

sec.⁻¹). The sample tube was rotated (10 r.p.m.) during the irradiation and absorption measurement periods. A series of e.p.r. absorptions were recorded which did not diminish in intensity for at least 8 hr. after cessation of irradiation. The persistence of these lines is interpreted as evidence for a ground-state species.¹⁰

The e.p.r. spectrum of II consisted of a comparatively sharp line at 1587 gauss (peak-to-peak width of 11 gauss) and a pair of absorptions occurring at 2973 and 3481 gauss. These absorptions are consistent with a spin Hamiltonian description¹¹

$$\mathcal{H} = g\beta H \cdot S + DS_z^2 + E(S_x^2 - S_y^2)$$

in which $|D| = 0.0521 \text{ cm.}^{-1}$ and $|E| < 0.002 \text{ cm.}^{-1}$.^{12,13}

The e.p.r. of the photolysis product of 1,4-diazidobenzene¹⁴ in fluorolube was obtained in a similar manner. A series of absorptions at 1578 (= H_{\min}), 2500, 3852, 3566, and 3972 gauss were recorded which can be described by the above spin Hamiltonian with $|D| = 0.0675 \text{ cm.}^{-1}$ and $E \approx 0$.¹⁵

The e.p.r. spectrum of both II and IV were quite different from that which would be expected of a species in which only one molecule of nitrogen had been expelled from I or III. If this process had occurred, the e.p.r. spectrum would have resembled that of diphenylmethylene¹ or phenylnitrene,³ respectively.

The close similarity between the e.p.r. absorption spectrum and the magnitude of the zero-field parameters for the two species suggests a common structural feature which is responsible for the low spin-spin interaction. The observed zero-field splittings for II¹⁶ correspond to a value of $(1/r^3)^{-1/3}$ of approximately 4 Å. The most reasonable structures which explain this low spin-spin interaction are II and IV where the two electron-deficient atoms are approximately 5.6 Å. apart. The fact that the observed values of $|D|$ are somewhat larger than expected may be due to a spin polarization through the benzene ring, causing an increased spin-spin interaction. The larger value of $|D|$ for IV as compared to II is partly explained by the absence of spin delocalization onto the end phenyl rings which can occur in II.

In II and IV where the two electron-deficient atoms are *para* to each other, it is not unexpected that the triplet states II and IV are of lower energy than the quintet states. In *m*-phenylene-bis-(phenylmethylene), and *m*-phenylenedinitrene, one might anticipate that the quintet would be of lower energy. The e.p.r. spectra of the photolytic products of 1,3-bis-(α -diazobenzyl)-benzene and 1,3-diazidobenzene have been obtained. The spectra are quite complex and are currently being analyzed. However, it is of interest that the spectra are quite similar to each other and quite distinct from those of II and IV.

Acknowledgment.—The authors wish to acknowledge the assistance of Richard M. R. Cramer and to thank

(10) Since experiments at 4°K. gave similar absorption lines, it is inferred that the observed species is probably the ground state, although the possibility that the e.p.r. is derived from a species only a few cm.⁻¹ above the ground state cannot be completely excluded.

(11) K. W. H. Stevens, *Proc. Roy. Soc. (London)*, **A214**, 237 (1952); C. A. Hutchison, Jr., and B. W. Mangum, *J. Chem. Phys.*, **34**, 908 (1961).

(12) In the calculation of D and E the 1587 gauss line was employed as " H_{\min} " or half-field line¹²; the other two lines were principal axis lines (when $E = 0$, the x - and y -axis lines are degenerate). The z -axis lines whose intensity would be expected to be weak were not observed in II but were seen in IV at 2500 and 3972 gauss.

(13) M. S. de Groot and J. H. van der Waals, *Mol. Phys.*, **3**, 190 (1960).

(14) Prepared from 1,4-diaminobenzene by the method of M. O. Ferster and H. E. Fierz, *J. Chem. Soc.*, **91**, 1953 (1907).

(15) An additional set of absorptions were recorded at 1227 (= H_{\min}), 1473, 2062, and 4115 gauss which can be fitted to the spin Hamiltonian where $|D| = 0.171 \text{ cm.}^{-1}$ and $E \approx 0$.

(16) For a recent theoretical calculation of the zero-field splittings based on this structure, see J. Higuchi, *J. Chem. Phys.*, **38**, 1237 (1963).

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Metal Nitrosyl Derivatives with Bridging Nitrosyl Groups

Sir:

No clear examples of metal nitrosyl derivatives with bridging nitrosyl groups have been reported. The cyclopentadienylmanganese nitrosyl derivative, $(C_5H_5)_3Mn_2(NO)_3$, claimed to have bridging nitrosyl groups on the basis of a band in the infrared spectrum at 1510 cm.⁻¹, was prepared several years ago.¹ However, this manganese compound apparently has not been investigated since its original discovery, and its relationship to other known metal nitrosyl, cyclopentadienyl, and carbonyl derivatives is not clear. Its structure therefore must be regarded as still uncertain.

This communication describes new nitrosyl derivatives of chromium and manganese where not only the presence of bridging nitrosyl groups is clearly indicated from the infrared spectrum, but also the relationship between the new compounds and well established metal carbonyl derivatives is quite clear.

For the preparation of the chromium derivative, an aqueous solution of $C_6H_5Cr(NO)_2Cl$ ^{1,2} was reduced with sodium borohydride. The product was extracted with benzene and purified by chromatography on alumina to give dark violet crystals of $[C_6H_5Cr(NO)_2]_2$, m.p. 158–159°, in 5–6% yield. *Anal.* Calcd. for $C_{10}H_{10}N_4O_4Cr_2$: C, 33.9; H, 2.8; N, 15.8; Cr, 29.4; O, 18.1; mol. wt., 354. Found: C, 34.0, 34.4; H, 2.8, 3.4; N, 16.1, 16.1; Cr, 28.2, 28.7; O, 18.1, 18.1; mol. wt., 347 (Mechrolab vapor pressure osmometer in benzene solution). This chromium derivative exhibited a single sharp cyclopentadienyl resonance at 4.82 τ demonstrating its diamagnetism.

For the preparation of the manganese derivative, a similar sodium borohydride reduction of an aqueous solution of the cation $[C_6H_5Mn(CO)_2NO]^+$ was carried out.³ The product was extracted from the reaction mixture with benzene. After evaporating the benzene solution at ~30 mm., the resulting purple-brown crystalline residue was purified by recrystallization from a dichloromethane-hexane mixture to give violet crystals of $[C_6H_5MnCONO]_2$ dec. >200°, in yields up to 60%. *Anal.* Calcd. for $C_{12}H_{10}N_2O_4Mn_2$: C, 40.4; H, 2.8; N, 7.9; Mn, 30.9; O, 18.0. Found: C, 39.6, 40.3; H, 2.9, 2.7; N, 8.0, 8.1; Mn, 31.2, 31.1; O, 18.1. The manganese derivative appeared to be too unstable in benzene solution for molecular weight determinations or for sharp n.m.r. spectra.

The new compounds $[C_6H_5Cr(NO)_2]_2$ and $[C_6H_5MnCONO]_2$ have physical properties very similar to the well known isoelectronic^{3,4} $[C_6H_5Fe(CO)_2]_2$, demonstrated to have structure I with two bridging carbonyl groups and two terminal carbonyl groups.⁵ The terminal carbonyl groups in the iron carbonyl derivative exhibit infrared bands⁶ at 1940 and 1955 cm.⁻¹,

(1) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **2**, 38 (1956).

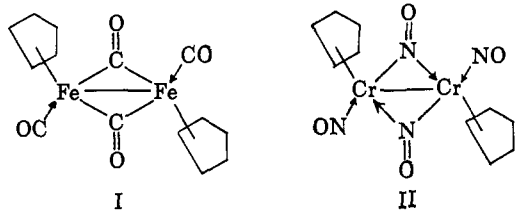
(2) E. O. Fischer and P. Kuzel, *Z. anorg. allgem. Chem.*, **317**, 226 (1962).

(3) T. S. Piper, F. A. Cotton, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **1**, 165 (1955).

(4) B. F. Hallam, O. S. Mills, and P. L. Pauson, *ibid.*, **1**, 313 (1955).

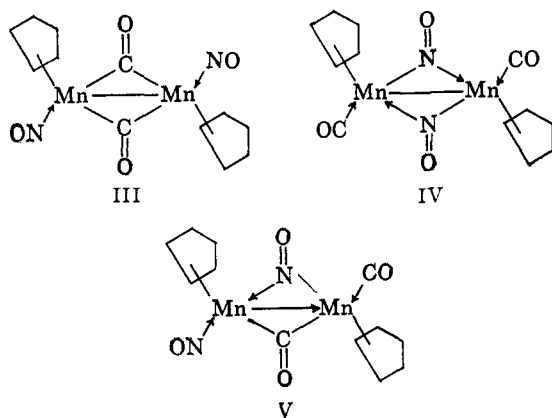
(5) O. S. Mills, *Acta Cryst.*, **11**, 620 (1958).

(6) The infrared spectra described here were taken either on the Beckman



whereas the bridging carbonyl groups exhibit an infrared band at 1756 cm.^{-1} , *i.e.*, at a frequency of $\sim 90\%$ of the frequency of the terminal carbonyls. In this connection it is of interest that the chromium derivative $[\text{C}_6\text{H}_5\text{Cr}(\text{NO})_2]_2$ exhibits a band at 1672 cm.^{-1} which may be attributed to the terminal nitrosyl groups and a band at 1505 cm.^{-1} due to bridging nitrosyl groups. As in the case of the iron carbonyl derivative the frequency of the bridging nitrosyl groups is $\sim 90\%$ of the frequency of the terminal nitrosyl groups. Moreover, it is of interest to compare the position of this band at 1505 cm.^{-1} in $[\text{C}_6\text{H}_5\text{Cr}(\text{NO})_2]_2$ with that of the band at 1510 cm.^{-1} in $(\text{C}_6\text{H}_5)_3\text{Mn}_2(\text{NO})_3$ assigned¹ to bridging nitrosyl groups. This infrared evidence indicates that the chromium complex $[\text{C}_6\text{H}_5\text{Cr}(\text{NO})_2]_2$ has structure II. This structure is entirely analogous to the structure of $[\text{C}_6\text{H}_5\text{Fe}(\text{CO})_2]_2$ (I) but with chromium atoms replacing iron atoms and nitrosyl groups replacing carbonyl groups.

The situation with the manganese derivative $[\text{C}_6\text{H}_5\text{MnCONO}]_2$ is more complex due to possible structures with two bridging carbonyl groups (III), two bridging nitrosyl groups (IV), and possibly even one bridging carbonyl group and one bridging nitrosyl group (V).⁷ The infrared spectrum of $[\text{C}_6\text{H}_5\text{MnCONO}]_2$ exhibits strong bands at 1956 , 1781 , 1707 , and 1509 cm.^{-1} which on the basis of the positions of the bands in $[\text{C}_6\text{H}_5\text{Fe}(\text{CO})_2]_2$ and $[\text{C}_6\text{H}_5\text{Cr}(\text{NO})_2]_2$ may be assigned to term-



inal carbonyl groups, bridging carbonyl groups, terminal nitrosyl groups, and bridging nitrosyl groups, respectively. This suggests that $[\text{C}_6\text{H}_5\text{MnCONO}]_2$ either has structure V, is a mixture of isomers with structures III and IV, or is a mixture of III and/or IV with V. Attempts to separate $[\text{C}_6\text{H}_5\text{MnCONO}]_2$ into two or more isomers by chromatography on alumina were unsuccessful. It is possible, however, that III, IV, and V might be rapidly interconvertible in solution

IR-9 machine with grating optics or on the Perkin-Elmer 112 machine with CaF_2 optics. Halocarbon oil mulls were used.

(7) In structure V the manganese-manganese bond instead of being analogous to the metal-metal bonds in structures I-IV may instead be regarded as analogous to the iron-iron bond in $\text{C}_4\text{H}_4\text{Fe}_2(\text{CO})_6$ (ref. 8) and its derivatives where one metal atom donates a lone pair to the other metal atom.

(8) W. Hübel and E. Weiss, *Chem. Ind.* (London), 703 (1959); W. Hübel and E. H. Bray, *J. Inorg. Nucl. Chem.*, **10**, 250 (1959); A. A. Hock and O. S. Mills, *Proc. Chem. Soc.*, 233 (1958).

and that the products always isolated might be an equilibrium mixture of the three compounds.

The compounds $[\text{C}_6\text{H}_5\text{Cr}(\text{NO})_2]_2$ and $[\text{C}_6\text{H}_5\text{MnCONO}]_2$ are much less stable than $[\text{C}_6\text{H}_5\text{Fe}(\text{CO})_2]_2$, decomposing slowly on prolonged storage at room temperature. The manganese compound is degraded by iodine to a carbonyl-free product under conditions where $[\text{C}_6\text{H}_5\text{Fe}(\text{CO})_2]_2$ forms the iodide $\text{C}_6\text{H}_5\text{Fe}(\text{CO})_2\text{I}$.¹ Sodium amalgam or sodium borohydride in tetrahydrofuran solution lead to very extensive destruction of $[\text{C}_6\text{H}_5\text{MnCONO}]_2$. The sensitivity of compounds of this type to strong reducing agents in ethereal solutions may explain the failure of Piper and Wilkinson to observe any $[\text{C}_6\text{H}_5\text{Cr}(\text{NO})_2]_2$ as a product in the treatment of the halides $\text{C}_6\text{H}_5\text{Cr}(\text{NO})_2\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) with ethereal Grignard reagents despite the fact that many of the reactions between $\text{C}_6\text{H}_5\text{Fe}(\text{CO})_2\text{I}$ and the same Grignard reagents produced significant quantities of $[\text{C}_6\text{H}_5\text{Fe}(\text{CO})_2]_2$.⁹

Further work on these and other nitrosyl derivatives is being carried out and will be described in forthcoming publications.

(9) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956).

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Even-Electron Paramagnetic Chelates¹

Sir:

Certain even-electron metal chelates of formula $\text{M}^{+2}(\text{R}^-)_2$ have been found to be paramagnetic. Electron spin resonance studies of these compounds show that they contain two unpaired electrons. All combinations in which M is Be, Mg, Ca, Sr, or Zn and R is 2,2'-bipyridine, 4,7-diphenyl-1,10-phenanthroline, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline, 2,2'-biquinoline, or 4,4'-diphenyl-2,2'-bipyridine have been investigated. The beryllium chelates were formed by the method of Coates and Green.² The other metal chelates were prepared by the reduction of R with a metal-mercury amalgam.

Solutions of most of the substances in rigid 2-methyltetrahydrofuran exhibited e.s.r. spectra characteristic of triplet molecules.³⁻⁶

The temperature dependence of the spectra indicate that the ground state is either triplet or lies within 100 cm.^{-1} of the triplet state. The splittings in the $\Delta M = 1$ region of the magnetic resonance absorption lie in the range between 50 and 135 gauss . These splittings, which are due to the intramolecular spin-spin interaction, generally vary as would be expected if the spins reside singly on each ligand and are separated by M^{+2} . The zinc chelates, however, are an exception. In each series, apart from 2,2'-bipyridine,⁸ the splitting for the zinc compound is largest. The increased dipolar interaction is probably accounted for by: (i) admixtures of states in which either one or two electrons are removed from the 3d shell of the zinc ion and are placed singly on either ligand and/or (ii) a spin polarization

(1) This work has been supported by the United States Air Force under contract, the National Science Foundation, the Petroleum Research Fund of the American Chemical Society, and an equipment loan contract with the Office of Naval Research.

(2) G. E. Coates and S. I. E. Green, *J. Chem. Soc.*, 3340 (1962).

(3) The products of 2,2'-bipyridine with calcium and strontium were paramagnetic but were insoluble in 2-methyltetrahydrofuran and showed a single e.s.r. line. Solutions of zinc amalgam and 2,2'-bipyridine were not paramagnetic.

(4) M. S. de Groot and J. H. van der Waals, *Mol. Phys.*, **3**, 190 (1960).

(5) R. W. Murray, A. M. Trozzolo, E. Wasserman, and W. A. Yager, *J. Am. Chem. Soc.*, **84**, 3213 (1962).

(6) N. Hirota and S. I. Weissman, *Mol. Phys.*, **5**, 537 (1962).