*Contribution from the Department of Chemistry, Rutgers University, the State University of New Jersey, Newark, N. J. 07102, and Frick Chemical Laboratory, Princeton University, Princeton, N. J. 08540, U.S.A.*

# Spin Delocalization in Nitrones and Imines Coordinated to Metal Acetylacetonates[1a]

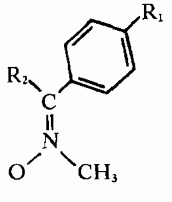
**R. W. Kluiber and W. De W. Horrocks, Jr.**[1b]

*Received September 20, 1969*

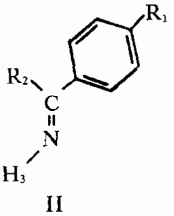
*Nitrone bis(2,4-pentanedionato)metal complexes of 1:1 and 2:1 stoichiometry have been isolated and characterized. Spin density in the nickel complexes is delocalized mainly in the nitrone π orbital. Nmr studies of both imine and nitrone complexes provide evidence for inhibition of spin density distribution due to twisting from coplanarity of a phenyl group in the π system.*

## Introduction

Nuclear magnetic resonance spectra of ligands coordinated to paramagnetic ions are frequently characterized by very large shifts in the nuclear resonances of the complexed ligands from their diamagnetic positions. These isotropic shifts and associated effects have been used to determine the distribution of spin density in the ligand orbitals and to provide information on structure and bonding in the complex. For example the shifts observed in proton magnetic resonance studies of heterocyclic amine oxides (*i.e.* pyridine 1-oxide) complexed with bis(2,4-pentanedionato)nickel(II), Ni(AA)$_2$, have been interpreted as being produced by spin density distribution in the highest filled ligand π orbital.[2,3] This contrasts with similar studies on pyridines and quinolines in which spin density appears to be delocalized principally in a ligand σ orbital.[3,4] The present work extends these studies to include M(AA)$_2$ complexes of the homologous nitrones, I, and imines, II.



I



II

## Experimental Section

*Ligands.* The aldonitrones,[5,6] ketonitrones,[7] aldimines[8] and ketimines[9] were prepared according to the literature. N-phenyl α-p-tolyl nitrone was supplied by Dr. I. Levine of Union Carbide Corporation. The mp and nmr spectra of .8 *M* $CDCl_3$ solutions of the principal ligands studied are as follows (nmr assignments were made on the basis of intensities, splitting, and in a few cases by extrapolation of isotropic shifts to zero paramagnetic species concentration): α-phenyl N-methylnitrone; (mp 81-82°)–8.20 (*o*), –7.42 (*m*), –7.35 (=CH), –3.83 ($NCH_3$); α-*p*-tolyl N-methylnitrone (mp 120°); –8.12 (*o*), –7.32 (=CH), –7.18 (*m*), –3.80 ($NCH_3$), –2.35 (*p*-$CH_3$); α-phenyl α, N-dimethyl nitrone (mp 114-116°); –7.42 (*m*), –7.39 (*p*), –7.33 (*o*), –3.65 ($NCH_3$), –2.43 ($CCH_3$); α-*p*-tolyl α, N-dimethyl nitrone (mp 79-81°); –7.23 (*m*), –7.14 (*o*), –3.65 ($NCH_3$), –2.43 ($CCH_3$), –2.40 (*p*-$CH_3$). For the N-methylimines: benzaldehyde methylimine; –8.25 (CH), –7.67 (*o*), –7.37 (*m*,*m*′,*p*,*p*′,*o*), –3.49 ($NCH_3$); *p*-tolualdehyde methylimine (mp 15°); –8.23 (=CH), –7.59 (*o*), –7.20 (*m*), –3.47 ($NCH_3$), –2.33 (*p*-$CH_3$); benzophenone methylimine –7.53 (*o*), approximately –7.25 (*o*′,*m*,*m*′,*p*,*p*′), –3.22 ,$NCH_3$); acetophenone methylimine; –7.80 (*o*), –7.35 (*m*, *p*), –3.33 ($NCH_3$), –2.17 (=$CCH_3$); *p*-methylacetophenone methylimine; –7.70 (*o*), –7.16 (*m*), –3.32 ($NCH_3$), –2.32 (*p*-$CH_3$), –2.13 (=$CCH_3$). Small concentration dependent variations in the *ortho* proton resonance were observed for some of the imines.

*α-p-Tolyl N-Methyl Nitrone: Co(AA)$_2$, 2:1 Complex.* A mixture of 130 mg (0.5 mmole) of Co(AA)$_2$ and 150 mg (1.0 mmole) of α-*p*-tolyl N-methyl nitrone was dissolved in 4 ml of benzene and traces of moisture were removed by azeotropic distillation. After addition of heptane (8 ml) and cooling, red-brown crystals of 2:1 complex were formed along with other products. The purest product, mp 113-115°, was obtained by seeding the hot solution with a preformed crystal of the 2:1 complex. *Anal.* Calcd. for $C_{28}H_{36}CoN_2O_6$; C, 60.53; H, 6.53. Found: C, 60.14;

---

(1) (a) Supported by the Research Council of Rutgers University and by the National Science Foundation through Grant No GP-6321. b) Present address: Department of Chemistry, Pennsylvania State University, University Park, Pennsylvania, 16802.

(2) R. W. Kluiber and W. D. Horrocks, Jr., *J. Am. Chem. Soc.*, *87*, 5350 (1965). R. W. Kluiber and W. D. Horrocks, Jr., *Inorg. Chem.*, *5*, 152 (1966).

(3) R. W. Kluiber and W. D. Horrocks, Jr., *J. Am. Chem. Soc.*, *88*, 1399 (1966).

(4) J. A. Happe and R. L.Ward, *J. Chem. Phys.*, *39*, 1211 (1963).

(5) O. L. Brady and F. P. Dunn, *J. Chem. Soc.*, 2411 (1926).

(6) T. Kubota, M. Yamakawa, and Y. Mori, *Bull. Chem. Soc. Japan*, 36, 1552 (1963).

(7) O. Exner, *Collection Czech. Chem. Commun.*, *16*, 258 (1951).

(8) R. B. Moffett, *Org. Syn.*, *34*, 65 (1954).

(9) C. R. Hauser and D. Lednicer, *J. Org. Chem.*, *24*, 46 (1959).

**Table I.** Relative Shifts of Proton Resonances in Ligands Complexed with $Ni(AA)_2$

| Structure | $R_1$ | $R_2$ | $NCH_3$ | $CR_2$ | ortho | meta | para | $p$—$CH_3$ |
|---|---|---|---|---|---|---|---|---|
| I | H | H | +1.00 [a] | +1.11 | +0.53 | –0.12 | +0.46 | — |
| I(calc) [b] | H [b] | H [b] | +1.00 [b] | +1.12 [b] | +0.57 [b] | +0.11 [b, c] | +0.94 | — |
| I(calc) [d] | H [d] | H [d] | +1.00 [d] | +1.21 [d] | +0.35 [d] | +0.00 [c, d] | +0.35 [d] | — |
| I | $CH_3$ | H | +1.00 [a] | +1.10 | +0.54 | –0.17 | — | –0.52 |
| I | H | $CH_3$ | +1.00 [a] | –2.2 | +0.27 | –0.16 | +0.17 | — |
| I | $CH_3$ | $CH_3$ | +1.00 [a] | –2.3 | +0.26 | –0.16 | — | –0.18 |
| II | H | H | –1.00 | –5.1 | [e] | [e] | [e] | — |
| II | $CH_3$ | H | –1.00 | –5.5 | –0.18 | +0.11 | — | +0.07 |
| II | H | $C_6H_5$ | –1.00 | ~[0] | –0.69 | +0.23 | –0.0 | — |
| II | H | $CH_3$ | –1.00 | +0.26 | –0.77 | +0.24 | –0.07 | — |
| II | $CH_3$ | $CH_3$ | –1.00 | +0.29 | –0.83 | +0.30 | — | +0.11 |

[a] For $CDCl_3$ solutions 0.8 *M* in nitrone and 0.078 *M* in $Ni(AA)_2$ the observed isotropic shifts of these N—$CH_3$ proton resonances were ($R_1$=H, $R_2$=H)+56 cps; ($R_1$=$CH_3$, $R_2$=H)+65 cps; ($R_1$=H, $R_2$=$CH_3$)+139 cps; ($R_1$=$CH_3$, $R_2$=$CH_3$)+139 cps. Observed line widths of the N—$CH_3$ resonance at half height are for the systems ($R_1$=$CH_3$, $R_2$=H) 30 cps and for ($R_1$=$CH_3$, $R_2$=$CH_3$)26 cps. [b] Calculated spin densities normalized to N—$CH_3$=1.00 (actual N—$CH_3$=0.11) for the Highest filled Hückel MO; uncorrected for spin correlation. [c] Should be negative owing to spin correlation effects. [d] Calculated spin densities as in *b* for lowest energy empty Hückel orbital. [e] Shifts are small and were not resolved.

H, 6.70. An analogous attempt to prepare the pure 2:1 nickel(II) complex resulted in a mixture of brown, green and white crystals.

*α-Phenyl α, N-Dimethyl Nitrone: $Ni(AA)_2$, 2:1 Complex.* To a hot solution of 515 mg (2.0 mmoles) of $Ni(AA)_2$ in 10 ml of $CCl_4$, was added 600 mg 4.0 mmole) of α-phenyl α, N-dimethyl nitrone. Hot ligroin (bp 66-75°), approximately 25 ml, was added and a preformed crystal of the 2:1 adduct was added to the green solution. A yellow brown precipitate (690 mg) was isolated by decantation and washed with petroleum ether (bp 30-60°). After drying at 56° *in vacuo* for one hour the compound melted at 131-133° to a green melt which partially resolidified to the brown adduct upon cooling. *Anal.* Calcd. for $C_{28}H_{36}N_2NiO_6$: C, 60.56; H, 6.54; N, 5.04. Found: C, 60.49; H, 6.65; N, 5.13. In the absence of seeding with preformed 2:1 complex, a green precipitate mixed with some crystalline starting nitrone formed. Upon standing this mixture was slowly converted into the brown 2:1 complex.

Analogously prepared was the brown green 2:1 complex with α-*p*-tolyl α,N-dimethyl nitrone and $Ni(AA)_2$, mp 114-118° with partial resolidification and remelting unsharply at about 130°. *Anal.* Calcd. for $C_{30}H_{40}N_2NiO_6$: C, 61.76; H, 6.91. Found: C, 61.67; H, 7.09.

*1:1 $M(AA)_2$ Complexes of Ketonitrones.* To 270 mg of $Ni(AA)_2$ in 5 ml $CCl_4$ was added 150 mg α-*p*-tolyl α,N-dimethyl nitrone. Water was azeotropically removed by concentrating at the boiling point to 3 ml, and 8 ml of ligroin was added. Bright green crystals of the 1:1 adduct were isolated and dried at 56° *in vacuo* for 1 hour, mp 140-141°. *Anal.* Calcd. for $C_{20}H_{27}NNiO_5$: C, 57.17; H, 6.48; N, 3.33. Found: C, 57.03; H, 6.68; N, 3.42. Also prepared was the 1:1 complex of α-phenyl α,N-dimethyl nitrone, mp 140-144°. *Anal.* Calcd. for $C_{19}H_{25}NO_5Ni$: C, 56.18; H, 6.20. Found: C, 56.59; H, 6.39.

Analogously prepared was the dark red 1:1 cobalt adduct of α-phenyl α,N-dimethyl nitrone, mp 130-133°. *Anal.* Calcd. for $C_{19}H_{25}CoNO_5$: C, 56.16; H, 6.20; N, 3.45. Found: C, 56.03; H, 6.32; N, 3.66. An attempt to prepare the 2:1 cobalt complex as above resulted only in isolation of the 1:1 complex.

*Spectra.* Infrared spectra in the region 4000-600 $cm^{-1}$ were recorded on a Perkin Elmer 237B or a Beckman IR-10 spectrometer. The visible near infrared spectra 5000-20,000 $cm^{-1}$) were obtained using a Cary 14 spectrometer. Nmr spectra were obtained using either a Varian A-60 or A60-A spectrometer (60 mc/sec) with tetramethyl silane as an internal standard and downfield being the negative direction. The data on the paramagnetic complexes were obtained under rapid exchange conditions as previously described,[2,3] using a number of samples containing varying excesses of ligand.

Relative isotropic shifts found for the protons of α-*p*-tolyl N-methyl nitrone, I ($R_1$=$CH_3$, $R_2$=H) complexes with other $M(AA)_2$ systems at concentrations comparable to those in Table I are (for N-$CH_3$, =CH, *o*, *m*, *p*-$CH_3$) M=$Co^{II}$, 1.00, 1.80, 0.70, –0.18, –0.46; M=$Fe^{II}$, 1.00, 1.80, 0.45, –0.13, –0.39; M=$Mn^{II}$, 1.00, too broad, 0.65, –0.14, –0.59. The corresponding cobalt(II) complex relative shifts for ($R_1$=H, $R_2$=H) are 1.00 (N—$CH_3$), 1.73 (C—H), 0.51 (*o*), –0.12 (*m*), 0.35 (*p*), with the absolute magnitude of the N—$CH_3$ shift for a solution 0.8 *M* in nitrone and 0.078 *M* in $M(AA)_2$ being +128 cps. Under these conditions the absolute magnitude for the α-*p*-tolyl N-methyl nitrone $Co(AA)_2$ complex N—$CH_3$ shift is +129 cps.

The nmr spectra of the imine complexes (except those of benzophenone methylimine) showed a slow decrease in the observed isotropic shifts with time which stopped after 24 hours. However the ratios of the isotropic shifts were independent of time and it is these invariant ratios obtained under conditions of rapid ligand exchange which are given in Table I.

## Results

Nitrone-$M(AA)_2$ complexes of both 2:1 and 1:1 stoichiometry were isolated and characterized. Mull infrared spectra of the nitrones, both complexed and uncomplexed, show a single strong absorption in the 1100-1300 $cm^{-1}$ region which has been assigned to the N-O stretching frequency.[10] This absorption, found at 1172 $cm^{-1}$ in uncomplexed $\alpha$-*p*-tolyl N-methyl nitrone, is shifted to 1152 $cm^{-1}$ in the $M(AA)_2$ complexes. For the ketonitrones, a peak at about 1250 $cm^{-1}$ in the free ligands is shifted to 1225-1230 $cm^{-1}$ in the isolated complexes. The absorptions $\nu_2$ and $\nu_{10}$ associated with the $\beta$-diketone group are also found in this region but are of lower intensity.[11] The observed shifts are in agreement with the coordination of the nitrones to the metal atoms through the oxygen atom.[12]

The visible near-infrared spectra of both the isolated cobalt nitrone complexes in mineral oil mull show maxima at about 8,150 and 21,500 $cm^{-1}$ and shoulders at about 17,700 and 21,000 $cm^{-1}$. The mull spectra of the 2:1 and 1:1 nitrone-$Ni(AA)_2$ complexes have d-d transition maxima at approximately 8,000-8,500 $cm^{-1}$ and 15,400 $cm^{-1}$. These data indicate that the donor atoms in all these isolated complexes have near octahedral symmetry around the central metal atom. However, methylene chloride solutions, 0.8 *M* in $\alpha$, N-dimethyl $\alpha$-phenyl nitrone and 0.03 *M* in $Co(AA)_2$, have maxima at 12,300 ($\varepsilon = 13\,M^{-1}\,cm^{-1}$) and 18,000 ($\varepsilon = 55\,M^{-1}\,cm^{-1}$) $cm^{-1}$. This indicates that in solution the predominant cobalt species is of lower than 2:1 stoichiometry[2] and probably not surrounded by an octahedral coordination shell.[13] Solutions of $Ni(AA)_2$ and excess nitrone show peaks at 8,600 and 15,100 $cm^{-1}$ in agreement with a near octahedral arrangement of donors but the solutions are more nearly the color of the isolated green 1:1 complex than the 2:1 complex. This suggests that in solution the principal nickel species is hexacoordinate but has a 1:1 ligand to $Ni(AA)_2$ stoichiometry and is therefore associated.[14]

Nmr isotropic shift data for nitrones complexed to $Ni(AA)_2$ under conditions of rapid ligand exchange, are presented in Table I. These are principally contact shifts since the shifts observed for the $CH_3$ and CH protons of the acetylacetonate group, $-2.9$ and $+17.0$ ppm respectively, are similar to those for nickel acetylacetonate complexes in which dipolar effects are known to be negligible.[15]

No complexes of imines with $M(AA)_2$ were isolated and the visible spectra of solutions indicate that the equilibrium constants for the formation of such complexes are small.

## Discussion

*Nitrones.* Spin density[16] in the aromatic nitrones complexed with $Ni(AA)_2$, in analogy with the corresponding pyridine 1-oxide complexes,[2,3] is distributed in ligand orbitals having predominantly $\pi$ character. Thus the isotropic shifts show an alternation in the sign of spin density on adjacent centers in the $\pi$ framework. Resonances of protons attached directly to the imine, *ortho* and *para* carbon atoms are shifted upfield whereas the resonances of methyl groups attached to these centers are shifted downfield in agreement with the presence of positive spin density. Negative spin density at the nitrogen atom is indicated by the upfield shift of the $N{-}CH_3$ resonance and is confirmed by an upfield shift of the *meta* and a downfield shift of the *ortho* proton resonances of the N-phenyl group in N-phenyl $\alpha$-*p*-tolylnitrone. Additional support for a $\pi$ type of spin distribution in the ligand is provided by data for the ketonitrones. These ligands, unlike the aldonitrones in which the aromatic ring and N-oxide groups are *cis*,[17] presumably have the ring and oxide *trans* to each other.[18] The absence of a large downfield shift of the *ortho* protons resonance and the uv spectral data,[6] indicate that in the free ligand there is twisting of the aromatic ring from coplanarity with the imine group and a reduction in conjugation. The decrease in the fraction of spin delocalized in the aromatic ring compared with that at the $N{-}CH_3$ group for the ketonitrones relative to the aldonitrones indicate that this loss in conjugation also affects the spin distribution in the complex. However a comparison of the isotropic shifts with calculated $\pi$ spin densities,[19] Table I, shows only a moderate agreement.[19b] In particular, the spin density on the nitrogen which is observed to be negative is predicted to be positive. The observed $N{-}CH_3$ upfield shift is also in contrast to the reported downfield shift of the $N{-}CH_3$ resonance in $\alpha$-2-pyridyl N-methylnitrone complexed with nickel chloride.[20]

The delocalization of unpaired spin in a ligand $\pi$ orbital of a hexacoordinate nickel(II) complex can arise through several mechanisms[21] and does not require the presence of ligand-metal $\pi$ bonding.[22] In the present work, spin delocalization into the ligand $\pi$ system is probably due to the non-orthogonality of the metal ligand $\sigma$ and the ligand $\pi$ orbitals caused by the noncoplanarity of the $Ni{-}O{-}N{=}C$ system. This noncoplanarity is supported by the observed general upfield bias of the isotropic shifts of the $Co(AA)_2$ nitrone complexes. This can be interpreted as being due to dipolar shifts in an axial complex having the Co–O–N plane twisted approximately 55° relative to the $O{-}N{=}C$ plane.[2,23] Qualitatively similar conclusions are reached from the observed $N{-}CH_3$ and $C{-}R_2$ nmr line width ratios based on a dominant dipolar term for line broadening in these complexes.[16]

---

(10) J. Hamer and A. Macaluso, *Chem. Rev.*, *64*, 473 (1964).

(11) K. Nakamoto, « Infrared Spectra of Inorganic and Coordination Compounds », John Wiley and Sons, New York, N. Y., 1963, p. 216.

(12) Y. Kakuiti, S. Kida, and J. W. Quagliano, *Spectrochim. Acta*, *19*, 201 (1963).

(13) M. Ciampolini and G. P. Speroni, *Inorg. Chem.*, *5*, 545 (1966).

(14) J. P. Fackler, Jr. *Progr. Inorg. Chem.*, *7*, 361 (1966).

(15) G. N. LaMar, *J. Mag. Res.*, *1*, 185 (1969).

(16) For a review of this and other aspects of spin delocalization in paramagnetic complexes see D. R. Eaton and W. D. Phillips, *Advan. Magnetic Resonances*, *1*, 103 (1965).

(17) K. Folting, W. N. Lipscomb, and B. Jerslev, *Acta Cryst.*, *17*, 1263 (1964).

(18) K. Tori, M. Ohtsuru, and T. Kubota, *Bull. Chem. Soc. Japan*, *39*, 1089 (1966).

(19) (a) T. Kubota and M. Yamakawa, *Bull. Chem. Soc. Japan*, *36*, 1564 (1963). (b) It should be noted that spin density introduced in a $\pi$ system via $\sigma$-$\pi$ non-orthogonality is not necessarily restricted to the *highest filled $\pi$-MO. Calculations which assume exclusive occupation* of a particular MO in such cases may not be entirely realistic. Further theoretical work is necessary in order to clarify this point.

(20) J. R. Hutchison, G. N. LaMar, and W. D. Horrocks, Jr., *Inorg. Chem.*, *8*, 126 (1969).

(21) G. N. LaMar, *Mol. Phys.*, *12*, 427 (1967).

(22) (a) R. W. Kluiber and W. D. Horrocks, Jr., *Inorg. Chem.*, *6*, 430 (1967). (b) R. S. Fitzgerald and R. S. Drago, *J. Am. Chem. Soc.*, *89*, 2879 (1967).

(23) R. W. Kluiber and W. D. Horrocks, Jr., *Inorg. Chem.*, *6*, 166 (1967).

($N-CH_3/C-R_2$ line width ratios of 1.00/0.75 for I, $R_1 = CH_3$, $R_2 = H$, and 1.00/1.92 for I, $R_1 = R_2 = CH_3$, are observed). Such twisting from coplanarity has also been reported in the interaction of iodine with nitrones[24] and in the analogous pyridine 1-oxide $Ni(AA)_2$ complex.[25]

*Imines.* The most notable feature of the spin delocalization data for the complexed imines is found in the system N-methyl benzophenone imine, II ($R_1 = H$, $R_2 = C_6H_5$), wherein only one of the phenyl groups participates effectively in the spin density distribution. Again this appears to be an example of steric inhibition of conjugation in the complexed ligand as evidenced by spin delocalization. In the uncomplexed ligand, steric factors allow only one of the phenyl groups to be near coplanar and thus conjugated with the imine group. In the fast exchange studies reported here, the group which accepts the delocalized spin in the complex can be identified as that which is also conjugated with the imine group in the uncomplexed ligand. This phenyl is identified by the downfield shift of the *ortho* protons resonance (in the absence of $Ni(AA)_2$) caused by the adjacent, conjugated imine group. Previous studies of aromatic N-methyl ketimines have assigned the conjugated aromatic ring to a position *trans* to the $N-CH_3$ group.[26] However models of possible complexes involved in the present study, based on the imine nitrogen bonding with the nickel atom using a $sp^2$ hybrid orbitals, indicate that due to steric effects of the nickel atom and its associated ligands, near coplanarity with the imine group is probable only if the phenyl group is *cis* to the $N-CH_3$. This discrepancy of the spin delocalization data with either the ligand stereochemistry or postulated bonding has not yet been resolved.

The other imine data presented in Table I can again be summarized using the qualitative concept of spin delocalization producing alternating centers of positive and negative spin density. The changes in sign of the resonance shifts found upon substitution of methyl groups for protons is characteristic of spin distribution in predominantly a ligand $\pi$ orbital, but the agreement of the observed shifts with calculated signs and magnitudes of spin densities[19] is poor. The large shifts observed for the $N-CH_3$ and the $R_2$ group relative to those of the aromatic protons in the aldimines is similar to that observed in salicylaldimine complexes[27] and may be due to either a combination of $\sigma$ and $\pi$ delocalization or to steric inhibition of conjugation of the phenyl group. An attempt to provide further experimental information on the spin delocalization mechanism using the system N-*p*-tolyl *p*-tolualdimine and $Ni(AA)_2$ was unsucessful. The observed shifts were very small owing to an unfavorable equilibrium with this weakly basic ligand.[28] Using the more basic N-*p*-anisyl *p*-N,'N'-dimethylaminobenzaldehydimine produced an nmr spectrum which indicated that appreciable metal complexing with the dimethylamino nitrogen rather than the imine group occurred.[22a]

---

[24] T. Kubota, *J. Am. Chem. Soc.*, *87*, 458 (1965).
[25] W. D. Horrocks, Jr. D. H. Templeton, and A. Zalkin, *Inorg. Chem.*, *7*, 1552 (1968).
[26] D. Y. Curtin, E. J. Grubbs, and C. G. McCarty, *J. Am. Chem. Soc.*, *88*, 2775 (1968).
[27] R. H. Holm, A. Chakravorty, and L. J. Theriot, *Inorg. Chem.*, *5*, 625 (1966).
[28] J. Weinstein and E. McIninch, *J. Am. Chem. Soc.*, *82*, 6064 (1960).