

the effect of the added ligand slightly smaller. H<sub>2</sub>O also competes more efficiently than D<sub>2</sub>O with ethylenediamine in the interactions with the Tl<sup>+</sup> ion; thus the effect of the added ligand is somewhat smaller in the H<sub>2</sub>O solution than in the D<sub>2</sub>O solution resulting in the

change in sign of the solvent isotope shifts as ethylenediamine is added.

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

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**Abstract:** The complexes (CO)<sub>4</sub>MA<sub>s</sub>(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>CH(R)CH<sub>2</sub>As(CH<sub>3</sub>)<sub>2</sub> (R = H, CH<sub>3</sub>, C(CH<sub>3</sub>)<sub>3</sub>; M = Cr, Mo, and W, but not all combinations) which contain six-membered chelate rings were prepared and their nuclear magnetic resonance spectra investigated. In order to solve the spectra it was necessary to prepare selectively deuterated analogs. When R = H the rings are undergoing fast conformational inversion between symmetric chair forms. When R = C(CH<sub>3</sub>)<sub>3</sub> the rings are locked in a chair conformation with R in an equatorial position.

Numerous conformational analyses on carbocyclic and heterocyclic six-membered ring systems have been documented and reviewed in the literature.<sup>2</sup> Recently, there has been an interest in the stereochemistry of metal complexes containing six-membered chelate rings.<sup>3-15</sup> In contrast to the carbocyclic systems that have only a tetrahedral arrangement of atoms, a site exists that can have a square planar or octahedral configuration, introducing interactions not formerly encountered.

Although X-ray studies give conformations of metal complexes in the solid state, it is apparent that the structures may be distorted by such factors as intermolecular hydrogen bonding and crystal packing.<sup>3,16</sup> Furthermore, since most chemical reactions are carried

out in solution, it is important to establish conformations in this state. We have initiated a program of nuclear magnetic resonance studies directed toward elucidating the effects of such factors as ring size, ring substituents, central metal size, and central metal geometry, on chelate ring conformations. We have chosen the nmr method because of its unique ability to give the desired information provided that the ligands are suitably designed.

The study of di(tertiary arsine) chelate complexes of metals for the investigation of factors influencing conformation in solution has some advantages over the use of the more conventional diamine-metal compounds. With the latter, one is hindered by the necessity of deuterating the N-H bonds when present and by the commonly encountered need to use such solvents as D<sub>2</sub>O and DMSO-*d*<sub>6</sub>, with high dielectric constants and hydrogen bonding and complexing capabilities.<sup>17</sup> Furthermore, the possible broadening resulting from the coupling of the proton nuclei with the nitrogen atoms is obviated with the use of diarsine complexes.

There also exists a distinct simplification in the study of six-membered rings as opposed to the much studied five-membered ring systems.<sup>3,16</sup> Whereas in the latter a number of conformers can have quite similar energies, it has been calculated<sup>18</sup> that, in octahedral systems, the symmetric chair form of the six-membered ring is the highly favored configuration relative to the symmetric

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(17) While studies in these media can produce interesting results such as the apparent axial preference of the hydroxy and chloro groups in the platinum complexes of the diamine H<sub>2</sub>NCH<sub>2</sub>CHXCH<sub>2</sub>NH<sub>2</sub> (X = OH, Cl)<sup>4</sup> (which contrasts with the equatorial preference of those groups in cyclohexane derivatives), it seems important to first establish conformational preferences in less polar solvents using spectra of well-defined complexes. A further necessity is that the spectra must be of a quality to allow complete and unambiguous assignments to be made.

- (18) J. R. Golligly and C. J. Hawkins, *Inorg. Chem.*, **11**, 156 (1972).

boat and various skew-boat forms.<sup>19</sup> This conclusion is borne out by the reported solid-state X-ray results<sup>7,10,13,15</sup> on a number of complexes.<sup>21</sup>

We report in this paper the study of some di(tertiary arsine) complexes of the group VI metal carbonyls containing six-membered chelate rings,  $(\text{CO})_4\text{M}(\text{As}-\text{As})$ . The ligands prepared and used were of the type  $\text{As}-\text{As} = (\text{CH}_3)_2\text{AsCH}_2\text{CH}(\text{R})\text{CH}_2\text{As}(\text{CH}_3)_2$  ( $\text{R} = \text{H}$ , **1**;  $\text{CH}_3$ , **2**;  $\text{C}(\text{CH}_3)_3$ , **3**). Having found it impossible to solve the nmr spectra of the five- and six-proton systems (even using a 220-MHz spectrometer in one case), we had to have recourse to the preparation and use of partially and selectively deuterated ligands  $(\text{CH}_3)_2\text{AsCH}_2\text{CH}(\text{R})\text{CD}_2\text{As}(\text{CH}_3)_2$  ( $\text{R} = \text{H}$ , **1-d**;  $\text{C}(\text{CH}_3)_3$ , **3-d**). The deuterium decoupled spectra of the complexes of these ligands were more amenable to complete and accurate calculation of both chemical shift and coupling constant data.

## Experimental Section

Iododimethylarsine was prepared from the reduction of dimethylarsinic acid using sulfur dioxide and potassium iodide.<sup>22</sup> The dideuterated diol  $\text{HOCH}_2\text{CH}_2\text{CD}_2\text{OH}$  was prepared following the method of Campbell and Hall.<sup>23</sup> The diol  $\text{HOCH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{OH}$  was obtained by the reduction of diethyl methylmalonate with  $\text{LiAlH}_4$ . All other reagents were of commercial origin.

Infrared spectra were recorded on a Perkin-Elmer 457 instrument. The nmr spectra were run on an extensively modified Varian HA-100 instrument.<sup>24</sup> The final refined nmr parameters were obtained using the iterative LAOCOON III program modified for use on the UBC IBM 360-67 computer. The 220-MHz spectra were recorded at the Canadian 220 MHz NMR Centre at the Ontario Research Foundation, Sheridan Park. Microanalyses were done by Mr. Peter Borda of this department.

Instead of giving the experimental details for the preparation of all the chemicals used, the general method will be exemplified by describing the preparation of the complex 1,3-bis(dimethylarsino)-1,1-dideuterio-2-*tert*-butylpropanechromium tetracarbonyl,  $(\text{CO})_4\text{CrAs}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{C}(\text{CH}_3)_3)\text{CD}_2\text{As}(\text{CH}_3)_2$ . All reactions were carried out under an atmosphere of nitrogen.

**1. Preparation of 2-Hydroxymethyl-3,3-dimethylbutyric Acid.** The method is a slightly modified version of that used by Durst<sup>25</sup> and will therefore be given in detail.

One mole of *n*-BuLi in *n*-hexane was added dropwise to 104 g (1 mol) of diisopropylamine (freshly distilled over NaOH) in 400 ml of freshly dried THF at 0°. To the resulting  $\text{LiN}(i\text{-Pr})_2$  solution was added 58 g (0.5 mol) of 3,3-dimethylbutyric acid. This was followed by 15 g of paraformaldehyde, and the resulting mixture was stirred overnight. The reaction mixture was poured into a large quantity of water and extracted with ether to remove the diisopropylamine. The water layer was then just acidified with HCl and extracted with dichloromethane. On removal of the volatile fraction an nmr spectrum indicated the almost exclusive presence of the starting acid (8 g). The water solution was acidified further and extracted several times with ether. The extract upon drying ( $\text{Na}_2\text{SO}_4$ ) and evaporation yielded 45 g (70% yield) of product, mp 148–150°.

**2. Preparation of 1,1-Dideuterio-2-*tert*-butyl-1,3-propanediol.**

(19) In trisdiamine complexes the calculations of Golligly and Hawkins<sup>18</sup> predict the tris chair configuration to be the most stable. Other predictions suggest that the tris (skew-boat)<sup>20</sup> configuration is more stable.

(20) F. Woldbye, "Studies on Optical Activity," Polyteknisk Forlag, Copenhagen, 1969, p 210; *Proc. Roy. Soc., Ser. A*, **297**, 79 (1967); K. R. Butler and M. R. Snow, *Inorg. Chem.*, **10**, 1838 (1971).

(21) In some instances, the six-membered ring in trimethylene complexes have been found by X-ray studies to be in the "twisted" or skew-boat configuration,<sup>10,11</sup> but these are usually part of a fused ring system.

(22) E. Roberts, E. E. Turner, and F. W. Bury, *J. Chem. Soc.*, 1443 (1926).

(23) J. R. Campbell and L. D. Hall, unpublished results.

(24) R. Burton and L. D. Hall, *Can. J. Chem.*, **48**, 59 (1970).

(25) T. Durst, *Tetrahedron Lett.*, 4171 (1971), and personal communication.

The acid-alcohol prepared above (20.0 g, 0.138 mol), in 250 ml of THF, was added dropwise into a solution of  $\text{LiAlD}_4$  (7.05 g, 0.168 mol) in 200 ml of THF at such a rate as to maintain gentle reflux. After the addition was complete, reflux was maintained for a further 3 hr. On cooling, 7 ml of  $\text{H}_2\text{O}$ , 7 ml of 15% NaOH, and 21 ml of  $\text{H}_2\text{O}$  were added in turn to the stirred reaction mixture. The resulting gelatinous precipitate was filtered off and dissolved in dilute HCl. This solution was then extracted with ether. The THF filtrate and the ether layer were combined and evaporated to yield an oil which was dissolved in ether and dried over  $\text{Na}_2\text{SO}_4$ . On removing the ether, a creamy white solid was obtained which was recrystallized slowly from ether-*n*-pentane to give large transparent crystals of the product (15 g, 82% yield), mp 56–68°.

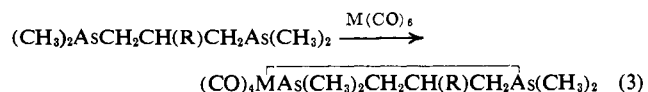
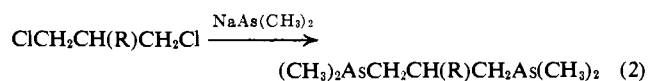
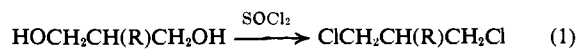
**3. Preparation of 1,3-Dichloro-1,1-dideuterio-2-*tert*-butylpropane.** The diol prepared above (5.8 g, 0.439 mol) was dissolved in pyridine (6.90 g, 0.874 mol) and to this solution was added thionyl chloride (10.50 g, 0.882 mol) over a period of 5 min. Fumes appeared initially on addition of each drop, and a white precipitate formed in an amber colored solution. After the addition the flask was heated slowly and at 80°  $\text{SO}_2$  began to evolve. The heating was continued between 85 and 90° until the evolution ceased (about 1 hr). Water and ether were added, and the ether layer was separated. The water layer was further washed with ether, and the combined ether layers were then washed with acidified water followed by 10%  $\text{Na}_2\text{CO}_3$ . The ether layer was then dried over  $\text{Na}_2\text{SO}_4$ . Evaporation of the ether gave the product (6.63 g, 89% crude yield).

**4. Preparation of 1,3-Bis(dimethylarsino)-1,1-dideuterio-2-*tert*-butylpropane.** Iododimethylarsine (27g, 0.116 mol) in THF was added in an exothermic reaction to sodium wire (12 g, 0.546 g atom) in THF. The solution turned green and a precipitate formed. The mixture was refluxed for a further 2 hr at which time the solution of  $\text{NaAs}(\text{CH}_3)_2$  was a very dark greenish black. (In some experiments, a white precipitate was first formed and the solution only turned green after heating. This is due to the initial formation of  $(\text{CH}_3)_2\text{As}-\text{As}(\text{CH}_3)_2$  and NaI, the former then being attacked further by sodium to give the green  $\text{NaAs}(\text{CH}_3)_2$ .) The solution was separated by decanting from the precipitated NaI and excess sodium and cooled to  $-78^\circ$ . To this was then added slowly with stirring a THF solution of the dichloride prepared above (6.0 g, 0.036 mol). The mixture was allowed to warm to room temperature and stirred for a further 0.5 hr. The THF was removed, and an  $\text{NH}_4\text{Cl}$  solution and ether were added. The ether layer was separated and the water layer was further extracted with ether. The combined ether layers were dried over  $\text{Na}_2\text{SO}_4$ . The product (~10 g), a fuming liquid which darkened on contact with air, was obtained on removal of the solvent.

**5. Preparation of  $(\text{CO})_4\text{CrAs}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{C}(\text{CH}_3)_3)\text{CD}_2\text{As}(\text{CH}_3)_2$ .** Equimolar quantities of  $\text{Cr}(\text{CO})_6$  and the di(tertiary arsine) were sealed along with 10 ml of benzene in a thick-walled Carius tube and maintained at 150° for 12 hr. After cooling, the tube was opened and 20 ml of heptane was added. The solution was filtered and reduced to half its volume on a rotary evaporator to give crystals of product. Filtration and cooling of the filtrate to  $-20^\circ$  afforded further well-defined crystals of the complex (yield 50–80%).

## Results and Discussion

The general scheme for the preparation of the complexes investigated is given in eq 1, 2, and 3. These reactions were carried out following the general methods given in the literature.<sup>26–28</sup>



(26) M. G. Darzens, *C. R. Acad. Sci.*, **152**, 1314 (1971).

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(28) W. R. Cullen, D. F. Dong, and J. A. J. Thompson, *Can. J. Chem.*, **47**, 4671 (1969).

Table I. Analytical Data and Carbonyl Infrared Spectra

Compound	Color	Chemical analysis		Ir, <sup>a</sup> cm <sup>-1</sup>	Mp, °C	
		Calcd	Found			
(CO) <sub>4</sub> CrAs(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>	Yellow	C H	31.8 4.4	32.0 4.6	2011, 1918, 1893	145-147
(CO) <sub>4</sub> MoAs(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>	White	C H	28.7 3.9	28.8 3.9	2021, 1925, 1907, 1899	145-147
(CO) <sub>4</sub> WAs(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>	Yellow	C H	24.1 3.3	24.0 3.4	2018, 1918, 1900 sh 1895	158-160
(CO) <sub>4</sub> CrAs(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )CH <sub>2</sub> As(CH <sub>3</sub> ) <sub>2</sub> <sup>b</sup>	Yellow	C H	33.5 4.7	33.4 4.9	2011, 1919, 1897	114-116
(CO) <sub>4</sub> CrAs(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>	Yellow	C H	38.2 5.6	38.1 5.6	2009, 1917, 1895	173-174
(CO) <sub>4</sub> MoAs(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>	White	C H	34.2 5.0	34.5 5.2	2020, 1925, 1908 1900	168-170
(CO) <sub>4</sub> WAs(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>	Pale cream	C H	29.8 4.4	29.5 4.5	2019, 1919, 1897	186-188

<sup>a</sup> Cyclohexane solution, all peaks are strong. <sup>b</sup> Molecular weight: calcd, 430; found, 416 (Mechrolab vapor pressure osmometer).

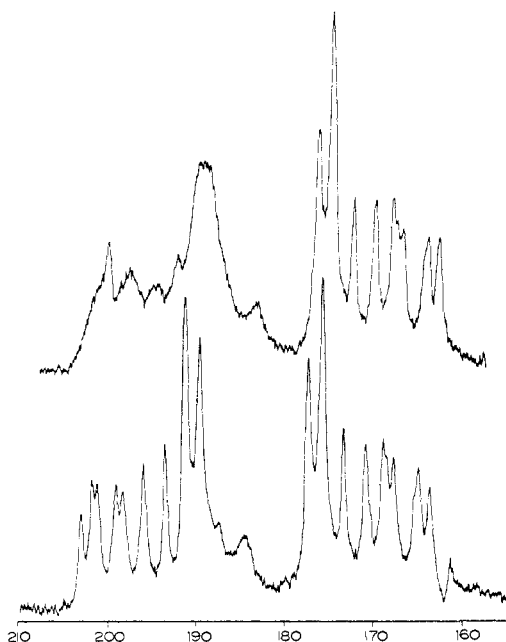


Figure 1. Part of the <sup>1</sup>H nmr spectrum of (CO)<sub>4</sub>CrAs(CH<sub>3</sub>)<sub>2</sub>CD<sub>2</sub>-CH<sub>2</sub>CH<sub>2</sub>As(CH<sub>3</sub>)<sub>2</sub>. The upper spectrum is the normal bridge proton region. The lower one is the same region run with deuterium decoupling.

The reaction shown in eq 2 appears to be a general one where R is an alkyl group. Also, 1,3-dibromopropane reacted in a similar fashion to the dichloropropane. The di(tertiary arsines) so obtained were not examined as such because of their sensitivity to oxidation and all investigations were performed on the much more stable carbonyl complexes.

Attempts at preparing a comparable di(tertiary arsine) where R is a phenyl group failed, both when the diiodide, 1,3-diiodo-2-phenylpropane, and the ditosylate 1,3-ditosyl-2-phenylpropane were used in reaction with NaAs(CH<sub>3</sub>)<sub>2</sub>. Instead, a highly unstable, apparently monodentate, arsine was obtained which reacted with the group VI hexacarbonyls to give unstable pentacarbonyl complexes (as seen from the infrared spectra in the carbonyl stretching region). Furthermore, the reactions of dihalides with NaAs(CH<sub>3</sub>)<sub>2</sub> give di(tertiary arsines) only if *primary dihalides* are used. Thus the

products from the reactions of 1,3-dichlorobutane or 1,2-dichloropropane when heated with the hexacarbonyls also afforded unstable pentacarbonyl derivatives. These reactions were not investigated further.

Analytical data and some physical properties for the carbonyl complexes prepared are given in Table I. The infrared spectra indicate the usual *cis* geometry of the ligands around the central metal. It is worth noting that the frequencies of  $\nu(\text{CO})$  for a given metal are almost constant and independent of ligand substitution and therefore, as will be seen below, of ligand conformation.

**Nmr Spectra of the Di(tertiary arsine)-Metal Complexes.** The Complexes (CO)<sub>4</sub>MAs(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>. The nmr spectrum of the chromium complex of the ligand 1-*d*<sub>2</sub> is shown in Figure 1. The simplification introduced by deuterium decoupling is very obvious. There appears to be virtually no cross-ring H-D coupling as is evidenced by the fact that no change occurred in half (the upfield portion) of the spectrum on decoupling. Thus the -CH<sub>2</sub>- groups adjacent to the arsenic atoms are more highly shielded than the central -CH<sub>2</sub>- group. This is presumably due to the basic properties of the As(CH<sub>3</sub>)<sub>2</sub> moiety. The spectra of all 1-*d*<sub>2</sub> complexes are very nearly symmetrical about their centers and yield solutions indicative of AA'BB' systems. The coupling constants obtained from analyses of the spectra, along with the chemical shifts, are listed in Table II. The symmetrical spectra are an immediate indication that the six-membered rings are undergoing fast conformational inversion since, if this had not been the case, more complicated spectra due to four inequivalent protons would have been obtained. Thus the six-membered ring is probably alternating rapidly between two equivalent chair conformations as shown in Figure 2 (R = H<sub>2</sub>).

Unfortunately because of the symmetry of the systems it is impossible to eliminate conclusively, on the basis of the nmr parameters, the possibility of a fast interconversion of symmetric skew-boat forms. However, Lambert<sup>29</sup> and Buys<sup>30,31</sup> in particular have developed the "R-value" method whereby the ring di-

(29) J. B. Lambert, *Accounts Chem. Res.*, **4**, 87 (1967), and references therein.

(30) H. R. Buys, *Recl. Trav. Chim. Pays-Bas*, **88**, 1003 (1969).

(31) H. R. Buys, *Recl. Trav. Chim. Pays-Bas*, **89**, 1253 (1970).

Table II. Nmr Parameters of Complexes<sup>a,b</sup>

Compound	$\delta_1, \delta_2$	$\delta_3, \delta_4$	$J_{12}, J_{34}$	$J_{13}$	$J_{14}, J_{23}$	$J_{24}$	$\delta_{As-CH_3}$	
$(CO)_4CrAs(CH_3)_2CH_2CH_2CD_2As(CH_3)_2$	1.711	1.959	2.2	-15.0	9.7	-12.8	1.350	
$(CO)_4MoAs(CH_3)_2CH_2CH_2CD_2As(CH_3)_2$	1.735	1.994	2.1	-15.0	9.7	-12.9	1.352	
$(CO)_4WAs(CH_3)_2CH_2CH_2CD_2As(CH_3)_2$	1.836	2.081	2.1	-15.6	9.7	-13.3	1.488	
$(CO)_4CrAs(CH_3)_2CH_2CH(C(CH_3)_3)CD_2As(CH_3)_2$	$\delta_1$ 1.098	$\delta_3$ 2.068	$\delta_4$ 1.132	$J_{13}$ -12.8	$J_{14}$ 11.7	$J_{34}$ 1.3	$\delta_{As-CH_3}$ 1.345	$\delta_{t-Bu}$ 0.882
$(CO)_4MoAs(CH_3)_2CH_2CH(C(CH_3)_3)CD_2As(CH_3)_2$	1.136 <sup>c</sup>	2.084	1.174	-12.4	11.3	0.8	1.353	0.888
$(CO)_4WAs(CH_3)_2CH_2CH(C(CH_3)_3)CD_2As(CH_3)_2$	1.188	2.181	1.225	-11.9	11.5	0.5	1.482	0.896

<sup>a</sup> CDCl<sub>3</sub> solution with ~20% by volume TMS. Chemical shifts are downfield from TMS in ppm, coupling constants are in Hz. <sup>b</sup> For 1-*d*<sub>2</sub> and 3-*d*<sub>2</sub> complexes, see notations in Figures 2a, 2b, and Figure 2a, respectively. <sup>c</sup> For the complex  $(CO)_4MoAs(CH_3)_2CD_2CH(C(CH_3)_3)CD_2As(CH_3)_2$   $\delta_1$  was found to be 1.153 ppm.<sup>34</sup>

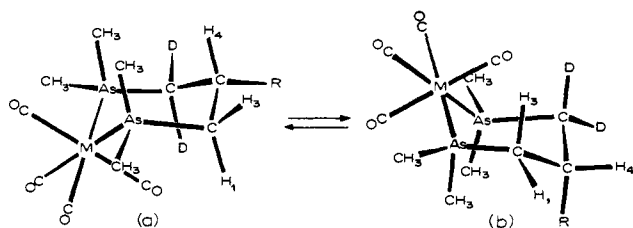


Figure 2. The conformational equilibrium proposed for six-membered chelate rings. In the 1-*d*<sub>2</sub> complexes, R = H<sub>2</sub>.

hedral angle  $\psi$  for the -CH<sub>2</sub>CH<sub>2</sub>- fragments in six-membered rings may be calculated from the vicinal proton-proton coupling constants using the equation

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

Defined in this way  $R$  is independent of the electro-negativity of substituents even though the individual couplings may be strongly dependent on the nature of the substituents.

It was found that for the ideal chair forms  $R$  would have a value of 1.9-2.2, for "puckered" chairs it would be >2.5, and for "flattened" chairs or flexible forms (various boat forms)  $R$  would be <1.8. For the group VI complexes of 1-*d*<sub>2</sub>  $R$  has a value of >4, and  $\psi$  is calculated to be 66-68°, indicating considerable puckering.

The results of a recent X-ray structure on the complex  $ClMn(CO)_3As(CH_3)_2CH_2CH_2CH_2As(CH_3)_2$ <sup>32</sup> show that the ring is indeed in a symmetrical chair form with a ring dihedral angle of 70-71°. Using the  $R$  method  $\psi$  for this complex is calculated as being 67-68°, indicating the applicability, at least in this case, of the method.<sup>33,34</sup>

Gollogly and Hawkins<sup>18</sup> predict that the ring of diamine complexes would flatten to accommodate any interaction between the ligand on the metal and axial substituents on the diamine ring, the flattening being achieved mainly by distortion of the MNC and NMN angles. However, the remaining ring angles are not much affected.

(32) C. Bear and J. Trotter, *J. Chem. Soc., Dalton Trans.*, 673 (1973).

(33) The parameters derived from the nmr spectrum of the manganese complex suggest that the chelate ring is "locked" in solution. Presumably the conformation in solution is the same as found in the solid state.

(34) W. R. Cullen, L. D. Hall, J. T. Price, and G. Spendjian, unpublished results.

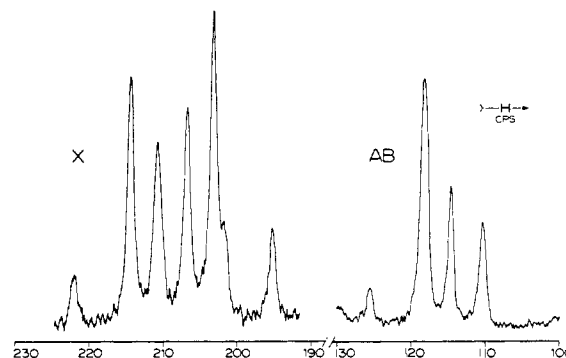


Figure 3. The deuterium decoupled <sup>1</sup>H nmr spectrum of the bridge proton region of  $(CO)_4MoAs(CH_3)_2CD_2CH(C(CH_3)_3)CH_2As(CH_3)_2$ ; the AB region was run at lower spectrometer gain than the X region.

There is virtually no change in the coupling constants derived from the spectra of the complexes on changing the central metal atom. This has also been noted in certain five-membered di(tertiary arsine) complexes.<sup>35</sup> It appears that changes in the As-M-As fragment geometry as a consequence of, for example, increasing bond length in the series Cr-As < Mo-As < W-As, are not reflected to any great extent by changes in the geometry of the propane moiety.

**The Complexes  $(CO)_4MAs(CH_3)_2CH_2CH(C(CH_3)_3)CD_2As(CH_3)_2$ .** The nmr spectrum of the molybdenum complex of the ligand 3-*d*<sub>2</sub> is shown in Figure 3 and is seen to be of the ABX type, as are those of the analogous chromium and tungsten complexes.

It was found that the X portion (downfield) of the spectrum sharpened up only slightly on deuterium decoupling, relative to the considerable sharpening observed in the AB portion of the spectrum. This means that the two protons on the carbon adjacent to the arsenic atom have widely different chemical shifts, the upfield one being close in chemical shift to the proton on the central carbon atom. With the help of this primary information the spectra were solved for both the magnitudes and signs of the coupling constants (assuming that geminal coupling constants are negative), and the chemical shift of each proton specifically. These are also given in Table II.

The choice of the *tert*-butyl group as a substituent on

(35) W. R. Cullen, L. D. Hall, and J. E. H. Ward, unpublished results.

the central carbon atom was spurred by the fact that this group to all practical purposes occupies almost exclusively the equatorial position in cyclohexane rings<sup>36</sup> and would therefore be the ideal locking group if one were required. From the high value of  $J_{14}$  it is evident that the *tert*-butyl group has indeed effectively locked the ring and taken up an equatorial position as shown in Figure 2a ( $R = C(CH_3)_3$ ). Although we would have expected from this that two As-CH<sub>3</sub> peaks would be observed, only one was seen in CDCl<sub>3</sub> solution. This is due to accidental degeneracy, rather than magnetic equivalence, since two peaks *are* distinctively resolved in benzene solution.

In the complexes of the ligand **3-d<sub>2</sub>** we can definitely eliminate the possibility of the existence of any skew-boat configurations whether locked or not. If the skew-boat conformers were locked, then depending on the positions of the -CD<sub>2</sub>- and -CH<sub>2</sub>- groups relative to the ring, two isomers would be expected. Only one compound was observed in each spectrum. Furthermore, if the skew-boats were undergoing fast interconversion, then we would expect coupling constants which are average values of  $J_{ax,ax}$ ,  $J_{eq,eq}$ , and  $J_{ax,eq}$ . The large couplings found thus preclude this stereochemistry.

The nmr spectrum of the complex  $(CO)_4CrAs(CH_3)_2-CH_2CH(CH_3)CH_2As(CH_3)_2$  was not solvable at 100 MHz; even the use of a 220-MHz spectrometer did not simplify the spectrum sufficiently to permit coupling constant and chemical shift data to be derived. The deuterated ligand was not prepared since the *tert*-butyl substituted complexes afforded essentially all the information presently required.

It must be emphasized at this stage that without the presence of the deuterium atoms and the simplification obtained by recording decoupled spectra, unique assignments of chemical shifts and coupling constants would have been impossible. That this is not simply due to the simplification of the spectra is illustrated by the following examples. In the AA'BB' systems observed for the complexes of **1-d<sub>2</sub>** it would have been impossible to differentiate which methylene groups were upfield and which were downfield. Also, if it had not

(36) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Wiley-Interscience, New York, N. Y., 1965.

been apparent in the complexes of **3-d<sub>2</sub>** that it was one of the -CH<sub>2</sub>- protons rather than the -CH(C(CH<sub>3</sub>)<sub>3</sub>)-proton which gave rise to the X portion in the ABX spectra, it would have been impossible to differentiate between  $^3J_{HH(ax,ax)}$  and  $^2J_{HH}$  (which have similar values but opposite signs) or to assign the calculated chemical shifts to specific protons.

The axial -CH<sub>2</sub>- proton on the **3-d<sub>2</sub>** complexes is about 95-100 Hz upfield from the equatorial proton. This value is significantly larger than the chemical shift of ~48 Hz observed between axial and equatorial protons in cyclohexane (at 100 MHz). For substituted trimethylenediamine complexes of Pt and Pd, Appleton and Hall found chemical shift differences of up to 65 Hz for the geminal protons (the axial proton being upfield) in the central methylene group of the complexes of *meso*-H<sub>2</sub>NCH(CH<sub>3</sub>)CH<sub>2</sub>CH(CH<sub>3</sub>)NH<sub>2</sub> where the chelate ring is reported to be locked with the two methyl groups equatorial.<sup>4</sup> These same workers report that the axial proton in the CH<sub>2</sub> group of the complexes of H<sub>2</sub>NCH<sub>2</sub>CHXCH<sub>2</sub>NH<sub>2</sub> (X = Cl, OH) is also upfield of the equatorial one in Pt<sup>II</sup> complexes but is *downfield* in Pt<sup>IV</sup> complexes of the same ligands<sup>5</sup> (see ref 17). With regard to the present results it is too early to speculate on the reasons for such a large axial-equatorial shielding difference, although the influences of the *tert*-butyl, and the carbonyl groups, are undoubtedly important.

Further work is now in progress in this laboratory to determine the effects of substituents on the metal atom and on the propane fragment, in both octahedral and tetrahedral systems. This will hopefully shed some additional light on the matter.<sup>37,38</sup>

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(37) A referee suggested that variable temperature nmr studies might help identify any fast conformational inversions; one such study was undertaken. The nmr spectrum of  $(CO)_4CrAs(CH_3)_2CH_2CH_2CD_2As(CH_3)_2$  in CH<sub>2</sub>Cl<sub>2</sub> containing a small amount of acetone was measured at temperatures in the range +20 to -85°. Although some changes were observed both in line widths and multiplet patterns, these were too complex to be simply interpreted.

(38) NOTE ADDED IN PROOF. More rigorous conformational calculations on six-membered chelate rings have been recently reported: L. J. DeHayes and D. H. Busch, *Inorg. Chem.*, **12**, 1505 (1973).