 1-butene or Zor E-2-butene (0.02 mol), tert-butyllithium (0.02 mol), and hexane (10 ml).⁶ After 0.5 hr at room temperature (or 24 hr if *n*-butyllithium is used instead), the reaction is essentially complete. If desired, the bulk of the hexane can be removed by vacuum.

The most obvious pmr spectral feature of crotyllithium prepared in this way is the 1:3:3:1 quartet (J =10.2 Hz) for the β -proton at δ 6.0, also observed in earlier preparations in diethyl⁵ and dimethyl ether.^{4,5} The other peaks for crotyllithium, visible though partially obscured by TMEDA or residual hexane, were shown by spin decoupling experiments to be consistent with the assignments on formula I and give essentially the same parameters observed in ether solvents.^{4,5} Indication that these parameters are due to an ionic species comes from the upfield location of the γ proton (δ 3.0; ionic 3-neopentylallyllithium (NAL), δ 3.3;^{3f} covalent Z-NAL^{3f} and crotylmagnesium bromide, δ 4.5⁷), downfield location of the α -proton (δ 1.2; ionic NAL, δ 1.2^{3f}; covalent Z-NAL^{3f} and crotylmagnesium bromide,⁷ δ 0.8), and especially from the nonequivalence of the α -protons at -90° when rotation about the C_{α} - C_{β}

(2) S. Bank, A. Schriesheim, and C. A. Rowe, J. Amer. Chem. Soc.,
87, 3244 (1965); S. Bank, *ibid.*, 87, 3245 (1965).
(3) (a) 1-Methyl-3-phenylallylpotassium, 83% Z, H. Kloosterziel and

J. A. A. van Drunen, Recl. Trav. Chim. Pays-Bas, 87, 1025 (1968); (b) 1-methylpentadienylpotassium, $\sim 100\% Z$, G. J. Heiszwolf, J. A. A. van Drunen, and H. Kloosterziel, *ibid.*, **88**, 1377 (1969); H. Kloosterziel and J. A. A. van Drunen, *ibid.*, **89**, 270 (1970); (c) 1-methylpentadienyllithium, 45% Z, D. E. Potter, Ph.D. Thesis, University of Arizona, 1969; (d) 1-methylpentadienyllithium, 96% Z, W. T. Ford and M Newcomb, J. Amer. Chem. Soc., 96, 309 (1974); (e) 1-methylheptatrienyllithium, 80% Z, H. Kloosterziel and J. A. A. van Drunen, Recl. Trav. Chim. Pays-Bas, 88, 1471 (1969); (f) 1-neopentylallyllithium, 57% Z, W. H. Glaze, J. E. Hanicak, J. Chaudhuri, M. L. Moore, and D. P. Duncan, J. Organometal. Chem., 51, 13 (1973), and earlier papers in this series. (4) E. R. Dolinskaya, I. Ya. Poddubnyi, and I. Yu. Tsereteli, Dokl.

(4) L. K. Johnskaya, I. Fair Jourdony, and T. T. Forteen, 2011.
 (5) D. Seyferth and T. F. Jula, J. Organometal. Chem., 8, P13 (1967).

(6) Metalations with this reagent have yielded allyllithium and 2-alkylallyllithiums, e.g., R. J. Crawford, W. F. Erman, and C. D. Broaddus, J. Amer. Chem. Soc., 94, 4298 (1972); S. Akiyama and J. Hooz, Tetrahedron Lett., 4115 (1973). Metalation derivatization of α -olefins involving 1-alkylallyllithium intermediates has been employed by C. D. Broaddus, Abstracts of the 159th American Chemical Society Meeting, Houston, Texas, Feb 22-27, 1970, Division of Petroleum Chemistry No. 91, and W. L. Mock, private communication, but the lithiated intermediates were not studied.

(7) D. A. Hutchison, K. R. Beck, R. A. Benkeser, and J. B. Grutzner J. Amer. Chem. Soc., 95, 7075 (1973), and references therein.

bond has been frozen out.^{4,8} The Z nature of the predominant isomer is shown by the relatively small magnitude of $J_{\beta\gamma}$ (10.2 Hz; cf. 8.7–10.2 Hz in related ionic Z anions and 13.4-14.3 Hz in related ionic E anions³). The amount of E isomer is difficult to estimate accurately from the β -proton absorption due to partial overlap, but in dimethyl ether the α and δ absorptions of the minor isomer are well resolved and show $\sim 15\%$ of the minor isomer to be present.4

Alkylation results correlate well with these pmr findings. When a solution of crotyllithium in TMEDAhexane prepared as described above was added at -78° to excess n-butyl bromide, the resulting C₈ alkene mixture was 46% Z-2-octene, 8% E-2-octene, and 46% 3methyl-1-heptene.9

These findings contrast with the report that in dimethyl ether the equilibrium mixture contains mostly Ecrotyllithium (II),⁴ with stereochemical assignments based on an interpretation of small chemical shift differences. These chemical shift arguments are evidently unreliable, since they give the answer opposite to that derived from the generally employed 3a-f method of coupling constant differences used above.

The 85% value of Z-crotyllithium (I) at equilibrium is higher than that found for NAL (57 $\%^{3f}$), presumably because in the latter the attractive interaction in the Zisomer¹⁰ is partially offset by a larger steric interaction. It is close to most of the values found for 3-substituted 1-methylallyl anions 3a-e and is sufficiently high that it can indeed serve as the major cause for the rapid basecatalyzed isomerization of 1-butene to Z-2-butene.²

Acknowledgment. We thank the National Science Foundation for financial support (Grants GU-1534 and GP-21115).

(8) Analogous appearance of such terminal protons at low temperature has been used to indicate the ionic nature of pentadienyllithium (R. B. Bates, D. W. Gosselink, and J. A. Kaczynski, Tetrahedron Lett., 205 (1967)), allyllithium (P. West, J. I. Purmort, and S. V. McKinley, J. Amer. Chem. Soc., 90, 797 (1968)), and polybutadienyllithium (M. Morton, R. D. Sanderson, and R. Sakata, J. Polymer Sci., Part B, 9, 61 (1971)).

(9) Analyzed by gc and pmr comparisons with authentic material from Chemical Samples Co.

(10) Of the many rationalizations of this effect, the most convincing involves increased 1,4-electronic attraction in the Z-isomer: R. Hoffmann and R. A. Olofson, J. Amer. Chem. Soc., 88, 943 (1966); I. Elphimoff-Felkin and J. Huet, C. R. Acad. Sci., Ser. C, 268, 2210 (1969); J. R. Grunwell and J. F. Sebastian, Tetrahedron, 27, 4387 (1971); N. D. Epiotis, D. Bjorquist, L. Bjorquist, and S. Sarkanen, J. Amer. Chem. Soc., 95, 7558 (1973).

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Stereochemical Control of Valence. II. The Behavior of the {MNO}ⁿ Group in Ligand Fields¹

Sir:

It is well-known that M-N-O angles ranging from 120 to 180° occur in mononitrosyl complexes.² Both valence-bond concepts³ and molecular orbital con-

(1) For part I see J. H. Enemark and R. D. Feltham, Proc. Nat. Acad. Sci. U. S., 69, 3534 (1972).

⁽²⁾ B. A. Frenz and J. A. Ibers, MTP (Med. Tech. Publ. Co.) Int. Rev.

<sup>Sci., Phys. Chem., Ser. One, 11, 33 (1972).
(3) (a) D. J. Hodgson, N. C. Payne, J. A. McGinnety, R. G. Pearson, and J. A. Ibers, J. Amer. Chem. Soc., 90, 4486 (1968); (b) D. M. P. Mingos and J. A. Ibers, Inorg. Chem., 10, 1035 (1971); (c) D. A. Snyder and D. L. Weaver,</sup> *ibid.*, 9, 2760 (1970).



Figure 1. Four possible molecular orbital diagrams for the metal d and $\pi^*(NO)$ orbitals of the covalent {MNO}ⁿ group with $C_{\infty v}$ symmetry. Diagrams a and b represent cases where the metal d orbitals of the free ion are of higher energy than the $\pi^*(NO)$ orbitals; diagrams c and d represent cases where the metal d orbitals of the free ion are lower in energy than the $\pi^*(NO)$ orbitals. The dependence of the M–N–O angle upon n is shown for each diagram.

cepts⁴ have been utilized to rationalize these angles for various complexes or groups of complexes. Recently we demonstrated¹ that the simple reaction [Co(NO)- $(das)_2$ ²⁺ + NCS⁻ \rightarrow [Co(NO)(das)₂(NCS)]⁺ (where das is o-phenylenebis(dimethylarsine)) and the concomitant change in stereochemistry about the Co atom from five- to six-coordination resulted in the conversion of a linear CoNO group to strongly bent CoNO group. We have chosen to call the process "stereochemical control of valence" because the distribution of valence electrons and the geometry of the [CoNO]²⁺ moiety are dictated by the overall stereochemistry of the complex ion. Here we show that such transformations can be understood by considering the $\{MNO\}^n$ moiety⁵ as an "inorganic functional group" that is perturbed by the coordination of other ligands to the metal.

Four possible molecular orbital diagrams for the covalent triatomic MNO group possessing $C_{\infty v}$ symmetry are shown in Figure 1. These diagrams have been constructed from the metal d orbitals and the $\pi^*(NO)$ orbitals, which detailed molecular orbital calculations have shown to be similar in energy and strongly interacting.⁶ Experimental evidence also indicates that the NO ligand is one of the strongest "back-accepting" ligands.7.8 Hence, in all of the diagrams of Figure 1 the orbital $2\pi(xz, yz, \pi^*(NO))$, which is antibonding with respect to N and O but bonding with respect to M and N, is shown as the lowest energy molecular orbital. The $\delta(xy, x^2 - y^2)$ orbital is nonbonding in $C_{\infty v}$ symmetry, and the $\sigma^+(z^2)$ orbital is σ antibonding with respect to M and N. Finally, the $3\pi(\pi^*(NO), xz, yz)$ orbital is antibonding with respect to M, N, and O. For triatomic molecules of the nontransition elements, the occupation of this latter type of orbital leads to a nonlinear triatomic species.9

(8) M. S. Quinby and R. D. Feltham, Inorg. Chem., 11, 2468 (1972). (9) A. D. Walsh, J. Chem. Soc., 2266 (1953).



Figure 2. An orbital correlation diagram showing the splitting of the molecular orbitals of the $\{MNO\}^n$ group from Figure 1a in a ligand field of C_{4r} symmetry. The dependence of the M-N-O angle upon n is shown for each symmetry.

Walsh's concepts⁹ can also be applied ^{4a} to the $\{MNO\}^n$ group then only the energy of the 3π orbital relative to the other orbitals need be considered in order to predict whether a given value of n will produce a linear or a bent nitrosyl group. Figure 1a and 1b has 3π higher in energy than δ , the nonbonding metal orbital. This ordering is reasonable if the metal d orbitals of the free ion are of lower energy than the $\pi^*(NO)$ orbitals. Figure 1c and 1d has 3π of lower energy than δ , an ordering expected only for strongly reducing metals. The dependence of the M–N–O angle upon n for each of the orderings is also shown in Figure 1.

The coordination of other ligands to the metal of the MNO triatomic species will lower the symmetry from $C_{\infty v}$ and can have important effects on the geometry of the MNO group. For example, Figure 2 shows that a large C_{4v} perturbation of Figure 1a raises the $b_1(x^2$ y^2) orbital higher in energy than $3e(\pi^*(NO), xz, yz)$ and can thereby convert a linear {MNO}^s group into a bent {MNO}⁸ group.¹⁰ Figure 3 depicts the splitting of the MNO orbitals of Figure 1c in a field of C_{4v} symmetry. For this example, a large C_{4v} perturbation results in $b_2(xy)$ becoming lower in energy than $3e(\pi^*-$ (NO), xz, yz). Here decreasing the magnitude of the C_{4v} perturbation will convert a linear {MNO}⁶ group into a bent {MNO}⁶ group. Thus, Figure 2 describes the conditions for the formal reduction of a coordinated NO ligand by an *increase* in the tetragonal ligand field splitting, and Figure 3 describes the conditions for the formal reduction of a coordinated NO ligand by a *decrease* in the tetragonal ligand field splitting.¹¹

Common to the $\{MNO\}^{8}$ case of Figure 2 and the {MNO}⁶ case of Figure 3 is a crossing point at intermediate perturbing fields where the highest occupied molecular orbital and the lowest unoccupied molecular orbital become degenerate. This crossing point repre-

^{(4) (}a) D. M. P. Mingos and J. A. Ibers, Inorg. Chem., 10, 1479 (1971); J. H. Enemark, ibid., 10, 1952 (1971); (b) C. G. Pierpont and R. Eisenberg, J. Amer. Chem. Soc., 93, 4905 (1971); (c) D. M. P. Mingos, Inorg. Chem., 12, 1209 (1973).

⁽⁵⁾ *n* is the number of electrons associated with the metal d orbitals and the $\pi^*(NO)$ orbitals of the MNO group; *n* corresponds to the familiar number of d electrons on the metal when the nitrosyl ligand is formally considered to be NO⁴

⁽⁶⁾ R. F. Fenske and R. L. DeKock, *Inorg. Chem.*, 11, 437 (1972).
(7) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed., Wiley, New York, N. Y., 1967, p 538.

⁽¹⁰⁾ In symmetries lower than C_{4n} the degeneracies of the 2e and 3e orbitals will also be lifted, but the discussion remains unchanged.

⁽¹¹⁾ Similar correlations can be drawn for diagrams 1b and 1d. perturbation of 1b by a field of $C_{1\tau}$ symmetry can result in a linear {MNO}¹⁰ group going to a bent {MNO}¹⁰ group. The perturbation of The perturbation of ld by field of C4v symmetry can result in a bent {MNO}^s group going to a linear {MNO}⁸ group.



Figure 3. An orbital correlation diagram showing the splitting of the molecular orbitals of the $\{MNO\}^n$ group from Figure 1c in a field of C_{4v} symmetry. The dependence of the M–N–O angle upon *n* is shown for each symmetry.

sents the transition state for the conversion of the MNO group from linear geometry to bent geometry. Several electronic states arise from such a degenerate crossing point, and a simple electrostatic calculation has been carried out for a representative example in C_{4v} symmetry.¹² The results of the calculation and relationship of the state symmetry diagram to the reactions of mononitrosyl complexes are discussed in the succeeding paper.13

Finally, we suggest that the concept of inorganic functional groups has general utility for understanding covalently bound transition metal complexes. The concept should be especially applicable to metal complexes of other small molecules (such as O_2 and N_2) and to metal cluster compounds.14.15

Acknowledgment. This research was supported by the National Science Foundation.

(12) R. D. Feltham and J. H. Enemark, Theoret. Chim. Acta, in press.

(13) J. H. Enemark and R. D. Feltham, J. Amer. Chem. Soc., 96, 5004 (1974).

(14) For example, see G. L. Simon and L. F. Dahl, J. Amer. Chem. Soc., 95, 2164 (1973), and references therein

(15) B. A. Averill, T. Herskovitz, R. H. Holm, and J. A. Ibers, J. Amer. Chem. Soc., 95, 3523 (1973).

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Stereochemical Control of Valence. III. The {CoNO}⁸ Group in Ligand Fields of C_{4v} , C_{2v} , and C_s Symmetry

Sir:

The role of symmetry in chemical reactions has received much attention.¹ Consideration of molecular orbital symmetry alone provides significant insight into the chemical reactivity of strongly bound compounds with no low-lying excited states.^{1a,d} However, molecular orbital symmetry by itself may be insufficient for understanding the reactions of transition metal complexes.^{1c} In the preceding communication² we introduced the concept of an inorganic functional group and showed that the properties of mononitrosyl complexes could be understood by examining the behavior of the $\{MNO\}^n$ group³ in ligand fields. In this communication, the concept is applied to the specific problem of understanding the properties of the {CoNO}⁸ group in ligand fields of various symmetries.

Five-coordinate complexes containing the {CoNO}⁸ group exhibit Co-N-O angles ranging from 120 to 180°. Moreover, to date all linear $\{CoNO\}^{\$}$ groups occur in trigonal bipyramidal (TBP) geometry and strongly bent {CoNO}8 groups occur in tetragonal pyramidal (TP) geometry.⁴ The molecular orbital correlation diagram appropriate for these complexes is shown in Figure 1. The maximum symmetry possible for CoNOL₄ is C_{4v} , and two possible molecular orbital orderings for it are shown in Figures 1b and 1c. If the molecular ordering is that depicted in Figure 1c, then the electron configuration will be $(2e)^4(1b_2)^2(3e)^2$. With the totally antibonding 3e orbital doubly occupied, the $\{CoNO\}^{8}$ group will bend² producing $CoNOL_{4}$ with C_s symmetry (Figure 1d). If the 4a₁ orbital is lowest (Figure 1b) then the electron configuration is $(2e)^{4-}$ $(1b_2)^2(4a_1)^2$. With two electrons in $4a_1$, the {CoNO}⁸ group will not bend, but the CoNOL₄ complex will distort to TBP geometry with C_{2v} symmetry. This distortion to TBP geometry makes $4a_1(d_{z^2})$ less antibonding thereby lowering the energy of the complex. A TBP distortion also allows the yz component of the e orbitals to interact with the σ orbitals of the other two ligands in the equatorial plane of the TBP complex, thereby facilitating delocalization of electron density from the σ orbitals of the equatorial ligands into the π^* orbitals of the NO group. Thus, for five-coordinate complexes of the $\{CoNO\}^{*}$ group, the choice between a TBP structure of C_{2v} symmetry (Figure 1a) and a TP structure with C_s symmetry (Figure 1d) is dictated by the relative energies of the $4a_1$ and 3e orbitals of the hypothetical C_{4v} species.⁵

The presence of two electrons in the $4a_1$ and 3emolecular orbitals gives rise to several electronic states.9 Figure 2 shows the relative energies of the manifold of singlet states arising from the $(4a_1, 3e)^2$ electronic configurations in C_{4v} symmetry and the behavior of these states in C_{2v} and C_s symmetry. The far left-hand

(2) J. H. Enemark and R. D. Feltham, J. Amer. Chem. Soc., 96, 5002 (1974).

(3) n is the number of electrons associated with the metal d orbitals and the $\pi * (NO)$ orbitals of the MNO group; *n* corresponds to the familiar number of d electrons on the metal when the nitrosyl ligand is formally considered to be NO. $^+$

(4) (a) B. A. Frenz and J. A. Ibers, MTP (Med. Tech. Publ. Co.) Int. Rev. Sci., Phys. Chem., Ser. One, 11, 33 (1972); (b) J. H. Enemark and R. D. Feltham, Coord. Chem. Rev., 13, 339 (1974).

(5) Molecular orbital correlation diagrams to account for the bending of MNO in M(NO)L₄ complexes have been proposed previously.⁶. However, those diagrams consider only ordering 1b of the C_{iv} case and correlate that ordering to both structures 1a and 1d. Such a scheme has no predictive power and is not consistent with Walsh's results⁸ for small molecules upon which the correlations are purportedly based.

(6) C. G. Pierpont and R. Eisenberg, J. Amer. Chem. Soc., 93, 4905 (1971); Inorg. Chem., 12, 199 (1973).
(7) D. M. P. Mingos, Inorg. Chem., 12, 1209 (1973).
(8) A. D. Walsh, J. Chem. Soc., 2266 (1953).

(9) R. D. Feltham and J. H. Enemark, Theor. Chim. Acta, in press.

⁽¹⁾ See especially (a) R. B. Woodward and R. Hoffmann, J. Amer. Chem. Soc., 87, 395 (1965); (b) H. C. Longuet-Higgins and E. W. Abrahamson, ibid., 87, 2045 (1965); (c) T. H. Whitesides, ibid., 91, 2395 (1969); (d) R. B. Woodward and R. Hoffmann, The Conservation of Orbital Symmetry," Verlag Chemie Gmbh, Academic Press, Weinheim, 1970; (e) R. G. Pearson, Accounts Chem. Res., 4, 152 (1971).