for the two molecules in this case were 2.167 (1) and 2.162 (1) Å, while that which we find here is 2.167 (2) Å. In the former, the average of the eight independent Mo–O distances (with the mean deviation) is 2.065 ± 0.010 Å, which may be compared to 2.061 (4) Å found here. Similarly, the S–O distances for coordinated oxygen atoms are 1.521 ± 0.003 Å formerly and 1.514 (4) Å in the present case, and those for the uncoordinated oxygen atoms are 1.442 ± 0.005 Å and 1.438 (6) Å, respectively.

Acknowledgment. We thank the National Science Foundation for financial support.

Registry No. $K_4[Mo_2(SO_4)_4]Cl \cdot 4H_2O$, 69429-51-2; $K_4Mo_2Cl_8$, 25448-39-9.

Supplementary Material Available: A table of observed and calculated structure factors (2 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) It should be remembered that a bond order of 3.5 also results from a $\sigma^2\pi^4\delta^2\delta^*$ configuration, the first example of this being the $Tc_2Cl_8^{3-}$ ion, whose structure,[1b] bonding,[1c] and electronic absorption spectrum[1d] are well-known. (b) Cotton, F. A.; Shive, L. W. *Inorg. Chem.* **1975**, *14*, 2032. (c) Cotton, F. A.; Kalbacher, B. J. *Ibid.* **1977**, *16*, 2386. (d) Cotton, F. A.; Fanwick, P. E.; Gage, L. D.; Kalbacher, B. J.; Martin, D. S. *J. Am. Chem. Soc.* **1977**, *99*, 5642.

(2) (a) Cotton, F. A.; Frenz, B. A.; Webb, T. R. *J. Am. Chem. Soc.* **1973**, *95*, 4431. (b) Cotton, F. A.; Frenz, B. A.; Pedersen, E.; Webb, T. R. *Inorg. Chem.* **1975**, *14*, 391.

(3) (a) Erwin, D. K.; Geoffroy, G. L.; Gray, H. B.; Hammond, G. S.; Solomon, E. I.; Trogler, W. E.; Zaggars, A. A. *J. Am. Chem. Soc.* **1977**, *99*, 3620. (b) Fanwick, P. E.; Martin, D. S., Jr.; Webb, T. R.; Robbins, G. A.; Newman, R. A. *Inorg. Chem.* **1978**, *17*, 2723.

(4) Lowenschuss, A.; Shamir, J.; Ardon, M. *Inorg. Chem.* **1976**, *15* 238.

(5) Block, T. F.; Fenske, R. F.; Lichtenberger, D. L.; Cotton, F. A. *J. Coord. Chem.* **1978**, *8* 109.

(6) Brencic, J. V.; Cotton, F. A. *Inorg. Chem.* **1969**, *8*, 7.

(7) Cotton, F. A.; Frenz, B. A.; Deganello, G.; Shaver, A. *J. Organomet. Chem.* **1973**, *50*, 227. Adams, R. D.; Collins, D. M.; Cotton, F. A. *J. Am. Chem. Soc.* **1974**, *96*, 749.

(8) All crystallographic computing was done on a PDP 11/45 computer at the Molecular Structure Corp., College Station, TX, with the Enraf-Nonius structure determination package.

Notes

Contribution from the IBM Research Laboratory, San Jose, California 95193

Structure of Thiotrithiazyl Tribromide $(S_4N_3^+)(Br_3^-)$: A Low Molecular Weight Sulfur–Nitrogen Compound Containing a Trihalide Counterion

J. J. Mayerle,* G. Wolmershäuser, and G. B. Street

Received September 15, 1978

The discovery of superconductivity in $(SN)_x$[1] and its brominated derivative $(SNBr_{0.4})_x$[2,3] has fostered a resurgence of interest in the chemistry of small S–N compounds and their reactions with halogens. Our efforts in this area have been twofold: to synthesize and characterize low molecular weight analogues of $(SN)_x$[4,5] and to unravel the complexities of the reaction of $(SN)_x$ precursors such as S_4N_4 with halogens. Recently it has been shown that the reaction of solid S_4N_4 with bromine *vapor* yields a brominated derivative of $(SN)_x$,[6,7] while reaction with *liquid* bromine yields the title compound, $(S_4N_3^+)(Br_3^-)$.[8] $(S_4N_3^+)(Br_3^-)$ is an interesting material for several reasons. In addition to being one of the few stable compounds containing the tribromide ion, it may be of importance because of the potential understanding its structure may shed on the unknown structure of $(SNBr_{0.4})_x$. Since brominated $(SN)_x$ does not lend itself to single-crystal X-ray diffraction studies, the question of what the major Br species are and their relationship to the $(SN)_x$ lattice have been attacked by such indirect methods as EXAFS, IR, and the like. In all of these methods some type of standard is necessary. $(S_4N_3^+)(Br_3^-)$ is one such excellent standard.

Experimental Section

The compound was prepared as previously described,[8] crystallizing in large clusters of fused single crystals. With considerable effort an irregularly shaped fragment of approximate dimensions 0.2 × 0.2 × 0.35 mm suitable for X-ray diffraction was found and mounted in a Lindemann glass capillary under an argon atmosphere. The crystal was transferred to an Enraf-Nonius CAD4 diffractometer where, subsequent to initial machine location and autoindexing of eight reflections, a preliminary unit cell and orientation matrix were computed. The least-squares refinement of the setting angles of 13 high-angle reflections ($2\theta \geq 30°$, graphite-monochromatized Mo $K\alpha_1$ radiation, λ 0.709 30 Å) then yielded the monoclinic cell dimensions $a = 6.105$ (2) Å, $b = 8.792$ (2) Å, $c = 18.060$ (4) Å, and $\beta = 91.58$ (1)°. There are four formula units per cell.

Data were collected by the θ–2θ scan method to $2\theta = 50°$. The scan range was calculated according to $\Delta\theta = (0.70 + 0.35 \tan \theta)°$ and was extended by 25% on each end for background measurement. The scan rate, based on a fast prescan, was computed such that 10^4 counts were to be obtained, if possible, in a maximum time of 90 s. An aperture 4 mm high and $(3.5 + 0.87 \tan \theta)$ mm wide was placed in front of the counter 173 mm from the crystal. The intensities of 3 standard reflections, measured after every 50 reflections, remained constant over the course of data collection.

The data were reduced as described previously,[9,10] with the value of ϵ in the expression for $\sigma(F_o^2)$ taken to be 0.04. An absorption correction ($\mu = 139.67$ cm^{-1}) was applied to the data, although the irregular shape of the crystal could only be grossly approximated. The values of the transmission coefficients ranged between 0.07 and 0.19. An analysis of the systematic absences ($0k0$, $k \neq 2n$; $h0l$, $l \neq 2n$) indicated the space group to be $P2_1/c$ (C_{2h}^5, No. 14).[11] The structure was solved by direct methods using MULTAN,[12] which revealed the positions of the Br atoms. Refinement and subsequent difference maps revealed the remaining atoms. Complete anisotropic refinement minimizing the function $\sum w(|F_o| - |F_c|)^2$ converged at $R = 0.065$ and $R_w = 0.074$, based on 91 variables and 1129 reflections for which $F_o^2 \geq 3\sigma(F_o^2)$. The weights were taken as $4F_o^2/\sigma^2(F_o^2)$. The error in an observation of unit weight was computed to be 2.48. In the last cycle no parameter changed by more than 0.002σ. The scattering factors were taken from ref 13. Corrections for the anomalous scattering[14] of Br and S were applied to the calculated structure factors. Final atomic positional and thermal parameters are compiled in Table I.

Results and Discussion

The atom numbering scheme for the $S_4N_3^+$ ring is shown

Table I. Positional (×10^4) and Thermal (×10^4) Parameters for $(S_4N_3^+)(Br_3^-)$[a]

atom	x	y	z	β_{11}[b]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br(1)	5230 (3)	4200 (3)	1461 (1)	195 (5)	116 (3)	30 (1)	−29 (3)	−16 (1)	6 (1)
Br(2)	2133 (3)	2080 (2)	1242 (1)	192 (5)	100 (2)	29 (1)	3 (3)	0 (1)	5 (1)
Br(3)	−714 (3)	176 (2)	1053 (1)	234 (6)	116 (3)	40 (1)	−43 (3)	0 (2)	−1 (1)
S(1)	4689 (6)	−1580 (5)	1847 (2)	158 (11)	115 (6)	25 (1)	−46 (7)	−10 (3)	2 (2)
S(2)	2023 (6)	−2617 (5)	2343 (2)	185 (12)	129 (7)	26 (1)	−42 (7)	2 (3)	1 (2)
S(3)	8 (7)	−4011 (5)	975 (2)	161 (12)	137 (7)	35 (2)	−50 (7)	−14 (3)	−7 (3)
S(4)	3725 (7)	−2564 (5)	284 (2)	229 (13)	146 (7)	23 (1)	−55 (8)	−3 (3)	1 (2)
N(1)	4753 (19)	−1883 (15)	999 (6)	144 (36)	137 (21)	23 (4)	−35 (23)	−21 (10)	8 (8)
N(2)	504 (20)	−3468 (15)	1768 (7)	172 (39)	131 (22)	30 (5)	−43 (24)	0 (11)	−4 (8)
N(3)	1569 (20)	−3531 (15)	350 (7)	189 (41)	131 (21)	30 (5)	−28 (24)	−22 (11)	−4 (8)

[a] Standard deviations in the least significant figure(s) are given in parentheses. [b] The form of the anisotropic thermal ellipsoids is given by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table II. Bond Lengths (Å) and Angles (deg)

Distances			
Br(1)-Br(2)	2.677 (2)	N(2)-S(3)	1.532 (13)
Br(3)-Br(2)	2.431 (2)	N(3)-S(3)	1.556 (14)
S(1)-S(2)	2.088 (5)	N(3)-S(4)	1.574 (13)
N(1)-S(1)	1.557 (12)	S(1)---Br(1)	3.130 (4)
N(1)-S(4)	1.541 (12)	S(2)---Br(1)	3.136 (4)
N(2)-S(2)	1.563 (13)		
Angles			
Br(1)-Br(2)-Br(3)	179 (1)	S(3)-N(3)-S(4)	137.0 (9)
N(1)-S(1)-S(2)	112.8 (5)	N(2)-S(3)-N(3)	119.0 (7)
S(4)-N(1)-S(1)	150.5 (9)	S(2)-N(2)-S(3)	150.2 (9)
N(3)-S(4)-N(1)	118.0 (7)	N(2)-S(2)-S(1)	112.3 (5)

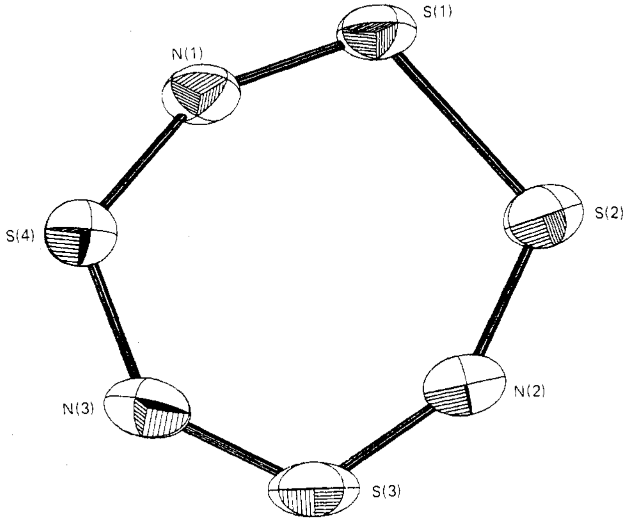


Figure 1. The thiotrithiazyl cation. The 50% probability ellipsoids are depicted.

in Figure 1, while bond lengths and angles are listed in Table II. A comparison of the data in Table II with that for $(S_4N_3^+)(NO_3^-)$ shows the geometry of the rings to be essentially the same for the two compounds, except for the S–S bond length of 2.088 (5) Å, which is slightly longer than the value of 2.070 (1) Å found for the nitrate salt.[15] The $S_4N_3^+$ ring is planar to within 0.017 Å. The bond lengths of the asymmetric Br_3^- ion are 2.431 (2) and 2.677 (2) Å. The degree of asymmetry of the anion, intermediate between that of the symmetric Br_3^- found in $[(CH_3)_3NH^+]_2Br^-Br_3^-$[16] and the extremely distorted Br_3^- in PBr_7,[17] is about the same as is found in $CsBr_3$.[18] The terminal Br atom, Br(1), involved in the longer of the two Br–Br bonds approaches the cation to within 3.13 Å, ~0.2 Å closer than does the other terminal Br, Br(3). It is generally the case with asymmetric trihalides that the terminal atom involved in the longest bond is most closely surrounded by cations.

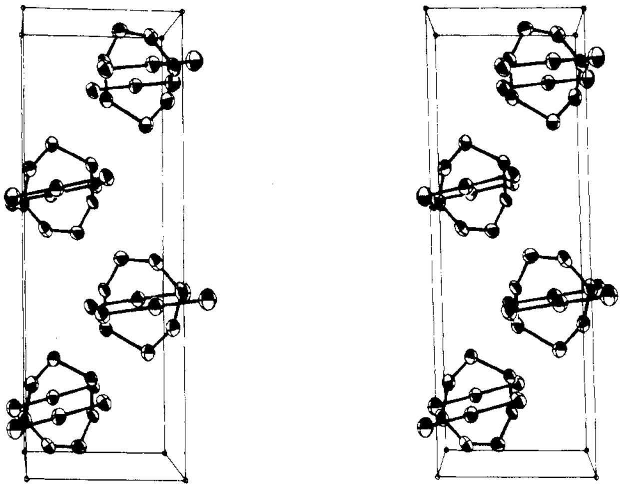


Figure 2. Stereoscopic view of the crystal packing. The origin of the cell is at the lower left front corner. The *a* axis runs horizontally from left to right, and *c*, vertically from bottom to top. The *b* axis completes the right-handed coordinate system.

The packing of cations and anions within the unit cell is represented stereoscopically in Figure 2. The dominant motif is one of stacks consisting of alternating cations and anions arrayed along *b*. The Br_3^- ion is slightly canted with respect to the rings between which it is sandwiched, making an angle of ~10° from the parallel. Furthermore, the Br_3^- ion does not lie equidistantly between the rings but is ~0.1 Å closer to one than the other. The mean spacings are 3.60 and 3.69 Å.

An important and perhaps the most interesting aspect of the structure is the relationship between Br_3^- ions in one stack with $S_4N_3^+$ rings in adjacent stacks and what this interaction portends for $(SNBr_{0.4})_x$. In particular, one of the terminal atoms, Br(1), of a Br_3^- ion in one stack approaches approximately equidistantly the two S atoms involved in the S–S bond of an $S_4N_3^+$ ring in an adjacent stack to within the relatively short distance of 3.13 Å, 0.68 Å less than the sum of the appropriate van der Waals radii. This distance expressed as a fraction of the sum of the van der Waals radii is 0.82, a value identical with the corresponding fraction determined for the S---O distance in $(S_4N_3^+)(NO_3^-)$[15] and is considered to mean a very short nonbonded distance. Furthermore, the terminal bromine atom in question lies within 0.1 Å of the plane of the $S_4N_3^+$ ring involved. Thus, this three-center interaction is similar to that found between one of the nitrate oxygen atoms and the –S–S– grouping in $(S_4N_3^+)(NO_3^-)$[15] and is consistent with the scheme of charge-transfer interactions proposed by Hordvik[19] and by Rosenfield et al.[20] to account for the geometric trends found for the interaction of divalent sulfur with electrophiles and nucleophiles in the solid state. Note also that, although nucleophilic Br(1) lies in the plane of the $S_4N_3^+$ ring, the Br_3^- itself is aligned slightly off the perpendicular to the plane, such that one of Br(1)'s lone pairs points approximately toward the disulfide group, thereby maximizing the charge-transfer interaction between the tribromide and disulfide moieties.

The structure provides some insight into the arrangement of Br_3^- in $(SNBr_{0.4})_x$. One of the terminal Br's would be expected to lie *in* the plane ($\bar{1}02$) of the $(SN)_x$ chain so as to maximize the type of interaction described in this paper. The orientation of the Br_3^- ion as a whole could then be either parallel or perpendicular to the chain. In either case, a nonbonded pair of the first Br would be directed at S. If the former (parallel) orientation were taken, this would allow both terminal Br atoms to interact with sulfur. Indeed, both electron diffraction[2] and spectroscopic[21] data suggest that whatever Br_3^- is present in $(SNBr_{0.4})_x$ (the question of the quantities of the various Br-containing species has not yet been resolved) is aligned parallel to *b*. This scheme not only provides a reason for that but would also predict that the Br_3^- is *in* the plane of the $(SN)_x$, not *between* the planes as would be required in a simpler intercalative model. In the absence of detailed knowledge of the MO picture of $(SN)_x$, this is, of course, speculative.

Registry No. $(S_4N_3^+)(Br_3^-)$, 67145-67-9.

Supplementary Material Available: A listing of structure factor amplitudes (9 pages). Ordering information is given on any current masthead page.

References and Notes

(1) R. L. Greene, G. B. Street, and L. J. Suter, *Phys. Rev. Lett.*, **34**, 577 (1975).
(2) G. B. Street, W. D. Gill, R. H. Geiss, R. L. Greene, and J. J. Mayerle, *J. Chem. Soc., Chem. Commun.*, 407 (1977).
(3) W. D. Gill, W. Bludau, R. H. Geiss, P. M. Grant, R. L. Greene, J. J. Mayerle, and G. B. Street, *Phys. Rev. Lett.*, **38**, 1305 (1978).
(4) J. Kuyper and G. B. Street, *J. Am. Chem. Soc.*, **99**, 7848 (1977).
(5) J. J. Mayerle, J. Kuyper, and G. B. Street, *Inorg. Chem.*, **17**, 2610 (1978).
(6) G. B. Street, R. L. Bingham, J. I. Crowley, and J. Kuyper, *J. Chem. Soc., Chem. Commun.*, 464 (1977).
(7) M. Akhtar, C. K. Chiang, A. J. Heeger, J. Milliken, and A. G. MacDiarmid, *Inorg. Chem.*, **17**, 1539 (1978).
(8) G. Wolmershäuser and G. B. Street, *Inorg. Chem.*, **17**, 2685 (1978).
(9) J. J. Mayerle, *Inorg. Chem.*, **16**, 916 (1977).
(10) The computer programs used were those mentioned in ref 9.
(11) "International Tables for X-Ray Crystallography", Vol. I, 3rd ed., Kynoch Press, Birmingham, England, 1969, p 99.
(12) G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. A*, **27**, 368 (1971).
(13) D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974, Table 2.2A.
(14) D. T. Cromer, "International Tables for X-Ray Crystallography", Vol. IV, Birmingham, England, 1974, Table 2.3.1.
(15) T. N. Guru Row and P. Coppens, *Inorg. Chem.*, **17**, 1670 (1978).
(16) C. Romers and E. W. M. Keulemans, *Proc. K. Ned. Akad. Wet., Ser. B*, **61**, 345 (1958), as quoted in ref 18.
(17) G. L. Breneman and R. D. Willett, *Acta Crystallogr.*, **23**, 467 (1967).
(18) G. L. Breneman and R. D. Willett, *Acta Crystallogr., Sect. B*, **25**, 1073 (1969).
(19) A. Hordvik, *Q. Rep. Sulfur Chem.*, **5**, 21 (1970).
(20) R. E. Rosenfield, Jr., R. Parthasarathy, and J. D. Dunitz, *J. Am. Chem. Soc.*, **99**, 4860 (1977).
(21) J. Macklin and G. B. Street, to be submitted for publication.

Contribution from the Department of Chemistry,
University of California, Los Angeles, California 90024

Simplified in Situ Syntheses of Anhydrous $HMn(CO)_5$

J. A. Gladysz,* Wilson Tam, G. M. Williams,
Dennis Lee Johnson, and David W. Parker

Received March 21, 1978

Hydride complexes of transition metals have played a critical role in the development of organometallic chemistry.[1,2] They are key intermediates in numerous stoichiometric and catalytic reactions and have been the object of a variety of structural,[3] spectroscopic, and theoretical studies.[1,2] A wide spectrum of methods has been utilized for their syntheses.[1,2]

One of the most extensively studied transition-metal hydrides has been $HMn(CO)_5$. Its physical properties have been examined in detail.[3-6] A number of novel and important manganese complexes have been synthesized from $HMn(CO)_5$,[7-12] and $HMn(CO)_5$ can be used to reduce organic compounds such as olefins and alkyl halides.[13]

In connection with several ongoing research projects, we required large amounts of anhydrous $HMn(CO)_5$ in THF. A literature survey revealed that most researchers employ the method of King.[14] This procedure is operationally cumbersome and requires (a) the generation of $Na[Mn(CO)_5]$ from $Mn_2(CO)_{10}$ and Na/Hg, (b) removal of mercury and solvent, (c) treatment of the $Na[Mn(CO)_5]$ residue with aqueous H_3PO_4, and (d) extensive vacuum line manipulations to separate H_2O and byproducts. A synthesis of $HMn(CO)_5$ from $Mn_2(CO)_{10}$ and H_2/CO (250 atm) at 200 °C has also been detailed.[15]

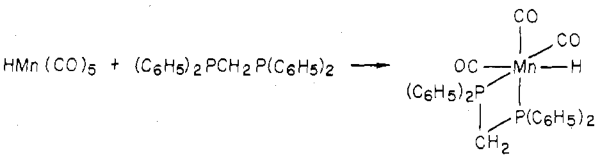
We report in this note the development of three rapid, convenient procedures for the in situ preparation of anhydrous $HMn(CO)_5$ in THF. They are complementary in terms of advantages and have been extensively used in our research group.

Results

Procedure A: $HMn(CO)_5$ from $Mn_2(CO)_{10}$. We recently described[16] a one-flask synthesis of $Li[Mn(CO)_5]$ from $Mn_2(CO)_{10}$ and $Li(C_2H_5)_3BH$[17] in THF. The formation of $Li[Mn(CO)_5]$ was found to be complete within a few minutes at room temperature. The only byproducts produced are H_2 and $(C_2H_5)_3B$, both of which are volatile. Consequently, it was of interest to determine if $HMn(CO)_5$ could be formed by protonation of $Li[Mn(CO)_5]$ in situ. For this purpose, an acid which was nonaqueous, nonoxidizing, and convenient to handle was sought. Trifluoromethanesulfonic acid (CF_3SO_3H)[18] was selected as meeting these criteria. Protonation of $Li[Mn(CO)_5]$ solutions, prepared as previously described,[16] with 1.1–1.2 equiv of CF_3SO_3H afforded $HMn(CO)_5$ in quantitative yield by IR (eq 1).

$$\begin{aligned} &\mathrm{Li(C_2H_5)_3BH + {}^1/_2Mn_2(CO)_{10} \rightarrow Li[Mn(CO)_5] + {}^1/_2H_2 + (C_2H_5)_3B} \\ &\qquad\qquad\qquad\qquad\qquad\quad \downarrow \mathrm{CF_3SO_3H} \\ &\qquad\qquad\qquad\qquad\qquad\quad \mathrm{HMn(CO)_5 + Li^+CF_3SO_3^-} \end{aligned} \qquad (1)$$

The $HMn(CO)_5$ solutions prepared according to eq 1 were chemically characterized by reactions with $(C_6H_5)_2PCH_2P(C_6H_5)_2$, $Li(C_2H_5)_3BH$, and $(CO)_5Mn(COC_6H_5)$, as depicted in eq 2–4. Thus three types of characteristic $HMn(CO)_5$ reactions (substitution, deprotonation, and substrate reduction) could be achieved in high yield in situ.



(2)

1

$$\mathrm{HMn(CO)_5 + Li(C_2H_5)_3BH \rightarrow Li[Mn(CO)_5] + (C_2H_5)_3B + H_2} \qquad (3)$$

$$\mathrm{HMn(CO)_5 + (CO)_5MnC({=}O)C_6H_5 \rightarrow HC({=}O)C_6H_5 + Mn_2(CO)_{10}} \qquad (4)$$

The synthesis of $HMn(CO)_5$ by procedure A yields $(C_2H_5)_3B$ and $Li^+CF_3SO_3^-$ as byproducts. For most preparative reactions utilizing $HMn(CO)_5$, these do not interfere. However, solvent and $HMn(CO)_5$ concentration may in some cases play important roles. For instance, acetylene hy-

0020-1669/79/1318-1163$01.00/0 © 1979 American Chemical Society