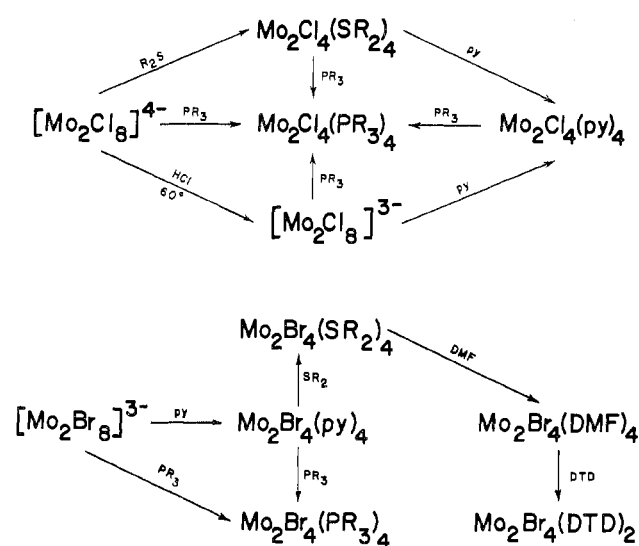


Scheme I. Some Reactions of Tetra- and Octahalodimolybdenum Complexes



ways involved? To what degree do electronic and steric factors manifested in ligands coordinated to the same molybdenum center affect substitution and other processes at the adjacent metal center? These and related questions now

under investigation will be discussed more fully in forthcoming papers.

Finally, we have observed that the  $[\text{Mo}_2\text{X}_8]^{3-}$  ion can be reduced to  $\text{Mo}_2\text{X}_4\text{L}_4$  by excess pyridine or tri-*n*-butylphosphine to produce the respective complexes of tetrahalodimolybdenum(II). The reaction, which may proceed with retention of the metal-metal bond, provides a convenient and at present the only procedure for preparing derivatives of tetrabromodimolybdenum(II) compounds. These and some related chemical relationships are summarized in Scheme I.

**Acknowledgments.** We are grateful to Professor R. A. Walton for communicating the results of related investigations prior to publication and to Professor M. Francia of Barnard College for helpful discussions.

**Registry No.**  $\text{Cs}_3\text{Mo}_2\text{Br}_8$ , 39469-89-1;  $\text{Mo}_2\text{Cl}_4[\text{S}(\text{C}_2\text{H}_5)_2]_4$ , 51731-32-9;  $\text{Mo}_2\text{Cl}_4[\text{S}(\text{CH}_3)_2]_4$ , 51731-33-0;  $\text{Mo}_2\text{Cl}_4(\text{DTH})_2$ , 51731-34-1;  $\text{Mo}_2\text{Cl}_4(\text{DTD})_2$ , 51731-35-2;  $\text{Mo}_2\text{Cl}_4(\text{DTDD})_2$ , 51731-36-3;  $\text{Mo}_2\text{Cl}_4(\text{S}_2\text{C}_2\text{H}_8)_2$ , 51731-38-5;  $\text{Mo}_2\text{Cl}_4(\text{C}_6\text{H}_5\text{N})_4$ , 51752-03-5;  $\text{Mo}_2\text{Cl}_4(\text{bipy})_2$ , 51731-39-6;  $\text{Mo}_2\text{Br}_4(\text{C}_6\text{H}_5\text{N})_4$ , 51731-40-9;  $\text{Mo}_2\text{Br}_4[\text{S}(\text{CH}_3)_2]_4$ , 51731-41-0;  $\text{Mo}_2\text{Br}_4(\text{DTD})_2$ , 51731-42-1;  $\text{Mo}_2\text{Br}_4(\text{bipy})_2$ , 51731-43-2;  $\text{Mo}_2\text{Br}_4[\text{P}(\text{n-C}_4\text{H}_9)_3]_4$ , 51731-44-3;  $\text{Mo}_2\text{Cl}_4(\text{TMEDP})_2$ , 51731-45-4;  $\text{Mo}_2\text{Cl}_4(\text{NCCCH}_3)_4$ , 51731-46-5;  $\text{Mo}_2\text{Cl}_4(\text{NCC}_6\text{H}_5)_4$ , 51731-47-6;  $\text{Mo}_2\text{Cl}_4(\text{DMF})_4$ , 51731-48-7;  $\text{Mo}_2\text{Br}_4(\text{DMF})_4$ , 51731-49-8;  $\text{Mo}_2\text{Cl}_4[\text{P}(\text{n-C}_4\text{H}_9)_3]_4$ , 38832-72-3;  $\text{Mo}_2\text{Cl}_4[\text{P}(\text{OCH}_3)_3]_4$ , 38832-74-5;  $(\text{NH}_4)_3\text{Mo}_2\text{Cl}_9 \cdot \text{H}_2\text{O}$ , 51794-31-1; 2,2'-bipyridine, 366-18-7; pyridine, 110-86-1; acetonitrile, 75-05-8; DMF, 68-12-2;  $\text{Cs}_3\text{Mo}_2\text{Cl}_8$ , 51795-65-4.

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## A Nuclear Magnetic Resonance Study of the Conformations of Six-Membered Chelate Rings in Manganese Carbonyl Halide Complexes of Di(tertiary arsines)

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The complexes  $\text{XMn}(\text{CO})_3\text{As}(\text{CH}_3)_2\text{CH}_2\text{CHRCH}_2\text{As}(\text{CH}_3)_2$  ( $\text{R} = \text{H}, \text{C}(\text{CH}_3)_3$ ;  $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) which contain six-membered chelate rings were prepared and their nmr spectra investigated. Selectively deuterated analogs were prepared in order to solve the spectra. The locked-chair configuration found when  $\text{R} = \text{H}$  shows the least interaction between the axial methyl group of the arsenic atoms and the axial halogen atom. When  $\text{R} = \text{C}(\text{CH}_3)_3$ , two isomers were observed for each complex; both have rings with locked-chair configurations and R equatorial. The more stable isomer has the same configuration as a complex with  $\text{R} = \text{H}$  except the *tert*-butyl group is in an equatorial position.

### Introduction

The stereochemistry of metal complexes that contain six-membered rings has been of recent interest.<sup>2-16</sup> In contrast

to five-membered ring systems which have a number of equal-energy conformers,<sup>3-17</sup> theoretical<sup>18</sup> and X-ray<sup>8,12,14,16</sup> studies of six-membered ring systems, containing an octahedral site, indicate the symmetrical chair conformer (a) (Figure 1) is favored over the symmetrical boat (b) or skew-boat conformers (c).

In an earlier publication<sup>2</sup> we discussed the nmr spectra of chromium, molybdenum, and tungsten tetracarbonyl com-

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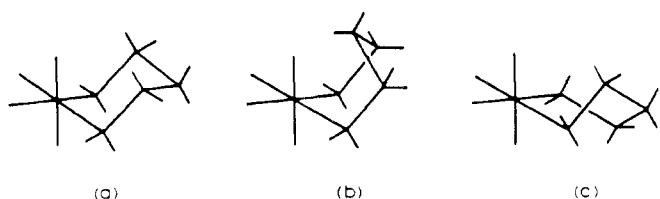


Figure 1. Chair (a), boat (b), and skew boat (c) conformations of a six-membered chelate ring.

plexes prepared from di(tertiary arsine) ligands of the type  $(\text{CH}_3)_2\text{AsCH}_2\text{CHRCH}_2\text{As}(\text{CH}_3)_2$  ( $\text{R} = \text{H}$ , **1**;  $\text{R} = \text{CH}_3$ , **2**;  $\text{R} = \text{C}(\text{CH}_3)_3$ , **3**).

The nmr parameters, not unexpectedly, indicated these six-membered ring complexes are chair conformers in solution. In complexes of ligand **1**, the rings undergo fast conformational inversion between the symmetric chair forms, while in complexes of **3** the rings are locked in a chair conformer with the *tert*-butyl group in an equatorial position.

The present work extends our nmr and conformational study to manganese tricarbonyl halide ( $\text{Cl}$ ,  $\text{Br}$ ,  $\text{I}$ ) complexes prepared from ligands **1** and **3**. The partially and selectively deuterated ligands  $(\text{CH}_3)_2\text{AsCH}_2\text{CDRCH}_2\text{As}(\text{CH}_3)_2$  ( $\text{R} = \text{H}$ , **1-d**<sub>1</sub>;  $\text{R} = \text{C}(\text{CH}_3)_3$ , **3-d**<sub>1</sub>),  $(\text{CH}_3)_2\text{AsCH}_2\text{CHRCD}_2\text{As}(\text{CH}_3)_2$  ( $\text{R} = \text{H}$ , **1-d**<sub>2</sub>;  $\text{R} = \text{C}(\text{CH}_3)_3$ , **3-d**<sub>2</sub>), and  $(\text{CH}_3)_2\text{AsCD}_2\text{CHRCD}_2\text{As}(\text{CH}_3)_2$  ( $\text{R} = \text{H}$ , **1-d**<sub>4</sub>;  $\text{R} = \text{C}(\text{CH}_3)_3$ , **3-d**<sub>4</sub>) were employed to solve the nmr spectra because satisfactory solutions could not be obtained for the five- and six-spin proton systems.

### Experimental Section

**Deuterated Diols.** The diols  $\text{HOCD}_2\text{CH}_2\text{CH}_2\text{OH}$  and  $\text{HOCD}_2\text{CH}_2\text{CD}_2\text{OH}$  were prepared according to the method of Campbell and Hall.<sup>19</sup> The preparation of  $\text{HOCD}_2\text{CH}(\text{C}(\text{CH}_3)_3)\text{CH}_2\text{OH}$  was previously reported in detail.<sup>2</sup>

(a) **1,1,3,3-Tetradeuterio-2-*tert*-butyl-1,3-propanediol.** Diethyl *tert*-butylmalonate<sup>20</sup> (10 g), dissolved in dry tetrahydrofuran (30 ml), was dropped onto a stirred heterogeneous mixture of lithium aluminum deuteride (1.8 g) and tetrahydrofuran (30 ml) at 0°. After refluxing (3 hr), the mixture was cooled and slowly hydrolyzed by the addition of water (1.8 ml), 15% sodium hydroxide solution (1.8 ml), and then additional water (5.4 g). The solution was filtered, dried over anhydrous sodium sulfate, filtered again, and then evaporated to give an oily product. Large transparent crystals (mp 56–58°) were obtained upon crystallization from ether-*n*-pentane.

(b) **2-Deuterio-2-*tert*-butylpropanediol.** This diol was prepared by the reduction of diethyl 2-deuterio-*tert*-butylmalonate<sup>21</sup> with lithium aluminum hydride according to published procedures.<sup>22</sup>

**Ligands.** The preparation of some of the di(tertiary arsine) ligands has been previously described<sup>2</sup> and the remainder were prepared by similar methods starting with the appropriately substituted 1,3-propanediols. The ligands prepared by this route include **1**, **1-d**<sub>2</sub>, **1-d**<sub>4</sub>, **3**, **3-d**<sub>1</sub>, **3-d**<sub>2</sub>, and **3-d**<sub>4</sub>.

**The Complexes  $\text{XMn}(\text{CO})_3\text{As}(\text{CH}_3)_2\text{CH}_2\text{CHRCH}_2\text{As}(\text{CH}_3)_2$ , ( $\text{X} = \text{Cl}$ ,  $\text{Br}$ ,  $\text{I}$ ;  $\text{R} = \text{H}$ ,  $\text{C}(\text{CH}_3)_3$ ).** Equimolar quantities of  $\text{Mn}(\text{CO})_5\text{X}^{23}$  and di(tertiary arsine) were heated (70°) in dry benzene until the infrared spectrum (cyclohexane) indicated all the pentacarbonyl complex had reacted ( $\text{Cl}$ , ~15 min;  $\text{Br}$ , ~30 min;  $\text{I}$ , ~45 min). The solution was evaporated to dryness and the residue crystallized from a dry benzene-heptane mixture (7°). The nmr spectrum of the complexes of **3** indicated the products contained two isomers, A and B. The ratio of isomer A to isomer B was 3:2 for  $\text{Cl}$  and  $\text{Br}$ ; and 4:1 for  $\text{I}$ . The isomers could not be separated by chromatography using an alumina column or by crystallization. Heating the mixture to 100°

in benzene (sealed nmr tube) increased the ratio of A to B to approximately 9:1. (Sublimation at 140° (0.01 mm) gave a mixture containing approximately 90% of isomer A.)

The nmr spectra of complexes of **1** indicated that only one isomer was present. These complexes were purified by crystallization followed by sublimation.

Complexes of deuterated ligands were prepared by similar routes.

**Instrumentation.** Melting points were determined using a Gallenkamp melting point apparatus and are uncorrected. The infrared spectra were recorded on a Perkin-Elmer 457 spectrometer (cyclohexane solvent) and calibrated using polystyrene film. The nmr spectra were measured in  $\text{CDCl}_3$  solution with 20% by volume TMS on an extensively modified Varian HA-100 instrument.<sup>24</sup> Chemical shifts are reported in ppm downfield from TMS; coupling constants are in Hz. The refined nmr parameters were obtained using the iterative LAOCOON III program modified for use on the University of British Columbia IBM 360-67 computer.

Microanalyses were made by Mr. Peter Borda of this department.

### Results

Analytical data, melting points, and carbonyl stretching frequencies for the metal chelate complexes are reported in Table I.

The  $\nu_{\text{CO}}$  frequencies and their intensity pattern indicate a *cis* geometry of the ligands about the manganese atom.<sup>25</sup> They are essentially independent of the diarsine ligand substituent and therefore of little use in determining ring conformations in solution.

**Nmr Spectra of the Di(tertiary arsine)-Manganese Complexes.**  $\text{XMn}(\text{CO})_3\text{As}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CH}_2\text{As}(\text{CH}_3)_2$ . The nmr spectra of these complexes exhibit two sharp signals (1:1) assigned to the arsenic methyl protons. The spectra also exhibit multiplets attributed to the six-spin propane fragment but were too difficult to solve. As a result, complexes of **1-d**<sub>2</sub> and **1-d**<sub>4</sub> were required to obtain the nmr parameters.

$\text{XMn}(\text{CO})_3\text{As}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CD}_2\text{As}(\text{CH}_3)_2$ . The nmr spectra of these complexes showed the arsenic methyl protons had the same chemical shift as complexes of the fully protonated ligand.

The nmr spectrum of the propane fragment of the iodide complex is shown in Figure 2. Deuterium decoupling sharpened and introduced signals in both the right and left portions of the spectrum. These signals were attributed to the protons on the central methylene carbon because of their proximity to the deuterium atoms. The remaining signals were attributed to the protons on the methylene group adjacent to the arsenic atom. With this information and a knowledge of the approximate values expected for the geminal coupling constants the spectrum was eventually solved as an ABCD system. The nmr parameters are listed in Table II. Protons 1 and 2 are located on a methylene carbon atom adjacent to an arsenic atom while protons 2 and 4 are on the central methylene carbon atom.<sup>26</sup> The nmr spectra of  $\text{Mn}(\text{CO})_3\text{Cl}$  and  $\text{Mn}(\text{CO})_3\text{Br}$  complexes of **1-d**<sub>2</sub> were solved in a similar manner and found to be ABCD systems. Parameters are also listed in Table II.

The axial position of the halide atom at the metal requires that all hydrogen atoms of the  $-\text{CH}_2\text{CH}_2\text{CD}_2-$  fragment be different (ABCD) systems with or without conformational inversion of the six-membered ring. The magnitude of  $J_{13}$ , however, indicates protons 1 and 3 are involved in a vicinal axial-axial interaction which requires the ring to be effectively locked in a boat, skew-boat, or chair conformation. The skew-boat conformers for the manganese tricarbonyl halide

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Table I. Analytical Data and Carbonyl Infrared Spectra of New Complexes

Compd	Chem anal		Ir, cm <sup>-1</sup>	Mp, °C	
	% calcd	% found			
ClMn(CO) <sub>3</sub> As(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> As(CH <sub>3</sub> ) <sub>2</sub>	C	28.2	28.4	2027, 1959, 1914	146-148
	H	4.2	4.2		
BrMn(CO) <sub>3</sub> As(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> As(CH <sub>3</sub> ) <sub>2</sub>	C	25.5	25.6	2026, 1959, 1916	169-172
	H	3.9	4.1		
IMn(CO) <sub>3</sub> As(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> As(CH <sub>3</sub> ) <sub>2</sub>	C	23.2	23.3	2023, 1958, 1915	223-125
	H	3.5	3.5		
ClMn(CO) <sub>3</sub> As(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> CH(C(CH <sub>3</sub> ) <sub>3</sub> )CH <sub>2</sub> As(CH <sub>3</sub> ) <sub>2</sub>	C	34.7	34.4	2029, 1959, 1913	182-184
	H	5.4	5.5		
BrMn(CO) <sub>3</sub> As(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> CH(C(CH <sub>3</sub> ) <sub>3</sub> )CH <sub>2</sub> As(CH <sub>3</sub> ) <sub>2</sub>	C	31.9	31.7	2023, 1957, 1913	126-128
	H	5.0	5.1		
IMn(CO) <sub>3</sub> As(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> CH(C(CH <sub>3</sub> ) <sub>3</sub> )CH <sub>2</sub> As(CH <sub>3</sub> ) <sub>2</sub>	C	29.3	29.0	2023, 1955, 1915	171-173
	H	4.6	4.9		

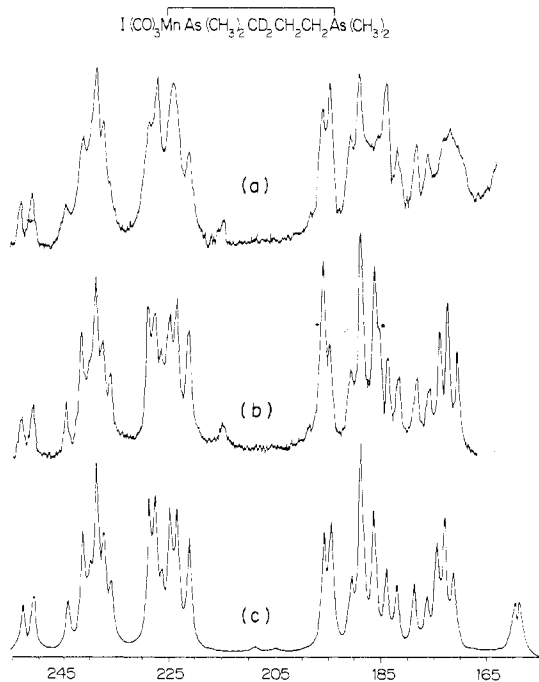


Figure 2. Nmr spectrum of the propane bridge in  $I(CO)_3MnAs(CH_3)_2-CH_2CH_2CD_2As(CH_3)_2$ : (a) raw spectrum; (b) deuterium-decoupled spectrum; (c) computer-simulated spectrum; asterisk, spinning side band.

derivatives of **1** can be eliminated because they have lower symmetry ( $C_1$ ) than the boat ( $C_2$ ) or chair ( $C_3$ ) conformers and should show four arsenic methyl signals rather than the two signals observed. Skew-boat conformers of the **1-d<sub>2</sub>** derivatives should also exhibit an nmr spectrum which represents two ABCD spin systems for the propane fragment of the ring.

Lambert<sup>27</sup> and Buys<sup>28,29</sup> have developed a method whereby the ring dihedral angle  $\psi$ , for carbocyclic six-membered rings, may be calculated from the vicinal proton-proton coupling using the equation

$$R = \frac{J_{trans}}{J_{cis}} = \frac{J_{ax,ax} + J_{eq,eq}}{J_{ax,eq} + J_{eq,ax}} = \frac{3 - 2 \cos^2 \psi}{4 \cos^2 \psi}$$

Ideal chair conformers are expected to have  $1.9 \leq R \leq 2.2$ , "puckered" chairs values of  $R > 2.5$ , and "flattened" chairs or flexible boat forms  $R < 1.8$ . All the manganese halide derivatives have  $R > 4$  indicating the chelate rings are locked in puckered chair conformers in solution. The ring dihedral

angles (As-C-C-C) were calculated to be 67-68° for these complexes.

#### $XMn(CO)_3As(CH_3)_2CH_2CH(C(CH_3)_3)CH_2As(CH_3)_2$ .

The nmr spectra of these complexes exhibit two *tert*-butyl signals and four arsenic methyl signals suggesting the presence of either two isomers or two conformers in solution. The chemical shifts are listed in Table II. The nmr spectra of the  $-CH_2CHRCH_2-$  fragments were very complicated and difficult to solve. As a result the **3-d<sub>1</sub>**, **3-d<sub>2</sub>**, and **3-d<sub>4</sub>** ligands and their complexes were prepared in order to simplify the proton spectra. In principle the complexes of **3-d<sub>2</sub>** are most valuable because all the nmr parameters desired can be obtained from the spectra of these systems. However, in some cases even these spectra could not be solved directly and complexes of **3-d<sub>1</sub>** and **3-d<sub>4</sub>** were required to obtain some of the parameters.

$XMn(CO)_3As(CH_3)_2CH_2CH(C(CH_3)_3)CD_2As(CH_3)_2$ . The nmr signals of the *tert*-butyl and arsenic methyl groups for these complexes are similar to those of the fully protonated complexes, again suggesting the complex has two structures. The nmr spectra of the propane fragments were difficult to solve because of overlapping spectra. This difficulty was overcome because a conversion to a preponderance of one structure (isomer A) was possible by heating the mixture.

**A Isomers.** The nmr spectrum of  $ClMn(CO)_3As(CH_3)_2-CH_2CH(C(CH_3)_3)CD_2As(CH_3)_2$  (Figure 3) is representative of this series. The propane fragment of these isomers gave ABX spectra that were readily solved. The AB portion of a spectrum corresponds to the geminal protons while the X portion of a spectrum is at higher field and represents the  $-CH(C(CH_3)_3)$  proton.<sup>30</sup> These spectra are examples of a deceptively simple case and therefore have a large probability for error in the values assigned to  $J_{13}$  and  $J_{23}$ .<sup>31</sup> The coupling constants, however, are in agreement with the values expected for six-membered rings having chair configurations.

**B Isomers.** These isomers which could not be separated from the more thermally stable isomers made up only 40% of the mixture found for the chloro and bromo compounds and 20% of the iodo complexes. It was difficult to assign nmr signals to isomer B even with a knowledge of the spectrum of isomer A. The nmr parameters for  $BrMn(CO)_3-As(CH_3)_2CH_2CH(C(CH_3)_3)CD_2As(CH_3)_2$  were eventually obtained with the aid of the solutions to the spectra of complexes of **3-d<sub>1</sub>** and **3-d<sub>4</sub>**. The spectrum of the bromo complex was an  $A'MX'$  system. The manganese chloride mixture has the M and X' parts of the spectrum of isomer B overlapped by the AB and X bands of isomer A. The A'

(30) The geminal protons in analogous group VIb metal complexes had quite different chemical shifts.<sup>2</sup>

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Table II. Nmr Data for New Complexes

Compd	$\delta_1$	$\delta_2$	$\delta_3$	$\delta_4$	$\delta(\text{As-CH}_3)$	$\delta(\text{C}(\text{CH}_3)_3)$	$J_{12}$	$J_{13}$	$J_{14}$	$J_{23}$	$J_{24}$	$J_{34}$
$\text{ClMn}(\text{CO})_3\text{As}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CD}_2\text{As}(\text{CH}_3)_2$	2.160	1.711	1.786	2.267	1.444	1.479	-12.6	13.4	2.2	2.2	6.4	-15.8
$\text{BrMn}(\text{CO})_3\text{As}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CD}_2\text{As}(\text{CH}_3)_2$	2.244	1.769	1.771	2.290	1.456	1.515	-12.3	13.4	2.6	2.0	6.0	-15.4
$\text{IMn}(\text{CO})_3\text{As}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CD}_2\text{As}(\text{CH}_3)_2$	2.373	1.867	1.741	2.311	1.477	1.586	-12.7	13.6	2.8	1.9	5.9	-15.5
$\text{IMn}(\text{CO})_3\text{As}(\text{CH}_3)_2\text{CD}_2\text{CH}_2\text{CD}_2\text{As}(\text{CH}_3)_2$		1.731	1.731	2.279								
Isomers A of 3												
$\text{ClMn}(\text{CO})_3\text{As}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{C}(\text{CH}_3)_3)\text{CD}_2\text{As}(\text{CH}_3)_2$	1.793	1.857	1.271 <sup>a</sup>		1.401	1.514	-12.4	12.6	0.7	0.7		
$\text{BrMn}(\text{CO})_3\text{As}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{C}(\text{CH}_3)_3)\text{CD}_2\text{As}(\text{CH}_3)_2$	1.863	1.913	1.246 <sup>a</sup>		1.416	1.554	-12.4	11.0	2.2	2.2		
$\text{IMn}(\text{CO})_3\text{As}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{C}(\text{CH}_3)_3)\text{CD}_2\text{As}(\text{CH}_3)_2$	1.979	2.003	1.200 <sup>b</sup>		1.432	1.629	-12.7	11.2	2.1	2.1		
Isomers B of 3												
$\text{ClMn}(\text{CO})_3\text{As}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{C}(\text{CH}_3)_3)\text{CD}_2\text{As}(\text{CH}_3)_2$	1.315 <sup>b</sup>	2.193	1.755 <sup>b</sup>		1.456	1.522	-12.3	11.6	1.8	1.8		
$\text{BrMn}(\text{CO})_3\text{As}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{C}(\text{CH}_3)_3)\text{CD}_2\text{As}(\text{CH}_3)_2$	1.32 <sup>b</sup>	2.176	1.886		1.466	1.597	-12.4		2.1	2.1		
$\text{IMn}(\text{CO})_3\text{As}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{C}(\text{CH}_3)_3)\text{CD}_2\text{As}(\text{CH}_3)_2$	1.31 <sup>b</sup>	2.16 <sup>b</sup>	2.011 <sup>b</sup>		1.467	1.708	-12.2 <sup>b</sup>					

<sup>a</sup> Values obtained from 3-*d*<sub>1</sub> complexes are 1.248 for Cl and 1.233 for Br. <sup>b</sup>  $\delta_1$  and  $\delta_2$  from 3-*d*<sub>1</sub> complexes;  $\delta_3$  from 3-*d*<sub>4</sub> complexes.

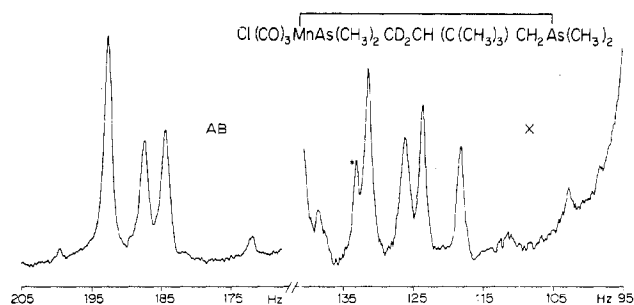


Figure 3. Nmr spectrum of the propane fragment of  $\text{ClMn}(\text{CO})_3\text{As}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{C}(\text{CH}_3)_3)\text{CD}_2\text{As}(\text{CH}_3)_2$ ; the asterisk indicates a spinning side band.

portion of the spectrum does provide one of the vicinal coupling constants. The iodide mixture has too little of isomer B present to solve its spectrum satisfactorily.

The nmr parameters obtained for the manganese halide complexes are listed in Table II. The vicinal coupling constants obtained for the bromide complex of isomer B are consistent with a locked configuration for the six-membered ring.

$\text{XMn}(\text{CO})_3\text{As}(\text{CH}_3)_2\text{CD}_2\text{CH}(\text{C}(\text{CH}_3)_3)\text{CD}_2\text{As}(\text{CH}_3)_2$ . The deuterium-decoupled nmr spectra for the propane fragments of these complexes exhibited two sharp bands, one for each isomer. Chemical shifts are listed in Table II.

$\text{XMn}(\text{CO})_3\text{As}(\text{CH}_3)_2\text{CH}_2\text{CD}(\text{C}(\text{CH}_3)_3)\text{CH}_2\text{As}(\text{CH}_3)_2$ . The deuterium-decoupled nmr spectra for the propane fragments of these complexes exhibited a broad singlet, (AB)<sub>2</sub> system of isomer A, and two doublets, <sup>32</sup>(AX)<sub>2</sub> system of isomer B.

## Discussion

A comparison of coupling constants of the protons of ligand 3 derivatives of manganese tricarbonyl halide with the group VIb tetracarbonyl complexes<sup>2</sup> indicates quite similar coupling constants for the geminal (~12 to -13 Hz) and two vicinal coupling constants (~11-13 and ~0.5-2.0 Hz). The similarity of the vicinal coupling constants suggests that the rings of these derivatives probably have similar "locked" conformations.

The manganese tricarbonyl halide derivatives of 1 have geminal proton coupling constants of ~-12.5 Hz (carbon 1) and ~-15.5 Hz (carbon 2) compared with the respective values of ~-13.0 and ~-15.0 Hz for the group VIb tetracarbonyl derivatives of 1. In contrast to the single vicinal coupling constant observed ( $J = 9.7$  Hz) for the group VIb tetracarbonyl derivatives of 1 shown to have flipping ring conformations,<sup>2</sup> four vicinal coupling constants (~13.5, ~2.5, ~2.0, and ~6.0 Hz) were observed for the manganese tricarbonyl halides of 1 and indicate the rings have either locked-chair or locked-boat configurations.

Lambert and Buys "R value" method, when applied to these manganese halide derivatives of ligand 1, suggests the locked configurations are strongly "puckered" chairs (*vide supra*). Figure 4 shows the four chair configurations that can exist for cis tricarbonylmanganese halide complexes with ligands 1 and 3. For ligand 1 (R = H), the configurations (a) and (d) and also (b) and (c) become equivalent and, thus, two forms [(a) and (c)] are expected to exist in a conformational equilibrium. The nmr results, however, indicate the predominance of only one of these configurations in solution. Any flipping process would lower  $J_{13}$ .

(32) Although the coupling constants were not determined, some small cross-ring coupling was observed.

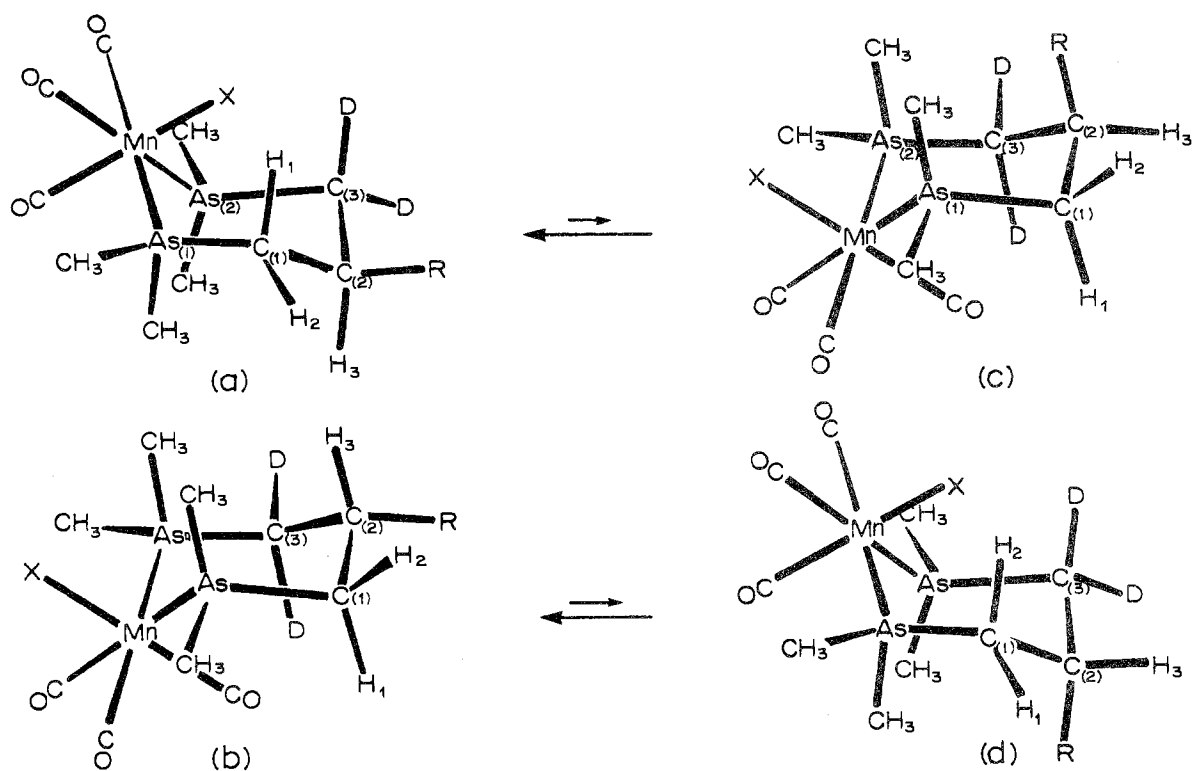


Figure 4. The four chair conformations possible for *fac*-Mn(CO)<sub>3</sub>X complexes of 3 (R = C(CH<sub>3</sub>)<sub>3</sub>).

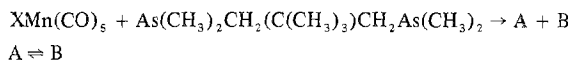
A recent X-ray investigation<sup>33</sup> of  $\text{ClMn}(\text{CO})_3\text{As}(\text{CH}_3)_2\text{-CH}_2\text{CH}_2\text{CH}_2\text{As}(\text{CH}_3)_2$  shows that the ring has a slightly distorted chair configuration of Figure 4(a), and it seems reasonable to assume that this is the structure of the conformer found in solution. The ring As-C-C-C dihedral angle of 70–71° compares well with the 67–68° calculated from the nmr parameters and demonstrates the applicability of the “R value” method to this complex. The X-ray results find the angle between the  $\text{As}_1\text{MnAs}_2$  plane and the  $\text{As}_1\text{As}_2\text{-C}_1\text{C}_3$  plane is only 31° indicating the chair configuration is flattened in the Mn-As-C fragment of the ring. Gollogly and Hawkins<sup>18</sup> have predicted that the rings of metal-diamine complexes flatten to accommodate an interaction between the axial ligand on the metal and axial substituents on the diamine ring.

Bear and Trotter<sup>33</sup> argued that it is the minimization of interaction between the arsenic methyl groups and the four other substituents that is responsible for the choice of structure (a) (Figure 4). There does not seem to be a repulsive interaction between the chlorine atom and the axial protons on C<sub>1</sub> and C<sub>3</sub> since the Mn-Cl bond is bent toward (85°) the As-Mn-As plane. This suggests the possibility of an attractive interaction between these atoms.

All four chair configurations (Figure 4) are possible for manganese complexes of 3 (R = *tert*-butyl). The  $J_{13}$  values, however, indicate an axial-axial interaction for these vicinal protons which necessitates the *tert*-butyl group be in an equatorial position. This result is not surprising in view of the well known tendency of this bulky group to occupy almost exclusively equatorial positions in cyclohexane rings.<sup>34</sup> The structures (c) and (d) of Figure 4 can be eliminated as significant configurations in solution and thus the two struc-

tures observed in the nmr spectra of the complexes of 3 must correspond to (a) and (b). The structures are isomers, not conformers, and cannot be interconverted by a ring-flipping process.

We have found that the proportion of the more stable isomer A is increased (90%) when a mixture of isomer A and isomer B is heated to 100°. The conversion is not complete and an equilibrium process may be involved, *i.e.*



These conversions probably involve a bond-breaking process but no attempt has yet been made to determine the mechanism although a five-coordinate intermediate could be implicated.

It seems likely that the A isomers have structure (a), since this would be analogous to the structure of the Mn(CO)<sub>3</sub>Cl complex of 1 with the *tert*-butyl group of 3 in an equatorial position. Isomers B would then have structure (b).

The chemical shift of the *tert*-butyl group changes only slightly with a variation of the halogen atom. Isomers A of 3 have their chemical shifts at slightly lower field than isomers B. The new complexes of 1 and 3 have two signals attributable to the arsenic methyls but these are at lower field than the arsenic methyl signals of corresponding group VIb metal complexes<sup>2</sup> presumably because of the inductive effect of the halide substituents. The arsenic methyl signals move progressively to lower field with a change from Cl to Br to I substituents. The opposite trend would be expected from the electronegativities or the diamagnetic shielding properties of the halogen atoms. The low-field methyl signal changes more than the upfield signal with variation of the halide substituent although a definite assignment of the chemical shifts to axial or equatorial methyl groups cannot be made from this study.

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Proton 3 (Figure 4) in manganese complexes of **3** (isomer A) has a chemical shift at higher field than analogous complexes of **1** reflecting the inductive effect of the *tert*-butyl group. Both sets of complexes have the chemical shifts of proton 3 in the order Cl > Br > I (highest field). Isomers B of **3** have this order reversed. The nmr spectra of complexes of **1** show proton 3 (axial) is at higher field than proton 4 (equatorial). The chloride complex has a chemical shift of 0.48 ppm between protons 3 and 4 which is about the difference usually observed between axial and equatorial protons in cyclohexane systems.<sup>35,36</sup>

Nmr spectra of group VIb complexes of **3** have the chemical shift of proton 1 (axial) at higher field (0.9–1.0 ppm) than proton 2 (equatorial)<sup>2</sup> and similar results are observed for isomers B of the manganese halide complexes. In contrast, the manganese halide complexes of **1** and **3** that have been assigned structure (a) (Figure 4) have chemical shifts for proton 1 at unusually low fields, and this similarity of chemical shifts provides additional support for our assignment of structure (a) to isomers A. As mentioned above, the X-ray

diffraction study<sup>33</sup> that showed the Mn–Cl bond is bent toward the chelate ring provides some evidence for an attractive interaction between the halide atom and the chelate ring, which could account for the low-field shifts. However, it is possible that the protons occupy a paramagnetically deshielded region of these metal carbonyl complexes.

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**Registry No.** ClMn(CO)<sub>3</sub>As(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>As(CH<sub>3</sub>)<sub>2</sub>, 41660-26-8; BrMn(CO)<sub>3</sub>As(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>As(CH<sub>3</sub>)<sub>2</sub>, 51652-94-9; IMn(CO)<sub>3</sub>As(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>As(CH<sub>3</sub>)<sub>2</sub>, 51652-95-0; ClMn(CO)<sub>3</sub>As(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>CH(C(CH<sub>3</sub>)<sub>3</sub>)CH<sub>2</sub>As(CH<sub>3</sub>)<sub>2</sub>, 51652-96-1; BrMn(CO)<sub>3</sub>As(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>CH(C(CH<sub>3</sub>)<sub>3</sub>)CH<sub>2</sub>As(CH<sub>3</sub>)<sub>2</sub>, 51652-97-2; IMn(CO)<sub>3</sub>As(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>CH(C(CH<sub>3</sub>)<sub>3</sub>)CH<sub>2</sub>As(CH<sub>3</sub>)<sub>2</sub>, 51652-98-3; ClMn(CO)<sub>3</sub>As(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CD<sub>2</sub>As(CH<sub>3</sub>)<sub>2</sub>, 51743-86-3; BrMn(CO)<sub>3</sub>As(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CD<sub>2</sub>As(CH<sub>3</sub>)<sub>2</sub>, 51743-87-4; IMn(CO)<sub>3</sub>As(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CD<sub>2</sub>As(CH<sub>3</sub>)<sub>2</sub>, 51743-88-5; IMn(CO)<sub>3</sub>As(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CD<sub>2</sub>As(CH<sub>3</sub>)<sub>2</sub>, 51652-99-4; ClMn(CO)<sub>3</sub>As(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>CH(C(CH<sub>3</sub>)<sub>3</sub>)CD<sub>2</sub>As(CH<sub>3</sub>)<sub>2</sub> (A), 51743-89-6; BrMn(CO)<sub>3</sub>As(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>CH(C(CH<sub>3</sub>)<sub>3</sub>)CD<sub>2</sub>As(CH<sub>3</sub>)<sub>2</sub> (A), 51743-90-9; IMn(CO)<sub>3</sub>As(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>CH(C(CH<sub>3</sub>)<sub>3</sub>)CD<sub>2</sub>As(CH<sub>3</sub>)<sub>2</sub> (A), 51743-91-0; ClMn(CO)<sub>3</sub>As(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>CH(C(CH<sub>3</sub>)<sub>3</sub>)CD<sub>2</sub>As(CH<sub>3</sub>)<sub>2</sub> (B), 51743-92-1; BrMn(CO)<sub>3</sub>As(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>CH(C(CH<sub>3</sub>)<sub>3</sub>)CD<sub>2</sub>As(CH<sub>3</sub>)<sub>2</sub> (B), 51743-93-2; IMn(CO)<sub>3</sub>As(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>CH(C(CH<sub>3</sub>)<sub>3</sub>)CD<sub>2</sub>As(CH<sub>3</sub>)<sub>2</sub> (B), 51743-94-3.

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## Detailed Analysis of the Carbonyl Stretching Vibrations in Axial and Equatorial Substituted Iron Carbonyl Compounds. Absolute Infrared Intensities and Force Constants of the Carbonyl Ligands

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Force constant calculations employing a restricted force field of CO stretching vibrations have been carried out for axially mono- and disubstituted phosphine, phosphite, and carbene and equatorially monosubstituted olefin derivatives of iron pentacarbonyl. The computations were made possible with the aid of frequency data obtained from <sup>13</sup>C photochemically enriched species. For the axially substituted LFe(CO)<sub>4</sub> species the force constant for the CO ligand opposite L (phosphines, phosphites, or carbene) was found to be greater than those cis to L by approximately 0.50 mdyn/Å. For the equatorially substituted (olefin)Fe(CO)<sub>4</sub> derivatives the two CO groups opposite the olefin ligand exhibited somewhat larger force constants as compared with the two CO ligands trans to one another. The calculated force constants for the equatorially substituted (olefin)Fe(CO)<sub>4</sub> species were all significantly larger than the corresponding values in the axially substituted LFe(CO)<sub>4</sub> derivatives. Absolute infrared intensities of ν<sub>CO</sub> were determined and used to calculate characteristic MCO group dipole moment derivatives in these complexes. The results of the intensity studies are discussed in terms of vibrational coupling and geometrical and electronic properties of the CO ligands as well as the substituent ligands. In addition, a combination of ν<sub>CO</sub> force constants and dipole moment derivatives have been employed in understanding and comparing the electron distributions in the metal carbonyl framework of the two isomeric forms of monosubstituted iron pentacarbonyl derivatives. These studies provide as well some criteria for distinguishing between the two types of infrared spectra commonly observed in the isomeric forms of monosubstituted iron pentacarbonyl species.

### Introduction

The measurement of infrared intensities of the CO stretching vibrations along with an appropriate normal-coordinate analysis can lead to assignment of relative dipole moment

derivatives, μ'<sub>MCO</sub>.<sup>3-13</sup> These quantities are very reliable

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