similar to that presented in the first part of the discussion of transition metal variations would predict that the dihedral angle of the ethane moiety in the chelate ring would decrease when the arsenic atoms are substituted by phosphorus atoms, since the metal-phosphorus and phosphorus–carbon bond lengths would be shorter than the corresponding bond lengths involving arsenic atoms. The calculated angles (Table IX) change in accordance with these arguments, but only by a small amount ($-0.75°$). However, it can be expected that such a donor atom change in the chelate complexes would cause more than simple geometric alterations in the two-carbon bridge. Electronic effects are anticipated to be more important for this type of substitution, because the donor atoms are bonded directly to the ethane bridge carbon atoms, in contrast

with variations in the metal atom, which involve changes farther removed from that part of the chelate ring. Perhaps this is the reason for the unusually high values of the Karplus coefficients obtained for the trifluorophosphorus derivatives 9 and 10.

It should be noted that much stereochemical information can be obtained from consideration of $^{31}P-^{1}H$ [31] couplings and it is our purpose to comment further on this in future publications.

A Nuclear Magnetic Resonance Study of the Conformational Preferences of Some Manganese Carbonyl Halide Chelate Complexes of Di(tertiary arsines)

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Abstract: The nmr parameters of some new di(tertiary arsine) chelate complexes of manganese carbonyl halides are presented and interpreted in terms of the conformational preferences of the five-membered chelate rings. The effects of the variations in cis-axial manganese substituents on the chelate ring conformations are described and discussed. It appears that changes in the metal atom substituent have little through-bond electronic effect. Thus, variations in bond lengths or substituent bond angles do not seem appreciable. Nevertheless, alterations in cis-axial manganese substituents have a marked effect on the conformational preferences of the five-membered chelate rings.

The conformational preferences of a number of di(tertiary arsine and phosphine) substituted group VI metal carbonyl chelate complexes have been the subject of work we have recently described.[2-4] For many chelate complexes of the general type A (M = Cr, Mo,

A
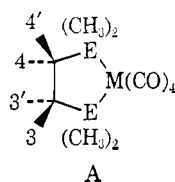
W; 3 = Si(CH$_3$)$_3$, SiCl$_3$, F, Cl, and CN and 3', 4 and 4' = H; 3 and 3' = H and 4 and 4' = F; 3 and 4 = F and 3' and 4' = H; and 3' = H and 3, 4, and 4' = F), it was found that a "bulky" substituent such as a trimethylsilyl group favors the "equatorial" position on

the puckered five-membered chelate ring, while a fluorine substituent usually prefers the "axial" orientation. In contrast, complexes of the ligand d,l-1,2-bis(dimethylarsino)-1,2-difluoroethane favor conformations in which the fluorine atoms exist gauche to one another, both adopting "equatorial" orientations.

The effects of variations of the solvents,[2,3] donor,[3] and transition metal atoms[3] were also described. While the solvent and donor atom alterations usually did not seem to systematically change the chelate ring conformations, perturbations of the geometries of the chelate rings caused by variations in the transition metal could be roughly estimated, and their subsequent effects on vicinal coupling constants were calculated and compared with those changes observed experimentally. In ideal cases, the signs and approximate magnitudes of the changes could be predicted.

We now report the results of our attempts to *systematically* investigate the interactions of axial transition metal atom substituents which are cis to a five-membered chelate ring in complexes such as B.

Gollogly and Hawkins[5a] have theoretically examined

(1) (a) Alfred P. Sloan Foundation Fellow, 1971–1973. (b) This work includes part of the material submitted by J. E. H. W. in partial fullment of the requirements for the Ph.D. degree in Chemistry, University of British Columbia.
(2) W. R. Cullen, L. D. Hall, and J. E. H. Ward, *J. Amer. Chem. Soc.*, 94, 5702 (1972).
(3) W. R. Cullen, L. D. Hall, and J. E. H. Ward, *J. Amer. Chem. Soc.*, 96, 3422 (1974).
(4) W. R. Cullen, L. D. Hall, and J. E. H. Ward, *Chem. Commun.*, 625 (1970).

(5) (a) J. R. Gollogly and C. J. Hawkins, *Inorg. Chem.*, 8, 1168 (1969); (b) L. J. De Hayes and D. H. Busch, *Inorg. Chem.*, 12, 1505 (1973).

4' (CH₃)₂ X
4 —As | CO
| Mn
| | CO
3' —As C
(CH₃)₂ O
3

B
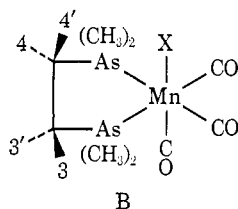
the interactions of cis-axial substituents such as NH_3 and Cl^- with the methyl groups in propylenediamine and N-methylethylenediamine chelate complexes of cobalt and report that the van der Waals interaction energies are sufficient to affect the conformations of the chelate rings. Similar conclusions were reached by De Hayes and Busch.[5b] Thus it appears that the interactions of most substituents on the five-membered chelate ring with cis-metal atom substituents could be significant, and these must be considered in the present work.

Experimental Section

The di(tertiary arsines) used to prepare the chelate complexes in this study were obtained by methods[2,3] which we have already described. The air-sensitive ligands were handled by syringe techniques in a nitrogen atmosphere.

Pentacarbonylmanganese chloride,[6] bromide,[7] and iodide[8] were obtained as described in the literature. Before use, these manganese complexes were sublimed, and their purity was checked by infrared spectroscopy.

Microanalyses were performed by Mr. Peter Borda of this department. Uncorrected melting points were determined with a Gallenkamp melting point apparatus. Infrared spectra were measured on cyclohexane solutions using a Perkin-Elmer Model 457 spectrometer and were calibrated against polystyrene and/or cyclohexane.

The ^1H nmr spectra were obtained using an extensively modified Varian HA-100 instrument. These spectra were recorded in the frequency sweep mode on carefully calibrated charts. All ^1H chemical shifts were recorded with tetramethylsilane as the internal reference. For ^{19}F measurements, the spectrometer was tuned to ca. 94.07 MHz and ca. 20% of trichlorofluoromethane was used as the internal reference for chemical shift calibration. Heteronuclear decoupling experiments with noise modulation used instrumentation already described in the literature.[9,10] Computer analysis of the nmr spectra were obtained with an IBM 360-67 computer and a modified version of the LAOCOON III program.[11]

The following procedure is representative of the methods used to synthesize the chelate complexes examined in this work.

Preparation of 1,2-Bis(dimethylarsino)-1,1-difluoroethanetricarbonylmanganese Chloride (1). A round-bottomed flask was charged with reagent grade benzene (50 ml). Following saturation of the solvent with nitrogen, pentacarbonylmanganese chloride (0.42 g, 1.82 mmol) was added together with the ligand 1,2-bis(dimethylarsino)-1,1-difluoroethane (0.5 g, 1.83 mmol). The reaction mixture was refluxed for 1 hr, cooled, and filtered. After removal of the solvent under reduced pressure, the resulting solid was washed with a small amount of light petroleum ether, dried under a high vacuum, and then sublimed (130°, 10^{-3} mm), yielding a pure sample of complex 1 (0.51 g, 62%).

The chelate complexes prepared during this work are summarized in Table I. The reaction conditions and analytical data are presented in Table II.

Results

In contrast to those obtained for the group VI metal carbonyl derivatives of $(CH_3)_2AsCH_2CF_2As(CH_3)_2$, the

(6) E. W. Abel and G. Wilkinson, *J. Chem. Soc.*, 1501 (1959).

(7) R. B. King in "Organometallic Synthesis," Vol. 1, J. J. Eisch and R. B. King, Ed., Academic Press, New York, N. Y., 1965, p 174.

(8) E. O. Brimm, M. A. Lynch, and W. J. Sesny, *J. Amer. Chem. Soc.*, 76, 3831 (1954).

(9) R. Ernst, *J. Chem. Phys.*, 45, 3845 (1966).

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

(11) LAOCOON III is a version of the least-squares nmr spectral fitting computer program described by S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, 41, 3863 (1964), modified by Mr. R. B. Malcolm, Chemistry Department, University of British Columbia.

Table I. The New Chelate Complexes[a]

1	3 = 3' = H; 4 = 4' = F; X = Cl
2	3 = 3' = H; 4 = 4' = F; X = Br
3	3 = 3' = H; 4 = 4' = F; X = I
4	3 = 4 = H; 3' = 4' = F; X = Cl
5	3 = 4 = H; 3' = 4' = F; X = Br
6	3 = 4 = H; 3' = 4' = F; X = I
7	3 = H; 3' = 4 = 4' = F; X = Cl
8	3 = H; 3' = 4 = 4' = F; X = Br
9	3 = H; 3' = 4 = 4' = F; X = I

[a] The numbering refers to B which is not intended to represent a fixed conformer in solution.

Table II. Analytical and Preparative Data for the New Chelate Complexes[a]

	Calcd C	Calcd H	Found C	Found H	Reaction time, hr	Yield, %	Mp, °C
1	24.1	3.15	23.9	3.19	1	62	149–153
2	21.9	2.86	21.8	2.78	0.5	81	171–173[b]
3	20.0	2.61	20.0	2.70	1.5	74	201–202
4	24.1	3.15	23.9	3.34	2	43	140–155[b]
5	21.9	2.86	21.8	2.85	0.5	23	157–159
6	20.0	2.61	20.3	2.86	2	21	186–188
7	23.2	2.81	23.2	3.01	0.25	55	145–149
8	21.2	2.56	21.2	2.79	1	74	173–187[b]
9	19.4	2.35	19.3	2.49	1.5	33	199–201

[a] The complexes were prepared as described in the Experimental Section except 4–6 which were eluted by petroleum ether–ether mixtures from an alumina column. [b] The compound melts with decomposition.

nmr spectra of the manganese derivatives $(CH_3)_2AsCH_2CF_2As(CH_3)_2Mn(CO)_3X$ **(1–3)** (X = Cl, Br, I) contain much more detail, and they were solved completely by iterative computer analyses. Figure 1 shows the methylene regions of the ^1H nmr spectra of the bromide complex, **2**.

The analyses of the proton spectra were complicated by two factors. Attempts to simplify the spectra by complete fluorine decoupling failed, probably because of the large chemical shift differences between the geminal pair of fluorine atoms. Also, the ^1H nmr spectra are very solvent dependent. Fortunately, the ^{19}F nmr spectra enabled the vicinal ^1H–^{19}F coupling constants to be estimated, and assignments of the transitions in the ^1H spectra could be made.

The ^{19}F spectrum of the same difluoromanganese chelate complex **2** (chloroform solution) is shown in Figure 2. Transitions in the normal spectrum (Figure 2A) are broadened by the interaction of the fluorine atoms with the arsenic methyl groups. By a ^{19}F–[^1H] noise-modulated heteronuclear decoupling experiment, the spectrum in Figure 2B was obtained in which both the arsenic methyl and methylene proton interactions have been removed.

It is interesting to note that the proton spectra of the bromide complex **2** in chloroform and benzene are best understood in terms of overlapping ABX subspectra. In each instance a fortuitous relationship between the magnitudes of some of the coupling constants and the chemical shift separation results in one of the subspectra showing fewer transitions than the other; that is, one of the subspectra corresponds to a deceptively simple ABX case.[12] If it is assumed that the relatively small coupling constants $J_{3'4'}$ and $J_{34'}$ are vicinal $^3J_{HF}$
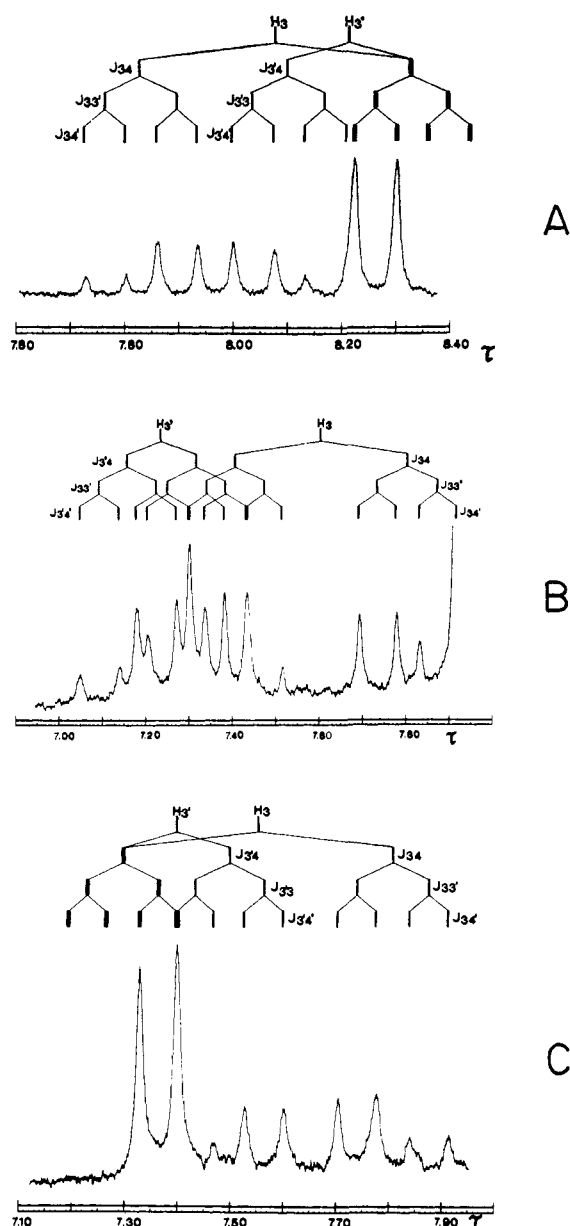
(12) L. D. Hall and R. B. Malcolm, unpublished results.

Figure 2. The ^{19}F nmr spectrum of $(CH_3)_2AsCH_2CF_2As(CH_3)_2$-$Mn(CO)_3Br$: A, normal spectrum; B, ^1H decoupled spectrum.

protons or fluorines had the higher chemical shifts. Thus the numbering of the nuclei in the tables that will be described below is arbitrary to the extent that the proton–fluorine coupling constants were not absolutely assigned nor were the absolute chemical shift assignments made.

The nmr spectra of the trifluoro derivatives **7–9** were very similar to those obtained for the related group VI metal carbonyl chelate complexes.[2,3] It was assumed that the relative signs of the coupling constants found in the present study would be the same.

The chemical shifts and coupling constants derived by iterative analyses of the nmr spectra of the chelate complexes **1–9** are presented in Tables III and IV.

Discussion

Characterization. The analytical data obtained for the new di(tertiary arsine) chelate complexes **1–9** are satisfactory (Tables I and II). The yields of the complexes do not reflect the ease of reaction since it is likely that some complexes decomposed slightly during sublimation. The generally lower yields of the difluoro complexes **4–6** can be accounted for by noting that the work-up of these derivatives involved chromatography in an attempt to separate the contaminating chelate complexes of the isomeric di(tertiary arsine), *meso*-1,2-bis(dimethylarsino)-1,2-difluoroethane.[3] This procedure was successful only in the case of the bromide chelate complex **5**. Fortunately the presence of the meso complexes together with the derivatives **4** and **6** did not interfere with the obtaining of good nmr data for the *d,l* complexes.

The infrared absorption frequencies for the carbonyl groups of the chelate complexes **1–9** are summarized in Table V. The complexes typically exhibit three almost equally intense absorptions in this region. Such a pattern is characteristic of the fac isomers, C, rather than the mer forms, D.[13] A recent X-ray determination of

Figure 1. The methylene regions of the ^1H nmr spectra of $(CH_3)_2$-$AsCH_2CF_2As(CH_3)_2Mn(CO)_3Br$ (**2**): A, C_6H_6 solution; B, $(CD_3)_2$-CO solution; C, $CHCl_3$ solution. The first-order assignment shown above each spectrum is solely intended as a diagramatic representation.

values, it follows that $J_{3'4}$ and J_{34} are also $^1H–^{19}F$ coupling constants, since they were found to have the same relative signs, while $J_{33'}$ corresponds to the geminal $^1H–^1H$ coupling constant.

The ^1H and ^{19}F nmr spectra of the difluoro derivatives **4–6** usually presented few problems. In one case, that of the bromide derivative **5** in acetone-d_6, the ^1H spectrum took on significant second-order characteristics due to the small chemical shift differences between the two protons (*ca.* 8 Hz) and it was necessary to solve the spectrum by several trial-and-error guesses. Since the coupling constant differences within the geminal and vicinal proton–fluorine pairs are very small, and because the fluorine nmr spectra are broadened by the arsenic methyl interactions, it was not possible to assign the geminal and vicinal J_{HF} values explicitly to individual fluorines nor was it possible to determine which of the
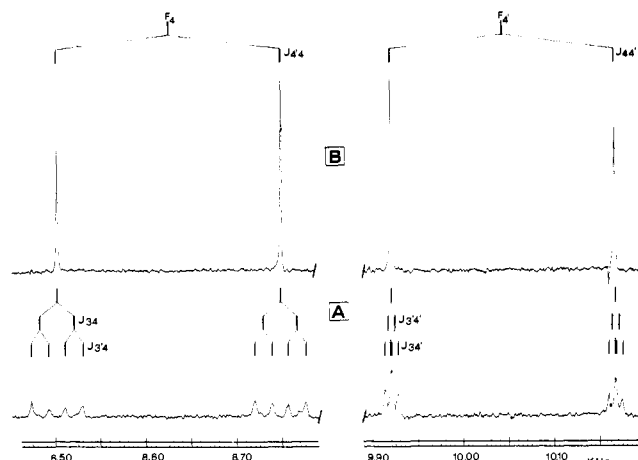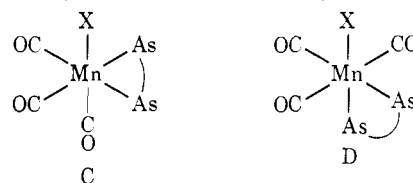

(13) R. J. Angelici, F. Basolo, and A. J. Poë, *J. Amer. Chem. Soc.*, **85**, 2215 (1963).

Table III. Chemical Shifts (τ and ϕ Values) for the Chelate Complexes 1-9

Compound	Solvent	3	3'	4	4'	Methyl groups			
1	CHCl₃	7.713	7.549	92.06	107.06	8.357	8.357	8.357	8.430
	(CD₃)₂CO	7.670	7.292	92.37	104.92	8.306	8.329	8.366	8.366
2	C₆H₆	8.079	8.197	91.45	106.42	8.530	8.660	8.806	8.959
	CHCl₃	7.673	7.546	91.79	106.62	8.273	8.273	8.358	8.484
	(CD₃)₂CO	7.607	7.272	92.28	104.64	8.252	8.273	8.312	8.360
3	CHCl₃	7.635	7.502	92.93	103.59	8.183	8.183	8.303	8.452
	(CD₃)₂CO	7.497	7.178	91.96	106.09	8.111	8.111	8.274	8.320
4	CHCl₃	4.146	214.42ᵃ	4.426	219.62ᵃ	8.218	8.313	8.373	8.386
	(CD₃)₂CO	3.861	214.06ᵃ	4.068	219.16ᵃ	8.309	8.341	8.370	8.469
5	CHCl₃	4.091	214.02ᵃ	4.454	218.66ᵃ	8.263	8.301	8.346	8.467
	(CD₃)₂CO	3.909	213.69ᵃ	3.987	219.21ᵃ	8.220	8.237	8.295	8.335
6	CHCl₃	3.998	213.73ᵃ	4.518	217.29ᵃ	8.150	8.150	8.339	8.447
	(CD₃)₂CO	3.883	213.49ᵃ	3.970	216.83ᵃ	8.119	8.144	8.209	8.309
7	CHCl₃	4.560	235.51	114.55	121.23	8.333	8.353	8.353	8.482
8	CHCl₃	4.443	234.27	114.42	120.92	8.219	8.219	8.313	8.395
	(CD₃)₂CO	4.261	232.51	114.78	119.46	8.191	8.191	8.227	8.324
9	CHCl₃	4.395	232.54	114.59	120.60	8.096	8.118	8.321	8.391

ᵃ The stereochemical assignment of the fluorine atoms was made arbitrarily.

Table IV. Coupling Constants (Hz) for the Chelate Complexes 1-9

Compound	Solvent	$J_{33'}$	J_{34}	$J_{34'}$	$J_{3'4}$	$J_{3'4'}$	$J_{44'}$
1	CHCl₃	−13.1	44.9	6.7	12.7	7.0	248.5
	(CD₃)₂CO	−13.1	40.6	7.9	15.2	9.5	245.7
2	C₆H₆	−13.1	40.5	7.4	17.2	7.3	247.2
	CHCl₃	−13.2	42.0	7.0	14.9	7.2	248.4
	(CD₃)₂CO	−13.3	39.9	7.9	15.0	9.5	246.2
3	CHCl₃	−13.1	40.5	7.7	14.5	8.2	245.1
	(CD₃)₂CO	−13.4	37.3	9.0	15.0	11.4	247.2
4	CHCl₃	52.8	10.3	17.4	16.9	−14.2	52.0
	(CD₃)₂CO	51.7	10.2	17.6	18.5	−14.6	53.1
5	CHCl₃	52.7	10.2	17.4	17.1	−15.3	51.9
	(CD₃)₂CO	51.6	10.0	17.8	18.7	−15.3	53.0
6	CHCl₃	52.6	9.9	17.9	17.1	−15.6	51.7
	(CD₃)₂CO	52.6	9.8	18.6	17.5	−15.9	51.3
7	CHCl₃	48.5	26.4	7.2	−10.9	−12.8	250.4
8	CHCl₃	48.5	26.2	7.3	−10.6	−13.2	251.4
	(CD₃)₂CO	48.1	24.8	7.9	−10.8	−13.8	252.2
9	CHCl₃	48.3	25.2	7.5	−10.9	−13.5	251.0

Table V. Carbonyl Infrared Stretching Frequencies (± 2 cm⁻¹) for the Chelate Complexes 1-9ᵃ

1	2038	1970	1923
2	2034	1967	1922
3	2030	1968	1924
4	2038	1967	1921
5	2036	1971	1919
6	2032	1971	1923
7	2038	1973	1925
8	2038	1973	1926
9	2034	1973	1927

ᵃ Cyclohexane solvent, 0.1 and 0.5 mm KBr cells.

the structure of a six-membered ring manganese chelate complex Cl(CO)₃MnAs(CH₃)₂CH₂CH₂CH₂As(CH₃)₂ which has a carbonyl infrared spectrum similar to those obtained for the chelate complexes examined in the present work[14] supports the fac assignment.

As expected, the frequencies of these absorptions are similar to those derived from related derivatives such as fac-1,2-bis(diphenylphosphino)ethane(tricarbonyl)-manganese halides[15] except that the complexes 1-9 have

(14) W. R. Cullen, L. D. Hall, J. T. Price, and G. Spendjian, *J. Amer. Chem. Soc.*, **96**, 410 (1974); C. A. Bear and J. Trotter, *J. Chem. Soc., Dalton Trans.*, 673 (1973).

(15) A. G. Osborne and M. H. B. Stiddard, *J. Chem. Soc.*, 4715 (1962).

absorptions *ca.* 5–15 cm⁻¹ higher in energy. This is probably due to the greater electronegativity of the two-carbon bridge of the di(tertiary arsines).

Chelate Ring Conformations. At the outset of this discussion, it is important to note that, although a particular conformation of a five-membered chelate ring may be very highly favored, it is not possible to assign a single, specific conformation to the chelate ring. This follows from the observation that the energy barriers to conformational inversion are relatively small,[5] and thus the conformations as determined by nmr will be to some extent time averaged.

(a) Vicinal Coupling Constants. We will start the discussion with the difluoro derivatives 1–3. The chelate rings in these complexes may exist in solution as an equilibrium mixture of two conformers E and F. Un-

E   F
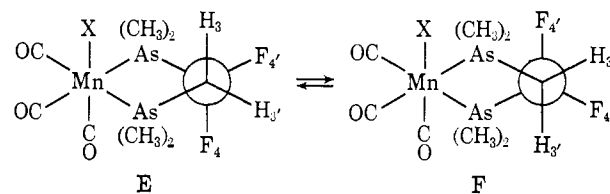
fortunately, both of these "locked" conformers are anticipated to exhibit very similar coupling constants. Therefore, the data cannot be readily interpreted on the

basis of dihedral angle relationships[16,17] of vicinal coupling constants, in terms of their relative conformer populations, even though it is tempting to suggest that form E would be favored by both steric and dipolar interactions between the manganese–halogen and fluorine atoms on the five-membered chelate ring.

The data for the difluoro derivatives 4–6 indicate unequivocally that the fluorine substituents have gauche relationships to vicinal protons and themselves, as in G.

G ⇌ H
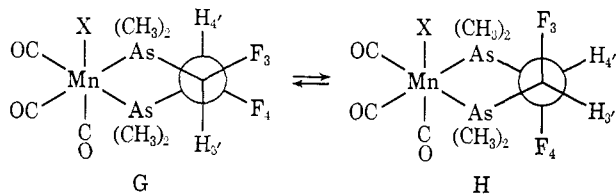
Thus the vicinal $^1H-^1H$ coupling constants are relatively large (ca. 10 Hz) while the vicinal $^1H-^{19}F$ coupling constants are relatively small (ca. 17–19 Hz). It seems that an equilibrium including species G and H would distinctly favor the former conformation. It is also important to note that the trans $^1H-^1H$ coupling constants (ca. 10 Hz) are significantly higher than those corresponding values derived from the related group VI metal carbonyl complexes (ca. 7–8 Hz). This difference will be considered later in the discussion.

Vicinal $^1H-^{19}F$[17] and $^{19}F-^{19}F$[18] coupling constant data indicate that the trifluoro chelate complexes 7–9 probably adopt similar conformations to those proposed for the related group VI complexes we have considered in previous work.[2,3] On comparison with the largest vicinal $^3J_{HF}$ values (ca. 15–19 Hz) obtained from the group VI trifluoro derivatives, the $^1H-^{19}F$ coupling constants in the manganese trifluoro derivatives 7–9 (ca. 26 Hz) seem to indicate a greater "axial" preference for the hydrogen atom, all other things being equal. However, the electronic and steric effects of changing the metal atom and its substituents have not been delineated, so it is unwise at this time to attribute all these coupling constant changes to purely conformational alteration. It is interesting to note that the nmr spectra of compounds 7–9 exhibit peaks corresponding to only one isomer. Possibly only one of the chelate complexes I or J is formed in the reaction. If the fluorine

I   J
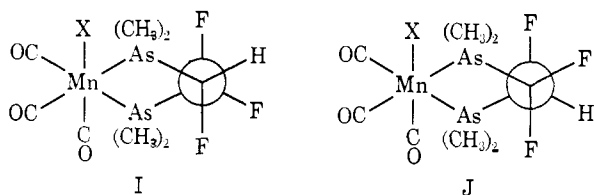
and hydrogen substituents in the two isomers had corresponding identical chemical shifts and coupling constants, the solution could contain a mixture of both I and J. However, this seems unlikely in view of the nmr results obtained for the chelate complexes 4–6 which had

two "equatorial" fluorine atoms significantly differing in chemical shift (ca. ϕ5). Thus we suggest that either one of the two possible forms I or J is formed specifically in the preparations of these derivatives.

(b) Chemical Shifts. As discussed in our previous studies,[3] the chemical shift data for the ethane-bridge substituents of the chelate complexes corroborate the interpretations based on the dihedral angle dependencies of vicinal coupling constants. In the complexes which had substituents predominantly favored in "axial" or "equatorial" orientations, it was found that the chemical shift of the "axial" proton of a geminal pair of protons is significantly higher than that of the "equatorial" methylene proton.[19]

In contrast, the difluoro complexes 1–3 studied in the present work exhibit relatively small chemical shift differences between the geminal protons. Indeed, by changing the solvent, these protons are sometimes observed to change their order. The ^1H nmr spectra in Figure 1 illustrate this phenomenon. In the spectrum determined in benzene (Figure 1A), H_3 has a lower chemical shift than $H_{3'}$. This order is reversed in the spectra determined in acetone-d_6 (Figure 1B) and chloroform (Figure 1C). These results are consistent with an equilibrium between the two conformations E and F. On the other hand, it does not seem possible to account for the variations of the chemical shifts of the arsenic methyl groups at this time.

(c) Solvent Effects. It is well known that conformers (or rotamers) having the higher dipole moment are more favored by solvents of higher dielectric constant,[20] and it was hoped that by varying the solvents in which the spectra were determined regular changes might be induced in the conformations and hence the nmr parameters of 1–9.

The largest variations in coupling constants (ca. 20%) of all the chelate complexes we have studied occur in the difluoromanganese chelate complexes 1–3. Unfortunately, the relative conformer populations have not been determined for these chelate derivatives, making it difficult to draw specific conclusions about the solvent dependency of the coupling constants, even though it seems that the conformational equilibrium is shifted in some direction with the solvent variations.

Solvent studies of the complexes 4–6 were made to investigate changes in the conformer populations as were carried out on the related group VI chelate derivatives. In the present study, the vicinal $^1H-^1H$ coupling constants indicate that the conformational equilibrium between G and H is not appreciably shifted. This may be taken as further evidence for the preference of the fluorine atoms to exist gauche to one another as in G.

The small variations in the $^1H-^{19}F$ and $^{19}F-^{19}F$ coupling constants in the trifluoro derivatives 7–9 can be accounted for in terms of those changes anticipated for rigid molecules,[21] and thus conformational changes would not be detected.

(16) For a discussion of $^1H-^1H$ vicinal coupling constants see (a) M. Karplus, J. Chem. Phys., 30, 11 (1959); (b) J. Amer. Chem. Soc., 85, 2870 (1963); (c) E. B. Whipple, J. Magn. Resonance, 5, 163 (1971).

(17) For a discussion of $^1H-^{19}F$ vicinal coupling constants see (a) A. M. Ihrig and S. L. Smith, J. Amer. Chem. Soc., 92, 751 (1970); (b) K. L. Williamson, Y.-F. L. Hsu, F. H. Hall, S. Swager, and M. S. Coulter, ibid., 90, 6717 (1968); (c) G. Govil, Mol. Phys., 21, 953 (1971); (d) M. S. Gopinathan and P. T. Narasimhan, ibid., 21, 1141 (1971).

(18) L. D. Hall, R. N. Johnson, J. Adamson, and A. B. Foster, Chem. Commun., 463 (1970).

(19) Similar results have been observed for propylenediamine chelate complexes: (a) S. Yanyo, H. Ito, Y. Koike, J. Fujita, and K. Saito, Bull. Chem. Soc. Jap., 42, 3184 (1969); (b) S. Yanyo, Y. Koike, J. Fujita, and K. Saito, Chem. Commun., 460 (1969).

(20) (a) R. J. Abraham, L. Cavalli, and K. G. R. Pachler, in "Nuclear Magnetic Resonance in Chemistry," B. Pesce, Ed., Academic Press, New York, N. Y., 1965, p 111; (b) N. Sheppard, Advan. Spectrosc., 1, 288 (1959); (c) R. J. Abraham, J. Phys. Chem., 73, 1192 (1969).

(21) A. M. Ihrig and S. L. Smith, J. Amer. Chem. Soc., 94, 34 (1972).

Table VI. Coupling Constants (Hz) for the Chelate Complexes Complexes 1-3, Their Sums,[a] and Lambert "R" Factor Data

Compound	Solvent	J_{34}	$J_{34'}$	$J_{3'4}$	$J_{3'4'}$	$\Sigma^3 J$	"R"	ϕ (deg)
1	CHCl₃	44.9	6.7	12.7	7.0	71.3	2.67	61
	(CD₃)₂CO	40.6	7.9	15.2	9.5	73.2	2.17	58
2	C₆H₆	40.5	7.4	17.2	7.3	72.4	1.94	57
	CHCl₃	42.0	7.0	14.9	7.2	71.1	2.24	59
	(CD₃)₂CO	39.9	7.9	15.0	9.5	72.3	2.16	58
3	CHCl₃	40.5	7.7	14.5	8.2	70.9	2.19	58
	(CD₃)₂CO	37.3	9.0	15.0	11.4	72.7	2.03	57

[a] For $(CH_3)_2AsCH_2CF_2As(CH_3)_2M(CO)_4$ in C_6H_6, $\Sigma^3 J$ is 72 (M = Cr), 73 (M = Mo), 72 (M = W). These data were obtained from spectra run on a Varian T-60 instrument.

(d) Cis-Axial Manganese Substituent Effects. The effects of alterations of the cis-axial halogen substituent on the coupling constants of the substituents on the chelate ring may be most easily delineated with the nmr parameters of the difluoro chelate complexes 1-3.

In order to proceed we will make the simplifying assumption that any through-bond electronic effects of the cis-axial halogen atom will be reflected equally in the Karplus coefficients[16,17] of the ethane-bridge substituents of E and F. Since the $^3J_{HF}$ values for 1-3 are likely weighted averages of the vicinal coupling constants of the individual conformers E and F, we cannot calculate the dihedral angles of these conformers directly as in our previous work.[3] However, the sums of the four vicinal ^1H–^{19}F coupling constants provide valuable information, and these are listed in Table VI as well as the $^3J_{HF}$ values for 1-3, the sums of $^3J_{HF}$ for the group VI tetracarbonyl analogs, and dihedral angles calculated from the Lambert "R" factors.

Assuming tetrahedral dispositions[22–24] about the ethane-bridge carbons, we may write

$$\sum {}^3J_{HF} = 2A \cos^2 \phi + A \cos^2 (120 - \phi) + B \cos^2 (120 + \phi) \quad (1)$$

Since $A \approx {}^2/_3 B$,[17c] eq 1 simplifies to

$$\sum {}^3J_{HF} = A \cos^2 \phi + \cos^2 (120 - \phi) + 1.5 \cos^2 (120 + \phi) \quad (2)$$

If E and F have the same dihedral angle about the C–C bond and all other bond angles and bond lengths are the same, then eq 2 may be used to obtain the Karplus coefficients. For example, for a dihedral angle of 58° (vide infra), we calculate $\Sigma^3 J_{HF}$ to be 2.280A; thus for a $\Sigma^3 J_{HF}$ value 70.9 Hz (as in 3, CHCl₃ solution), A and B are 31.1 and 46.6 Hz, respectively. These values are in general agreement with those obtained from direct calculations on "locked" five-membered ring chelate complexes.[3]

On the other hand, it is possible that conformers E and F have different dihedral angles, while all the remaining bond angles and bond lengths are the same. In that case, it is interesting to calculate the $\Sigma^3 J_{HF}$ values for dihedral angles of 56° (E) and 60° (F) for example. Using the Karplus coefficients calculated above, we

find that $\Sigma^3 J_{HF}$ (56°) and $\Sigma^3 J_{HF}$ (60°) are significantly different being 71.8 and 70.0 Hz, respectively, spanning a range of ca. 2 Hz. For equal populations of E and F, we would anticipate that $\Sigma^3 J_{HF}$ would be an average of these two values, 70.9 Hz, the same $\Sigma^3 J_{HF}$ value obtained for the intermediate angle ϕ 58°. On the other hand, for varying proportions of E and F, we would expect $\Sigma^3 J_{HF}$ values intermediate between 70.0 and 71.8 Hz.

The sums of the $^3J_{HF}$ values should also be sensitive to the electronegativity differences in the ethane-bridge substituents. Because of the inverse proportionality of Karplus coefficients to the electronegativity of the substituents,[25,26] we would anticipate that $\Sigma^3 J_{HF}$ would be greater for the iodo complex 3 than the chloro complex 1, for a given solvent.

It is interesting now to consider the observed $\Sigma^3 J_{HF}$ values in view of these dihedral angle and electronegativity considerations. For a given solvent, we find that the $\Sigma^3 J_{HF}$ values are virtually constant, all falling in the range ca. 71–73 Hz. The data may be interpreted in several different ways: (1) the dihedral angles of E and F are the same and the ethane-bridge substituent electronegativities do not vary, (2) the dihedral angles of E and F are different and the changes in electronegativities of the ethane-bridge substituents cancel these effects, or (3) variations on these effects are insufficient to cause appreciable coupling constant sum variations. It seems that (3) is the most reasonable alternative.

The sums of the vicinal $^3J_{HF}$ values for the group VI analogs are very similar to those of the manganese derivatives. Thus, it appears that changing from a group VI to a manganese metal atom with appropriate adjustment of the remaining ligands neither results in any significant electronic variation in the chelating di-(tertiary arsine) nor does it appreciably affect the bond angles and bond lengths in the ethane bridge. Consequently, it appears that the vicinal ^1H–^{19}F coupling constants may be *compared and interpreted on a conformational basis*.

Turning now to the vicinal coupling constants themselves, it seems that the conformational preferences of the chelate rings in E and F are definitely changing with alterations in the cis-axial substituent. For example, for 1 (CHCl₃, solution) J_{34} is reduced from 44.9 to 40.5 Hz when a chloro substituent is replaced by an iodo substituent. This change must arise from a shift in the populations of E and F, because it does not appear to arise from differences in the dihedral angles of E and F or variations in the electronegativities of the ethane-bridge substituents. Both steric and dipolar interaction

(22) This treatment like those of other workers,[23] assumes a tetrahedral disposition about the carbon atoms in the ethane bridge. Recent reports[24] indicate that the assumption may not be valid.

(23) (a) J. L. Sudmeier, G. L. Blackmer, C. H. Bradley, and F. A. L. Anet, J. Amer. Chem. Soc., **94**, 757 (1972); (b) J. L. Sudmeier and G. L. Blackmer, Inorg. Chem., **10**, 2010 (1971); (c) J. B. Lambert, Accounts Chem. Res., **4**, 87 (1971); (d) H. R. Buys, Recl. Trav. Chim. Pays-Bas, **88**, 1003 (1969).

(24) (a) R. E. Cramer, Inorg. Chem., **11**, 1019 (1972); (b) J. B. Lambert, J. J. Popay, E. S. Magyar, and M. K. Neuberg, J. Amer. Chem. Soc., **95**, 4458 (1973).

(25) K. L. Williamson, J. Amer. Chem. Soc., **85**, 516 (1963).
(26) L. D. Hall and D. L. Jones, Can. J. Chem., **51**, 2925 (1973).

may be involved to account for this population shift (*vide supra*).

Dihedral angles calculated by the "*R*" factor method[23c,24b] do not seem to be reliable on an absolute basis; however, their qualitative application to a homologous series seems valid. The angles calculated by this method (Table VI) are very similar, all falling in the range $58 \pm 1°$, except for the chloro chelate complex 1 (determined in chloroform). These values are in good agreement with those obtained by calculation and X-ray studies of related group VI carbonyl complexes[3,27] and do not seem to be greatly overestimated.[24b] There seems to be slight trend for the dihedral angles to decrease in the order Cl > Br > I. In the absence of other structural data, it is difficult to determine whether or not this trend is significant and whether these alterations, if appreciable, affect other bond angles in the chelate rings. In any event, we can conclude that the solvent effects are at least as important as those changes caused by halogen substituent variations. We calculate that solvent changes[21] may cause an apparent deviation of as much as $\pm 2°$ in the dihedral angle. These alterations are sufficient to account for the deviations between angles determined from the nmr spectra taken in different solvents. The data could be taken to indicate that an equilibrium exists between conformers with differing dihedral angles, but the evidence does not seem clear cut in favor of this interpretation.

Only small changes were observed for the coupling constants of the chelate complexes 4–6 for a given solvent. The alterations are on the borderline of experimental uncertainty in measuring the coupling constants (± 0.1 Hz). Since we have shown that the electronic and geometric effects of changing from a group VI metal to a manganese atom are likely not conformationally important, it seems reasonably certain that the conformational preferences for K in the manganese
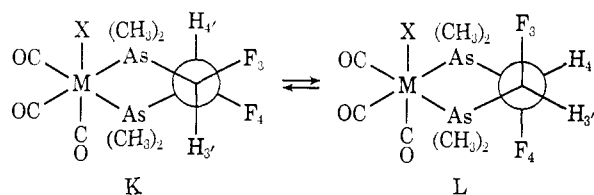
complexes are indeed greater than those in the group VI complexes as we have previously suggested in the discussion. Moreover it also appears that the conformational preferences in the manganese derivatives 4–6 are almost equally affected by the various halogen substituents in the cis-axial position on the manganese atom.

Similar considerations may be applied to the trifluoro chelate complexes 7–9. It seems that in contrast to the group VI trifluoro derivatives, the conformer in which the hydrogen atom adopts an "axial" position on the chelate ring M has an appreciable population in equilibrium with N. This conclusion is based on the magnitudes of the gauche $^1\text{H}-^{19}\text{F}$ coupling constants, which

(27) X-Ray crystallographic investigations of the related group VI metal carbonyl derivatives have revealed that the solids are highly disordered: I. W. Nowell, S. Rettig, and J. Trotter, *J. Chem. Soc., Dalton Trans.*, 2381 (1972).
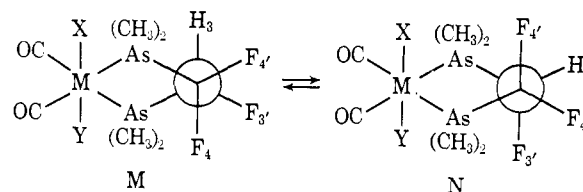
are *ca*. 25 Hz in the manganese derivatives and *ca*. 15–19 Hz in the group VI metal chelate complexes. For these compounds, as in the difluoro derivatives 4–6, apparently steric and/or dipolar interactions differ significantly from those in the related group VI chelate complexes. In view of these rather large differences, however, it is possible that the average dihedral angles of the group VI and manganese derivatives are not equal, and this inequality may at least partially give rise to the different gauche $^1\text{H}-^{19}\text{F}$ coupling constants in the group VI and manganese complexes.

At this time we cannot attach any significance to the small variations in coupling constants of the trifluoro complexes 7–9 with changes in halogen substituent. Perhaps when the precise sources of the steric and dipolar interactions in these compounds are determined, these differences will take on more meaning.

(e) The Arsenic Methyl Groups. For all the chelate complexes examined in this work, the arsenic methyl interactions with the cis-axial metal substituent seem relatively unimportant; extreme conformations of the derivatives 1–6 are anticipated to have very similar interactions of this nature, due to the symmetry of the chelated ligands. However, it may be that the interactions of the arsenic methyl groups with the other ethane-bridge substituents are significant. The delineation of these interactions cannot be made from the data we have already reported nor from this study. Conversely, the arsenic methyl interactions may have more significance in the trifluoro complexes 7–9. Unfortunately, since we cannot determine which of the two possible isomers I or J is formed, further discussion is not possible.

Since the chelate rings of several of the chelate complexes in this and our other studies seem to exist as an equilibrium mixture of two conformers, we have carried out variable temperature investigations on a selected number of derivatives. It is our intention to report the results of these experiments in a subsequent paper. As well, this work suggests that the interactions of the substituents on the arsenic donor atoms may be fruitfully studied. The conformational properties of six-membered chelate complexes of the type $(CO)_3Cr(L-L)$ and $X(CO)_3Mn(L-L)$, $(L-L)$ = di(tertiary arsine), are currently being investigated,[14,28] and it does seem that arsenic methyl interactions with axial ligands are responsible for "locking" the six-membered ring in Cl-$(CO)_3Mn(CH_3)_2AsCH_2CH_2CH_2As(CH_3)_2$.

(28) W. R. Cullen, L. D. Hall, J. T. Price, and G. Spendjian, *Inorg. Chem.*, in press.