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Bonding Properties of the Methyl Isocyanide Ligand. A Single-Crystal X-Ray Diffraction and Molecular Orbital Study of Bromotricarbonylbis(methyl isocyanide)manganese, $Mn(CO)_3(CNCH_3)_2Br$

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A single-crystal X-ray diffraction study on bromotricarbonylbis(methyl isocyanide)manganese, $Mn(CO)_3(CNCH_3)_2Br$, has been completed. In addition, a nonparameterized approximate molecular orbital calculation has been carried out on the compound for the purpose of aiding in the interpretation of the bonding. The crystal structure is triclinic, space group $P\bar{1}$ with two discrete molecules per unit cell, a = 8.900 (2) Å, b = 10.907 (3) Å, c = 6.155 (2) Å, α = 97.93 (1)°, β = 108.45 (1)°, γ = 81.86 (1)°, V = 558.3 Å^3, ρ_m = 1.77 ± 0.02 g/cm^3, and ρ_c = 1.79 g/cm^3. Diffractometer data were collected using Mo Kα radiation and the structure was refined by full-matrix least-squares methods with anisotropic thermal parameters for all but the hydrogen atoms to a final conventional R = 0.040 for 831 independent reflections. The molecule has a nearly octahedral configuration with cis methyl isocyanide ligands. The three Mn–CO distances are 1.854 (12), 1.815 (11), and 1.789 (11) Å, with the shortest of these being the carbonyl trans to the bromine. The $Mn-CNCH_3$ bond distances are 1.992 (11) and 1.950 (12) Å, and the C–N–C angle does not deviate from linearity by more than 3°. The Mn–Br distance of 2.537 (2) Å corresponds to a single-bond distance. Comparisons are made between the present structure and other reported methyl isocyanide complexes, as well as with the electronically related compounds, $Mn(CO)_5X$, X = Cl and Br. Bond length considerations and the molecular orbital results confirm that back-bonding to the methyl isocyanide ligand is taking place, even in the presence of carbonyl, a much stronger π-electron acceptor. For the methyl isocyanide complexes studied to date comparisons of the metal to isocyanide bond length show a striking similarity to the metal to cyanide distance in related molecules.

Introduction

A primary source of evidence for the strong π-acceptor ability of the methyl isocyanide ligand on bonding with transition metals has been a shortening of the metal to carbon bond distance relative to the expected single-bond length in such complexes as $[Co(CNCH_3)_5]^+$,[1] *trans*-$Fe(CN)_2(CNCH_3)_4$,[2] and other species in which the methyl isocyanide ligand is competing for electron density on the metal either with itself or with cyanide. However, prior to the present study, structural data have not been presented in which the methyl isocyanide ligand is present in a complex which also contains a potentially much stronger π acceptor such as carbonyl. Since previous theoretical work in our laboratory has suggested that the π-acceptor ability of a ligand may be dependent upon the total intramolecular environment,[3,4] we undertook the structural determination and molecular orbital study of bromotricarbonylbis(methyl isocyanide)manganese, $Mn(CO)_3(CNCH_3)_2Br$.

This particular compound was chosen for several reasons. It provides an opportunity for direct comparison of the structural geometry for carbonyl and methyl isocyanide bound to a transition metal in the same complex. Also, the expected idealized octahedral geometry about the manganese atom facilitates interpretation of the molecular orbital results in that σ and π effects are readily separable. Further, in the same sense that Cotton considers $CNCH_3$ and CO to be electronically similar,[5] this complex is analogous to the halopentacarbonylmanganese compounds $Mn(CO)_5Cl$ and $Mn(CO)_5Br$. Comparisons of the present structure with the structures for these compounds, as well as with structures of other reported methyl isocyanide complexes, provides an opportunity for additional insight into the bonding properties of the methyl isocyanide ligand. Finally, the present work is the only reported structural study for an isocyanide bound to manganese.

Crystal Preparation

The preparation of $Mn(CNCH_3)_2(CO)_3Br$ has been described elsewhere.[6] Suitable single crystals were obtained by vapor diffusion of pentane into an ethyl acetate solution of the compound. The crystals are amber with well-formed faces.

Crystal Data and Collection of Intensity Data

Preliminary Weissenberg and precession photographs revealed that $Mn(CNCH_3)_2(CO)_3Br$ crystallizes in the triclinic system, while the initial choice of unit cell gave an unconventional B-centered cell. A crystal of dimensions 0.32 × 0.18 × 0.08 mm was mounted on the end of a glass fiber using Canadian Balsam with the c^* axis parallel to the spindle axis on a General Electric Datex-automated, full-circle diffractometer. Sixteen independent reflections were carefully centered and reindexed in terms of a reduced cell obtained from a Delauney reduction. These sixteen reflections were subsequently refined to convergence using a least-squares procedure to furnish the reduced cell dimensions a = 8.900 (2) Å, b = 10.907 (3) Å, c = 6.155 (2) Å, α = 97.93 (1)°, β = 108.45 (1)°, γ = 81.86 (1)°, and V = 558.3 Å^3. The density calculated on the basis of two molecules of $Mn(CNCH_3)_2(CO)_3Br$ per unit cell, ρ = 1.79 g/cm^3, is in good agreement with the observed density of 1.77 ± 0.02 g/cm^3, as obtained by flotation in a tetrachloroethane–iodoethane solution.

Intensities of some 1353 reflections, constituting a complete asymmetric unit with $5° < 2\theta < 40°$, were collected employing a scintillation counter and pulse height analyzer set to admit 90% of the Zr-filtered Mo Kα radiation. Intensity data were collected using the θ–2θ scan technique utilizing a 2°/min scan speed and a scan width of 2.2° that was 0.1° asymmetric toward the high 2θ side of the centered peak. Background was counted for 20 sec on each side of the peak with a stationary crystal and stationary counter. The intensities of four standard reflections distributed in various octants of reciprocal space were measured at intervals of every 100 reflections. The raw data were treated according

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(1) F. A. Cotton, T. G. Dunne, and J. S. Wood, *Inorg. Chem.*, **4**, 318 (1965).

(2) R. Hulme and H. M. Powell, *J. Chem. Soc.*, 719 (1957).

(3) R. L. DeKock, A. C. Sarapu, and R. F. Fenske, *Inorg. Chem.*, **10**, 38 (1971).

(4) R. F. Fenske and R. L. DeKock, *ibid.*, **11**, 437 (1972).

(5) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience, New York, N. Y., 1966, pp 744–745.

(6) P. M. Treichel, G. E. Direen, and H. J. Mueh, *J. Organometal. Chem.*, in press.

TABLE I

POSITIONAL AND THERMAL PARAMETERS FOR $Mn(CNCH_3)_2(CO)_3Br^{a,b}$

	x	y	z	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Mn	0.3021 (1)	0.3103 (1)	0.6259 (2)	118 (3)	65 (2)	243 (5)	−17 (1)	49 (3)	−4 (2)
Br	0.2768 (1)	0.1122 (0.8)	0.3529 (2)	204 (2)	77 (1)	282 (4)	−21 (1)	64 (2)	−17 (1)
C(1)	0.1577 (12)	0.3929 (9)	0.3890 (18)	132 (19)	77 (11)	390 (46)	−19 (11)	38 (23)	−26 (18)
O(1)	0.0739 (9)	0.4452 (7)	0.2525 (13)	216 (17)	148 (10)	431 (33)	27 (10)	35 (18)	55 (14)
C(2)	0.4669 (12)	0.3418 (8)	0.5353 (15)	148 (19)	62 (10)	282 (37)	4 (11)	73 (22)	25 (14)
O(2)	0.5692 (9)	0.3598 (6)	0.4747 (12)	213 (15)	115 (9)	505 (32)	−21 (9)	194 (19)	19 (12)
C(3)	0.3107 (10)	0.4501 (10)	0.8172 (17)	116 (17)	87 (11)	372 (39)	−11 (11)	70 (20)	−5 (17)
O(3)	0.3150 (8)	0.5402 (7)	0.9391 (12)	180 (14)	115 (8)	509 (30)	−33 (8)	117 (17)	−119 (14)
C(4)	0.4587 (11)	0.2158 (8)	0.8706 (17)	110 (17)	70 (10)	302 (38)	−31 (11)	95 (21)	−58 (16)
N(1)	0.5526 (10)	0.1636 (7)	1.0049 (14)	133 (16)	91 (9)	290 (32)	−13 (10)	37 (18)	7 (14)
C(6)	0.6675 (11)	0.0974 (9)	1.1789 (15)	171 (18)	100 (11)	227 (33)	8 (11)	10 (20)	36 (16)
C(5)	0.1303 (13)	0.2609 (8)	0.7170 (16)	166 (21)	74 (11)	230 (36)	−7 (12)	54 (22)	−10 (15)
N(2)	0.0314 (10)	0.2334 (7)	0.7748 (13)	166 (18)	96 (9)	322 (33)	−27 (10)	89 (20)	0.6 (13)
C(7)	−0.0887 (12)	0.1980 (10)	0.8571 (17)	166 (20)	124 (13)	451 (44)	−50 (12)	87 (24)	20 (19)

[a] The form of the anisotropic temperature factor which is used here is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] The standard deviations of the last significant figure are given in parentheses.

to the formulas $I = S - B(T/t)$, and $\sigma(I) = [S + B(T/t)^2 + (0.0016)I^2]^{1/2}$, where I is the integrated intensity, S is the total scan count measured over time T, B is the total background count measured over time t, and $\sigma(I)$ is the standard deviation of the integrated intensity. It was observed that during the course of data collection there was a small but steady movement of the crystal resulting in a net reduction in intensity of the standard reflections by 15%. This effect was remarkably systematic and was corrected for by treatment of the data in linear blocks as simple decay. There did not appear to be any significant X-ray sensitivity on the part of the crystal itself. After merging of the data to treat redundant data a total of 831 independent reflections with $I > 2\sigma(I)$ were obtained and structure factors used for the structure determination were calculated according to $|F| = (I/Lp)^{1/2}$ and $\sigma(F) = \sigma(I)/2|F|Lp$, where Lp is the usual Lorentz-polarization correction term.

Determination of the Structure

All calculations were carrid out on the UNIVAC 1108 computer of the Academic Computing Center at the University of Wisconsin.[7] Atomic scattering factors for neutral atoms were used.[8]

A Patterson synthesis could clearly be interpreted as arising from two manganese and two bromine atoms related by a center of symmetry, so at this point the space group $P\bar{1}$ appeared to be the correct choice and was subsequently confirmed by the refinement. We therefore have two asymmetric molecules per unit cell related by a center of symmetry. A Fourier synthesis phased on the heavy atoms revealed the position of the light atoms adjacent to the manganese atom. Subsequent Fourier syntheses ultimately located all the nonhydrogen atoms.

Isotropic least-squares refinement on all atoms except hydrogen converged with $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.079$ and $R_2 = [\Sigma w_i||F_o| - |F_c||^2/\Sigma w_i|F_o|^2]^{1/2} = 0.097$, where $w_i = 1/\sigma(F_o)^2$. At this point absorption corrections were applied ($\mu = 50.1\ cm^{-1}$), the transimission coefficients varying from 0.48 to 0.69. Corrections for both the real and imaginary parts of the anomalous dispersion for the manganese and bromine atoms were made as well.[9] Subsequent anisotropic refinement on all nonhydrogen atoms converged with $R_1 = 0.044$ and $R_2 = 0.056$. A difference Fourier vaguely showed what appeared to be one of the hydrogen atoms on each methyl isocyanide ligand. The remaining hydrogen positions were generated assuming optimized sp^3 hybridization about the methyl carbon atom and a C–H bond distance of 1.1 Å. These positional parameters and an arbitrary isotropic thermal parameter value of 5 Å^2 were not allowed at any point to enter into the least-squares refinement procedure since we were making no attempt to locate accurately the hydrogen peaks. We were interested instead in a more accurate determination of the methyl carbon parameters. Two further anisotropic least-squares refinements on all the nonhydrogen atoms, reoptimizing the hydrogen positions after the first cycle, resulted in no significant positional or thermal parameter changes, with the final $R_1 = 0.040$ and $R_2 = 0.048$. A final difference Fourier revealed no residual electron density greater than 0.5 e/Å^3, except for a peak near Br of 0.54 e/Å^3. The final positional and thermal parameters are listed in Table I. Structure factors are compiled elsewhere.[10]

General Description of the Structure

The crystal structure consists of distinct monomeric units of $Mn(CO)_3(CNCH_3)_2Br$ with the methyl isocyanide ligands cis to one another and the bromine trans to a carbonyl. Table II lists the bond angles and distances in the monomeric unit whose structural parameters are given in Table I, and Figure 1 illustrates the numbering scheme. The crystal packing shows nò

TABLE II

TABLE OF BOND DISTANCES (Å) AND ANGLES (DEG)

Mn–Br	2.537 (2)	Br–Mn–C(1)	88.2 (3)
Mn–C(1)	1.854 (12)	Br–Mn–C(2)	89.3 (3)
Mn–C(2)	1.815 (11)	Br–Mn–C(4)	89.5 (2)
Mn–C(3)	1.789 (11)	Br–Mn–C(5)	86.3 (3)
Mn–C(4)	1.992 (11)		
Mn–C(5)	1.950 (12)	Mn–C(1)–O(1)	177.7 (9)
		Mn–C(2)–O(2)	178.6 (8)
C(1)–O(1)	1.097 (10)	Mn–C(3)–O(3)	179.5 (8)
C(2)–O(2)	1.137 (10)		
C(3)–O(3)	1.148 (10)	Br–Mn–C(3)	177.4 (3)
		C(5)–Mn–C(2)	174.9 (4)
C(4)–N(1)	1.124 (10)	C(1)–Mn–C(4)	177.6 (3)
N(1)–C(6)	1.423 (12)		
C(5)–N(2)	1.138 (11)	Mn–C(5)–N(2)	178.5 (9)
N(2)–C(7)	1.436 (14)	Mn–C(4)–N(1)	176.7 (8)
		C(5)–N(2)–C(7)	177.6 (10)
		C(4)–N(1)–C(6)	178.0 (7)
		C(1)–Mn–C(2)	90.8 (4)
		C(1)–Mn–C(5)	91.4 (4)
		C(5)–Mn–C(4)	89.1 (4)
		C(4)–Mn–C(2)	88.4 (4)

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(7) The following programs were used for the refinement and error calculations: (a) J. F. Blount, "A Three-Dimensional Crystallographic Fourier Summation Program," Ph.D. Thesis (Appendix), University of Wisconsin, 1965; (b) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, a Fortran Crystallographic Least-Squares Program," Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962; (c) J. F. Blount, "DEAR," an absorption correction program based on a method given by W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **10**, 180 (1957); (d) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE, a Fortran Crystallographic Function and Error Program," Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

(8) (a) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, **17**, 1040 (1964), for nonhydrogen atoms; (b) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965), for hydrogen.

(9) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1968, pp 215–216.

(10) A compilation of observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number INORG-72-3021. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

abnormally close contacts, with the most noteworthy interaction being van der Waals contacts between the methyl group of the methyl isocyanide ligand and bromine. This contact indicates probable hydrogen bonding, though this is not proven since the hydrogen positions have not been accurately determined. Table III lists some important intermolecular distances. The immediate coordination geometry about the manganese atom is nearly perfectly octahedral, with the biggest deviation being a bending of the equatorial ligands toward the bromine atom.[11] This type of bend seems to be a general feature of the $Mn(CO)_5L$ compounds as well. For example, in $Mn(CO)_5Cl$ the two independent X–Mn–C_{eq} angles are 88.1 (2) and 88.4 (2)°[12] and for the neutron diffraction results on $HMn(CO)_5$ the bending ranges from 81.8 (5) to 85.1 (5)°.[13] The analogous bending we observe ranges from 86.3 (3) to 89.5 (3)°.

TABLE III

SELECTED INTERMOLECULAR DISTANCES (Å)

Contact	Symmetry operation on primed atom[a]	Distance, Å
C(6)···Br′	$1 - x, -y, 1 - z$	3.851 (9)
C(6)···Br′	$x, y, 1 + z$	3.926 (10)
C(6)···Br′	$1 - x, -y, 2 - z$	3.791 (9)
C(7)···Br′	$x, y, 1 + z$	3.797 (10)
O(1)···O(3)′	$-x, 1 - y, 1 - z$	3.273 (10)
O(2)···O(2)′	$1 - x, 1 - y, 1 - z$	3.143 (14)
O(3)···O(3)′	$1 - x, 1 - y, 2 - z$	3.158 (13)

[a] This symmetry operation is applied to the corresponding x, y, z position in Table I to generate the position of the primed atom.

TABLE IV

STRUCTURAL DATA ON METHYL ISOCYANIDE COMPLEXES[g]

		Av bond lengths, Å			
Compound	Ref	M—CNCH₃	C≡N	N—CH₃	CNC angle, deg
$Mn(CNCH_3)_2(CO)Br$	*a*	1.97 ± 0.01	1.13 ± 0.01	1.43 ± 0.01	178 ± 1
$Co_2(CNCH_3)_{10}(ClO_4)_4$	*b*	1.87 ± 0.03 (eq) 1.92 ± 0.04 (ax)	1.15 ± 0.04	1.50 ± 0.05	172 ± 3
$Co(CNCH_3)_5ClO_4$	*c*	1.87 ± 0.02	1.14 ± 0.02	1.44 ± 0.03	175 ± 2.0
$Mo(CNCH_3)_4(CN)_4$	*d*	2.14 ± 0.01	1.13 ± 0.01	1.44 ± 0.01	174–180[f]
$CNCH_3$	*e*		1.166 ± 0.001	1.424 ± 0.001	180 (by symmetry)

[a] This work. [b] F. A. Cotton, T. G. Dunne, and J. S. Wood, *Inorg. Chem.*, **3**, 1495 (1964). [c] Reference 1. [d] F. H. Cano and D. W. J. Cruickshank, *Chem. Commun.*, 1617 (1971). [e] Reference 23. [f] The authors report that the MoCN and CNC angles are in this range. [g] Several structures of accuracy too low for meaningful comparisons of bond lengths and angles have been omitted from this table. They are *cis*-$(CN)_2Fe(CNCH_3)_4 \cdot 4CHCl_3$ [J. B. Wiford, N. O. Smith, and H. M. Powell, *J. Chem. Soc. A*, 1544 (1968)], *trans*-$(CN)_2Fe(CNCH_3)_4$ [R. Hulme and H. M. Powell, *J. Chem. Soc.*, 719 (1957)], $Fe(CNCH_3)_6Cl_2 \cdot 3H_2O$ [H. M. Powell and G. W. R. Bartindale, *ibid.*, 799 (1945)], and $CuICNCH_3$ [P. J. Fisher, N. E. Taylor, and M. M. Harding, *ibid.*, 2303 (1960)].

The two equatorial manganese to carbonyl distances we report, 1.815 (11) and 1.854 (12) Å, appear to be larger than the value for the axial carbonyl, 1.789 (11) Å, though the shorter of the equatorial distances is within 3σ of the axial value and thus is not statistically different from it. The structure of $Mn(CO)_5Cl$ shows an axial Mn–C bond shortening of approximately 0.08 Å, with the equatorial Mn–C bond distance reported as 1.893 (6) Å. The $HMn(CO)_5$ structure shows a similar shortening of about 0.03 Å, and in $Mn_2(CO)_{10}$ a shortening of about 0.04 Å was observed.[14] However, Greene and Bryan in their paper reporting the structure of $Mn(CO)_5Cl$ cautioned against assigning too much physical significance to the apparent differences in equatorial *vs.* axial carbonyl bond distances.[12] Uncertainty arises from the present lack of an adequate model for corrections to bond lengths that arise from anisotropic thermal motion. The bond lengths that we report, and all the values for other compounds we reference in this paper, are thermally uncorrected.

The bonding of the methyl isocyanide ligand itself appears nearly linear in the present work, varying from linearity by not more than 3°. In Table IV we have listed the presently known X-ray structural studies of transition metal complexes containing methyl isocyanide as a ligand and also the microwave structure of free methyl isocyanide. Those listed are the only structures that have appeared to date that are of sufficient accuracy to make meaningful comparisons of bond lengths and angles. From the table it is clear that the C–N–C linkage is nearly linear in all cases. In a structure of *cis*-$(CN)_2Fe(CNCH_3)_4 \cdot 4CHCl_3$ it is reported that methyl isocyanide groups trans to one another are linear, while the Fe–C–N–C linkages trans to the cyanide groups are bent by 22° at the carbon atom and 24° at the nitrogen atom.[15] Relative to the data presented in Table IV, such bending is exceptionally large, though the reported uncertainty in the bond angles for this case is considerable, and the situation is unique in that the crystal is at least 60% chloroform by volume. Extensive distortions could result from packing forces. The isocyanide C≡N distances we

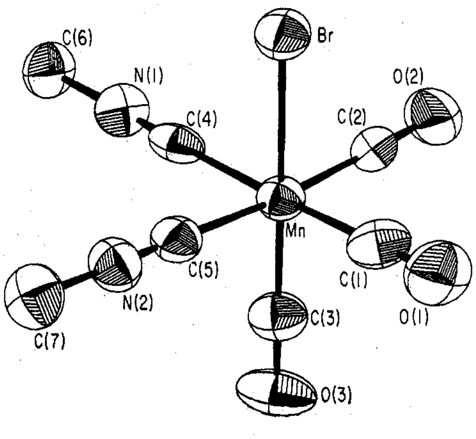

Figure 1.—ORTEP 50% probability thermal ellipsoid plot of $Mn(CO)_3(CNCH_3)_2Br$. Numbering scheme corresponds to Table II.

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(11) We refer to the carbonyl trans to the ligand X in $Mn(CO)_5X$ as axial, while the remaining two carbonyls and the methyl isocyanide ligands are referred to as equatorial.

(12) P. T. Greene and R. F. Bryan, *J. Chem. Soc. A*, 1559 (1971).

(13) S. J. La Placa, W. C. Hamilton, J. A. Ibers, and A. Davison, *Inorg. Chem.*, **8**, 1928 (1969).

(14) L. F. Dahl and R. E. Rundle, *Acta Crystallogr.*, **16**, 419 (1963).

(15) J. B. Wilford, N. O. Smith, and H. M. Powell, *J. Chem. Soc. A*, 1544 (1968).

TABLE V

PER CENT CHARACTER AND EIGENVALUES FOR LIGAND ORBITALS IMPORTANT IN BONDING TO THE METAL ATOM

		s(C)	p(C)	s(O)	p(O)	Eigenvalue, eV
CO	5σ	34.4	47.8	1.0	16.7	−13.79
	2π		66.8		33.3	+0.29

(1) (2)		s(C_1)	p(C_1)	s(N)	p(N)	s(C_2)	p(C_2)	H(total)	Eigenvalue, eV
$CNCH_3$	7 A_1	40.7	56.0	0.7	0.8	0.0	1.7	0.1	−13.39
	3 E		59.3		36.6		0.1	4.0	+3.17

report, 1.124 (10) and 1.138 (14) Å, are close to those distances in Table IV reported for both the bound and free methyl isocyanide. Likewise the N—CH_3 bond length is seen to be essentially the same for the cases cited.

Calculational Method

The approximate molecular orbital method we use has been described elsewhere.[16] It is most important to note that our method is completely nonparameterized, requiring only the wave functions and appropriate bond distances as input to produce the complete SCF calculation. Further, the wave functions and distances used are chosen in a consistent fashion described below.

Basis Functions.—Clementi's double-ζ functions for neutral atoms were used for carbon, oxygen, and nitrogen.[17] The 1s and 2s functions were curve fit to single ζ using the maximum-overlap criterion,[18] while being held orthogonal to one another. For the bromine the "best atom" functions of Clementi and Raimondi were used,[19] after the Schmidt orthogonalization, so that all one-center overlaps with core functions are zero. For hydrogen an exponent of 1.16 was used, which corresponds to the minimum energy exponent for methane.[20] For manganese the 1s–3d functions were taken from the results of Richardson, *et al.*[21] For the 3d case we used the function corresponding to the Mn^+ ($3d^6$) configuration. The 4s and 4p orbitals for manganese were constructed in a manner described previously by maximizing their overlap with the carbonyl carbon atom.[22]

Bond Distances and Angles.—The bond distances and angles for free methyl isocyanide are those determined from a rotational study by Costain.[23] Since it is useful to be able to transform the MO results for the complexed ligands into a single set of free ligand basis functions (*vide infra*), we have maintained the free ligand values for the ligand in the complex. Similarly, the free CO carbon–oxygen bond distance of 1.128 Å[24] was used for bound CO. This simplification is well justified since the bound ligand parameters in the present X-ray study are not significantly different from the free ligand values. One further simplification we have made is that we have set all C_{ax}–Mn–C_{eq} and Br–Mn–C_{eq} bond angles to 90°, since the deviations from this value that occur are small and the effect on the eigenvectors such deviations would cause is slight.[25] For the metal to equatorial carbonyl bond distance we chose the average of the two separate values, 1.83 Å. Likewise, for the two methyl isocyanides an average value of 1.97 Å was used. A preliminary calculation where we chose to use both reported equatorial carbonyl and methyl isocyanide values (±0.02 Å around the average value) showed very small differences in the orbital occupations and in no way affects the conclusions drawn from our reported calculation. The axial carbonyl was maintained at 1.79 Å from the manganese atom and the manganese to bromine distance was maintained at 2.537 Å.

Free Ligand Results.—In Table V we have tabulated the eigenvalues and per cent character for the highest occupied and lowest unoccupied molecular orbitals for both methyl isocyanide and carbonyl. For both ligands these two MO's are important in the metal–ligand bonding; the other orbitals are found to remain essentially unaffected when the ligand bonds. The carbonyl results have been presented previously[16] and are included here merely for comparison.

The methyl isocyanide and carbonyl ligands can form a σ bond to the metal atom by donating electron density from their highest occupied orbital, the 5σ for carbonyl and the 7 A_1 for methyl isocyanide. These orbitals correspond to the traditional "lone pair" orbitals of the respective ligands. However, while they do consist largely of s and p_σ orbitals at the carbon site used for bonding, they are not totally localized there, especially in the carbonyl case. In addition, both the carbonyl and methyl isocyanide free ligands are observed to have low-lying empty antibonding orbitals of π symmetry, the 2π and 3 E orbitals, respectively. Both of these orbitals have a large contribution from the p_π orbitals of the carbon site used for bonding to the metal and are suitable for overlap with occupied metal levels of π symmetry. Because of this favorable overlap and the low energetics of these orbitals, the 2π and 3 E orbitals of the ligands are available for accepting π electron density from the metal. This acceptance of electron density into unoccupied ligand orbitals comprises the familiar back-bonding property.

From the free ligand calculation, therefore, it is apparent that the methyl isocyanide ligands, as for the carbonyl case, possess orbitals of appropriate symmetry and energetics for bond formation *via* both donation from an occupied orbital of σ symmetry and back-acceptance into an empty antibonding orbital of π symmetry.

MO Results for $Mn(CO)_3(CNCH_3)_2Br$.—The orbital occupations for the methyl isocyanide and carbonyl

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orbitals used in bonding to the manganese are listed in Table VI. These occupations are listed in terms of the free ligand basis set. Hence, occupations less than two for the 5σ and 7 A_1 orbitals reflect the σ-donating ability of the ligands and occupations greater than zero for the 2π and 3 E orbitals reflect the amount of π back-bonding into these orbitals, which, of course, are empty in the free ligands. We have also listed the occupations of the 4p_π, 4p_σ, and 4s orbitals on bromine, as these are relevant to the discussion that follows.

TABLE VI

LIGAND ORBITAL MULLIKEN POPULATIONS IN $Mn(CO)_3(CNCH_3)_2Br$

	CO_{ax}	CO_{eq}	$CNCH_3$		Br
5σ	1.373	1.390		4s	1.977
2π	0.598	0.527		4p_σ	1.422
7 A_1			1.465	4p_π	3.992
3 E			0.267		

Discussion

The existence of π back-bonding for a ligand may be inferred by multiple-bond character in the metal to ligand bond, resulting in a shortening of that bond over the normal single-bond distance. One must, however, have available single-bond covalent radii of the atoms involved in the bond to determine this normal single-bond distance. Cotton has pointed out the difficulty that arises when one attempts to assign a covalent radius to the metal atom unless in the same molecule there is some other bond, M–X, that must be single.[26] In the present structure just such a single bond is present, the Mn–Br bond. If one takes the covalent radius of bromine to be Slater's value of 1.15 Å,[27] then the Mn–Br distance in the present structure, 2.537 Å, gives a covalent radius for Mn in this molecule of 1.39 Å. This is essentially identical with the manganese radius of 1.38 Å calculated for $Mn(CO)_5Cl$ by Greene and Bryan[12] and the estimated Mn(1+) atomic radius of 1.38 Å from the metal to ring bond distance in $(C_5H_5)Mn(CO)_3$.[28] Slater's value for the atomic radius of Mn, 1.40 Å, is seen to be very near our derived value, and thus our choice of 1.15 Å for the covalent radius of Br is consistent. The results of our molecular orbital calculation further substantiate the notion that the manganese to bromine bond involves no π character. Examination of Table VI shows that donation of electron density from bromine to the metal is essentially *via* the p_σ halogen orbitals with the p_π orbitals remaining filled. This is the same conclusion reached in a previous extensive molecular orbital study on the manganese pentacarbonyl halides.[25] Mn–Br bonds in $Mn(CO)_5Br$ (2.50 Å)[12] and in $[BrMn(CO)_4]_2$ (2.526 Å)[29] may be similarly interpreted as involving little, if any, π character.

Using the value of 1.39 Å, then, for the covalent radius of manganese and estimating the radius of sp-hybridized carbon as 0.70 Å, after Cotton,[26] give an Mn–C single bond distance of 2.09 Å. This value should probably represent a minimum for a single-bond distance since the σ orbitals in our free ligand molecular orbital calculations (see Table V) have more p character than "sp" hybridization warrants. The range of Mn–CO distances we report for $Mn(CO)_3(CNCH_3)_2Br$, 1.79–1.85 Å, represents a shortening of 0.24–0.30 Å over the single-bond distance, while for the methyl isocyanide ligands the corresponding values of 1.95–1.99 Å represent a shortening of 0.10–0.14 Å. Thus, the experimental bond shortenings observed suggest that methyl isocyanide is capable of accepting π-electron density from the metal, even in the presence of a stronger π acceptor such as carbonyl. The molecular orbital results of Table VI support this conclusion, with the 3 E occupation of the methyl isocyanide ligands being 0.267 electron. That carbonyl is a much stronger π acceptor than methyl isocyanide in this complex is reflected in its higher 2π occupation of 0.527 electron for the equatorial carbonyls and 0.598 electron for the axial carbon. The higher 2π occupation for the axial carbonyl results by virtue of the reduced competition for π-electron density with the bromine trans to it. This property is thoroughly discussed in the molecular orbital study of the manganese pentacarbonyl halides.[25]

A final feature of interest in the present structure is the striking similarity of the manganese to *methyl isocyanide* bond distances and the manganese to *cyanide* bond distances in related compounds. For example, compare the mean Mn–CN bond distances in $K_3Mn(CN)_6$, 2.00 (1) Å,[30] and in $K_3Mn(CN)_5NO \cdot 2H_2O$, 1.98 (2) Å,[31] to the values of 1.950 (12) and 1.992 (11) Å that we obtain for the $Mn-CNCH_3$ bond distance in $Mn(CO)_3(CNCH_3)_2Br$. Such an observation applies to the other compounds listed in Table IV as well. The reported values for the mean equatorial and axial Co–CN bond lengths in the $Co_2(CN)_{10}{}^{6-}$ dimer are 1.886 (5) and 1.961 (9) Å,[32] respectively, while the corresponding values in $Co_2(CNCH_3)_{10}{}^{4+}$ are 1.87 (3) and 1.92 (4) Å. The mean $Co-CNCH_3$ distance in $Co(CNCH_3)_5{}^+$ of 1.87 (2) Å can be compared with the mean value of 1.869 (13) Å in the $Co(CN)_6{}^{3-}$ anion.[33] For $Mo(CN)_4(CNCH_3)_4$ the reported Mo–CN distance is 2.17 (1) Å *vs.* the $Mo-CNCH_3$ distance of 2.14 (1) Å. With these data it appears that a metal to methyl isocyanide distance will be very near to the expected metal to cyanide bond distance, or only slightly shorter. Further structural studies would be needed to verify this prediction, but the similarity for the compounds cited above is worthy of note.

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