

proton ($^3J_{\text{HH}} = 7.3$ Hz). The lower field methyl is split by phosphorus ($^3J_{\text{PH}} = 15.9$ Hz) and by the methine proton ($^3J_{\text{HH}} = 7.3$ Hz). These are in reasonable agreement with the coordination compounds of the isopropyl-containing ligands discussed above.

In general, most of the proton data other than for the methyl groups are rather uninformative. The ethylene bridge region is too complex (presumably ABCDXY or A₂BCXY patterns) for resolution and is often superimposed on the methylene region of the alkyl groups. However, correct integration ratios of aryl:alkyl protons were obtained for all compounds. The methyl group in Ph₂PCH₂CH₂PPhMe appears as a doublet ($^2J_{\text{PH}} = 3.2$ Hz) at τ 8.77 ppm and in the dioxide of the same ligand as a doublet ($^2J_{\text{PH}} = 12.4$ Hz) at τ 8.30

ppm. The methyl group in Ph₂PCH₂CH₂PPhEt appears as a doublet ($^3J_{\text{PH}} = 15.2$ Hz) of triplets ($^3J_{\text{HH}} = 6.0$ Hz) at τ 9.12. In the dioxide the corresponding values are $^3J_{\text{PH}} = 17.1$ Hz, $^3J_{\text{HH}} = 7.3$ Hz, and τ 8.93.

The infrared spectra of the coordination compounds in the carbonyl stretching are helpful in confirming the structural assignments. For example, the bridging ligand complexes



and the monodentate ligand complexes, IV, both have the absorptions expected for local symmetry C_{4v} at the metal.³⁶ Likewise the chelate complexes have the absorptions expected for C_{2v} local symmetry.

(36) L. M. Haines and M. H. B. Stiddard, *Advan. Inorg. Chem. Radiochem.*, **12**, 53 (1969).

A Nuclear Magnetic Resonance Study of Some Five-Membered Rings in Chelate Complexes of the Group VI Metal Carbonyls

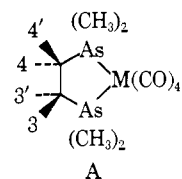
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Abstract: The synthesis of some new di(tertiary arsine) and di(tertiary phosphine) chelate derivatives of group VI hexacarbonyls is described. Parameters determined from analysis of the nmr spectra of the ligands and complexes are interpreted in terms of ligand rotamer populations and of conformational preferences of the chelate rings. The effects of systematic variations of solvent, donor atoms, and metal atoms are discussed. Changes in the puckering of the chelate rings induced by metal atom variations are predicted. Calculations of the dihedral angles and coefficients in the Karplus relationships pertaining to these complexes are also described.

In a recent report² we described the synthesis of a number of chromium carbonyl complexes of substituted ditertiary arsines A (M = Cr; 3 = Si(CH₃)₃, SiCl₃, F, Cl, CN; 3', 4, and 4' = H; and 3 = H; 3', 4, and 4' = F). The ligands were deliberately chosen so that the nmr spectra of their chelate complexes would be suitable for complete analysis. As anticipated, we found that a "bulky" substituent such as a trimethylsilyl group adopted an "equatorial" orientation on the five-membered chelate ring, but unexpectedly, a fluorine substituent showed a strong "axial" preference.^{2,3} Other substituents such as chlorine and a cyano group did not seem to strongly favor particular orientations.

The object of the present investigation was to systematically examine the effects of varying the transition metal atom, donor atom, and solvent on the conformations of a number of related chelate complexes. Thus complexes of type A (M = Mo and W) were prepared using many of the same ditertiary arsine ligands used to synthesize the analogous chromium



chelate complexes.² In addition, we also describe five-membered ring chelate complexes obtained from four ligands not considered in our earlier work. Future work will be concerned with variations in ring size and the effect of cis and trans substituents on the conformations of the chelate ring.

Experimental Section

Dimethylarsinic acid, the group VI hexacarbonyls, and the various olefins were purchased commercially and were used without further purification. Tetramethyldiarsine was obtained by the reduction of dimethylarsinic acid in 2 M hydrochloric acid with hypophosphorous acid;⁴ the diarsine was used without further purification. 1,2-Bis(dimethylphosphino)-1,1,2-trifluoroethane (**1**) was prepared by the photolytic addition of tetramethyldiphosphine to trifluoroethylene as described by Haszeldine and coworkers.⁵ 2,3-Dimethylarsino-1,1,1,2,3,3-hexafluoropropane was synthesized by a previously published method,⁶ but the yield of this compound

(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 fulfillment 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, *Chem. Commun.*, 625 (1970).

(4) V. Auger, *C. R. Acad. Sci.*, **142**, 1151 (1906).

(5) R. Fields, R. N. Haszeldine, and N. F. Wood, *J. Chem. Soc. C*, 744 (1970).

(6) W. R. Cullen and N. K. Hota, *Can. J. Chem.*, **42**, 1123 (1964).

was considerably improved when the reactants were irradiated. Two of the ditertiary arsines used in this paper have not been described before and their preparations are given in detail below. The remaining ligands were synthesized as previously described.²

All reactions, unless otherwise noted, were carried out in sealed Pyrex Carius tubes. Decomposition of air-sensitive starting materials and products was avoided by working in a nitrogen atmosphere. Volatile compounds were manipulated in a conventional vacuum system, while involatile liquid samples were handled by syringe techniques. A Swagelok fitting equipped with an injection gasket⁷ enabled the transfer of air-sensitive, involatile liquids to the Carius tubes.

Microanalyses were performed by Mr. Peter Borda of this Department or by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Uncorrected melting points were determined with a Gallenkamp melting point apparatus. Mass spectra were obtained with an AEI-MS-9 instrument with direct introduction of solid samples.

Infrared spectra were measured on a Perkin-Elmer 457 spectrometer and were calibrated against polystyrene and/or cyclohexane. Spectra of the new ditertiary arsine and phosphine chelate complexes were run on cyclohexane solutions in potassium bromide or calcium fluoride cells.

The ¹H nmr spectra were obtained using a Varian A-60, XL-100, or an extensively modified HA-100 spectrometer. The majority of these spectra were recorded in the frequency sweep mode on carefully calibrated charts using the HA-100 instrument. Unless otherwise noted, all ¹H chemical shifts were recorded with tetramethylsilane as the internal reference. For ¹⁹F measurements, the Varian HA-100 spectrometer was tuned to 94.07 MHz and *ca.* 20% of trichlorofluoromethane was used as the internal reference for chemical shift calibration. Computer analyses of the nmr spectra were obtained with an IBM 360-67 computer and a modified version of the LAOCOON III program.⁸ Heteronuclear decoupling experiments with noise modulation used instrumentation already described in the literature.^{9,10}

Reaction of Tetramethyldiarsine with 1,1-Difluoroethylene. A Carius tube was evacuated, cooled in liquid nitrogen, and charged with the diarsine (7.3 g, 34 mmol) and the olefin (4.1 g, 6.4 mmol). After sealing, the tube was irradiated for 24 hr with a 200-W Hanovia ultraviolet lamp placed at a distance of *ca.* 20 cm. The tube was continuously shaken and cooled with a stream of air. When the reaction was completed, the tube was cooled in liquid nitrogen and opened to a vacuum system, and the volatile contents were removed, leaving a residue (7.9 g, 84%) of the colorless, air-sensitive, liquid product, 1,2-bis(dimethylarsino)-1,1-difluoroethane (2). *Anal.* Calcd: C, 26.3; H, 5.15. Found: C, 26.5; H, 5.25.

Reaction of Tetramethyldiarsine with 1,2-Difluoroethylene. A Carius tube was charged as described for the previous preparation with the diarsine (8.7 g, 41 mmol) and a mixture of *cis*- and *trans*-1,2-difluoroethylene (3.3 g, 52 mmol). After irradiation of the reaction mixture for 120 hr, the contents of the tube were worked up in the usual manner yielding the product (10.1 g, 90%), 1,2-bis(dimethylarsino)-1,2-difluoroethane (3). *Anal.* Calcd: C, 26.3; H, 5.15. Found: C, 26.6; H, 5.14.

Subsequent nmr experiments showed that the product consisted of two compounds. The major component (*ca.* 75% of the total) was isolated by gas chromatography on a 10% FFAP on Chromosorb W column at 205°. Computer analysis of the nmr spectrum of this isomer showed it to be the racemic ligand. Details of the assignment to the racemic ditertiary arsine will be presented below. Experiments on a reduced scale with the pure *cis* and *trans* olefins showed that approximately the same 1:3 proportions of *meso*- and *rac*-1,2-bis(dimethylarsino)-1,2-difluoroethane (3) were formed as in the reaction with the mixture of the two olefins; however, the *trans* reacted more easily than the *cis*.

All the new chelate complexes 4–20 were prepared by heating the ligand with the appropriate group VI hexacarbonyl in benzene solution² except (CH₃)₂AsCH(CN)CH₂As(CH₃)₂Mo(CO)₆ (14) which was obtained by the following procedure.

Preparation of 1,2-Bis(dimethylarsino)-1-cyanoethane(tetracarbonyl)molybdenum (14). A round-bottomed flask was charged

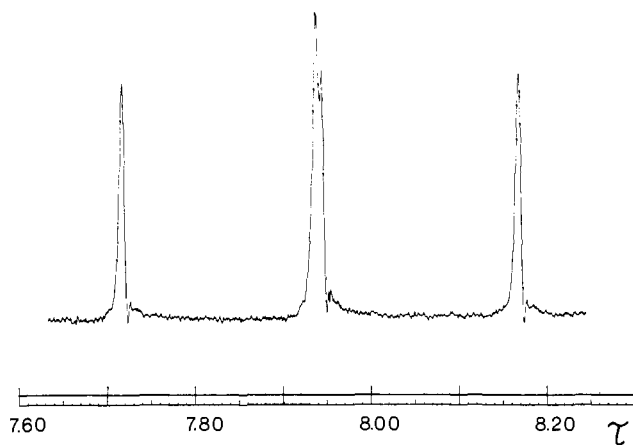


Figure 1. Partial ¹H nmr spectrum (100 MHz) of neat (CH₃)₂AsCF₂CH₂As(CH₃)₂.

Table I. New Chelate Complexes^{a,b}

| | |
|----|---|
| 4 | 3 = Si(CH ₃) ₃ ; 3', 4, and 4' = H; M = Mo |
| 5 | 3 = Si(CH ₃) ₃ ; 3', 4, and 4' = H; M = W |
| 6 | 3' = F; 3, 4, and 4' = H; M = Mo |
| 7 | 3 = H; 3', 4, and 4' = F; M = Mo |
| 8 | 3 = H; 3', 4, and 4' = F; M = W |
| 9 | 3 = H; 3', 4, and 4' = F; M = Cr |
| 10 | 3 = H; 3', 4, and 4' = F; M = Mo |
| 11 | 3 and 3' = H; 4 and 4' = F; M = Cr |
| 12 | 3 and 3' = H; 4 and 4' = F; M = Mo |
| 13 | 3 and 3' = H; 4 and 4' = F; M = W |
| 14 | 3 = CN; 3', 4, and 4' = H; M = Mo |
| 15 | 3 = CN; 3', 4, and 4' = H; M = W |
| 16 | 3 and 4 = F; 3' and 4' = H; M = Cr |
| 17 | 3 and 4 = F; 3' and 4' = H; M = Mo |
| 18 | 3 = CF ₃ ; 3', 4, and 4' = F; M = Cr |
| 19 | 3 = CF ₃ ; 3', 4, and 4' = F; M = Mo |
| 20 | 3 = CF ₃ ; 3', 4, and 4' = F; M = W |

^a The numbering refers to A which is not intended to represent a fixed conformer in solution. ^b In 9 and 10 As is replaced by P in A.

with 30 ml of reagent grade dioxane saturated with nitrogen, 2,5-norbornadiene(tetracarbonyl)molybdenum (0.5 g, 1.66 mmol), and 1,2-bis(dimethylarsino)-1-cyanoethane (0.44 g, 1.66 mmol). The mixture was refluxed for 15 min. After cooling and filtering the solution, the solvent was removed under vacuum and the product crystallized from a mixture of benzene and light petroleum ether, yielding pure 1,2-bis(dimethylarsino)-1-cyanoethane(tetracarbonyl)molybdenum (14, 0.38 g, 49%).

The chelate complexes prepared for investigation are listed in Table I. Preparative and analytical data are summarized in Table II.

Results

The ¹H and ¹⁹F nmr spectra of the trifluoro ditertiary phosphine (CH₃)₂PCFHC₂P(CH₃)₂ (1) were simplified and analyzed with the aid of ¹H–¹⁹F, ¹H–³¹P, ¹⁹F–¹H, and ¹⁹F–³¹P heteronuclear decoupling experiments; nevertheless, all the coupling constants and chemical shifts could not be exactly obtained. The chemical shift separation between the geminal fluorine atoms is insufficient to yield a completely first-order ¹⁹F spectrum. The outer multiplets of the AB “quartet” are not intense enough to be observed and it was necessary to estimate the values of the chemical shift difference δAB as well as the geminal ¹⁹F–¹⁹F coupling constant J_{AB}, in order to obtain sufficient data to analyze the remainder of the spectrum. These approximations were made using data from the related ditertiary arsine.

The ¹H nmr spectrum of the methylene protons of (CH₃)₂AsCH₂CF₂As(CH₃)₂ (2) is shown in Figure 1.

(7) M. C. Waldman, *J. Chem. Educ.*, **46**, 364 (1969).

(8) 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.

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

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

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

| Complex | Calcd, % | | Found, % | | Rxn time, hr | Rxn temp, °C | Yield, % | Mp, °C |
|-----------------|----------|------|----------|------|--------------|--------------|----------|----------------------|
| | C | H | C | H | | | | |
| 4 | 30.1 | 4.67 | 30.0 | 4.79 | 2.5 | 150 | 38 | 109–111 |
| 5 | 25.8 | 3.99 | 25.6 | 3.90 | 6 | 135 | 32 | 127–128 |
| 6 | 25.9 | 3.26 | 25.9 | 3.16 | 2 | 140 | 40 | 151–152 |
| 7 | 24.0 | 2.62 | 23.9 | 2.51 | 2 | 150 | 64 | 162–166 |
| 8 | 20.4 | 2.23 | 20.8 | 2.15 | 24 | 150 | 33 | 197–198 |
| 9 | 32.6 | 3.56 | 32.5 | 3.63 | 3 | 145 | 61 | 205–215 ^b |
| 10 | 29.2 | 3.18 | 29.3 | 3.08 | 1.5 | 145 | 55 | 190–193 ^b |
| 11 | 27.4 | 3.22 | 27.7 | 3.21 | 2 | 150 | 50 | 169–170 |
| 12 | 24.9 | 2.93 | 24.9 | 2.99 | 2 | 150 | 77 | 151–154 ^b |
| 13 | 21.1 | 2.48 | 21.3 | 2.49 | 18 | 150 | 11 | 176–177 |
| 14 ^c | 28.1 | 3.21 | 28.1 | 3.22 | 0.25 | <i>d</i> | 49 | 161–163 |
| 15 | 23.6 | 2.71 | 23.5 | 2.66 | 14 | 150 | 39 | 186–188 |
| 16 | 27.4 | 3.22 | 27.7 | 3.36 | 2 | 150 | 35 | 152–156 |
| 17 | 24.9 | 2.93 | 24.9 | 3.01 | 2 | 130 | 22 | 149–153 |
| 18 | 25.2 | 2.31 | 25.2 | 2.56 | 18 | 135 | 59 | 128–130 |
| 19 | 23.3 | 2.13 | 23.3 | 2.17 | 3 | 135 | 53 | 117–118 |
| 20 | 20.1 | 1.84 | 20.3 | 1.92 | 18 | 135 | 14 | 133–134 |

^a Complexes were prepared as described in the Experimental Section. ^b Compound melted with decomposition. ^c Compound was purified by crystallization from a pentane–acetone mixture. ^d Compound prepared in refluxing dioxane solution.

Table III. Chemical Shifts (τ and ϕ Values) for the Neat Ligands

| Compd | Chemical Shifts (τ) | | | | Methyl groups (ϕ) | | | |
|---|----------------------------|--------|--------------------|--------------------|--------------------------|-------|-------|-------|
| | 1 | 1' | 2 | 2' | | | | |
| (CH ₃) ₂ PCHF ₂ CF ₂ P(CH ₃) ₂ (1) | 5.122 | 214.88 | 111 ^{a,d} | 113 ^{a,d} | <i>b</i> | | | |
| (CH ₃) ₂ AsCH ₂ CF ₂ As(CH ₃) ₂ (2) | 7.939 | 7.939 | 90.76 | 90.76 | 8.870 | 8.870 | 8.940 | 8.940 |
| (CH ₃) ₂ AsCHF ₂ CF ₂ As(CH ₃) ₂ (3) ^e | 4.922 | 199.26 | 4.922 | 199.26 | 8.947 | 8.947 | 8.966 | 8.966 |

^a The stereochemical assignment was made arbitrarily since the angular dependence of ¹⁹F–¹⁹F coupling constants is not well known. ^b Data are not reported due to complexity of methyl resonances. ^c Phosphorus chemical shifts were not determined. ^d These are estimated values, see text. ^e Spectrum obtained in CHCl₃ solution.

Table IV. Coupling Constants (Hz) for the Neat Ligands

| Compd | Coupling Constants (Hz) | | | | | | |
|--|-------------------------|------------------------|-------------------------|-------------------------|--------------------------|-------------------------|--|
| | <i>J</i> _{11'} | <i>J</i> ₁₂ | <i>J</i> _{12'} | <i>J</i> _{1/2} | <i>J</i> _{1/2'} | <i>J</i> _{22'} | |
| (CH ₃) ₂ PCHF ₂ CF ₂ P(CH ₃) ₂ (1) | 47.2 | 17.0 | 14.7 | –18.6 | –20.0 | ≈261 ^{a,b} | |
| (CH ₃) ₂ AsCH ₂ CF ₂ As(CH ₃) ₂ (2) | ≈–13 ^c | 13.3 | 31.0 | 31.0 | 13.3 | ≈260 ^c | |
| (CH ₃) ₂ AsCHF ₂ CF ₂ As(CH ₃) ₂ (3) | 49.7 | 4.6 | 35.9 | 35.9 | 49.7 | –12.3 | |

^a Estimated value, computer analysis iterated to 0.150 RMS error. ^b Phosphorus coupling constants are *J*_{P,1} = 6.0 Hz, *J*_{P,1'} = 50.5 Hz, *J*_{P,2} = 10.2 Hz, *J*_{P,2'} = 8.4 Hz, *J*_{1P,2} = 2.7 Hz, *J*_{1',P,2} = 17.0 Hz, *J*_{2P,2} = 23.0 Hz, *J*_{2',P,2} = 24.0 Hz. ^c Estimated value, see text.

The center line of the triplet is slightly split into a doublet with 0.6-Hz separation. Using this spacing and estimates of the geminal ¹H–¹H and ¹⁹F–¹⁹F coupling constants, –13.0 and 260 Hz, obtained from the nmr parameters of manganese complexes of this and related ligands,¹¹ the spectrum was analyzed yielding the vicinal ¹H–¹⁹F coupling constants.^{12,13} These derived ³*J*_{HF} values are essentially independent of the estimates for both of the geminal coupling constants, since variations of ±0.5 Hz in the ²*J*_{HH} value and of ±15 Hz in the ²*J*_{FF} value result in changes of only ±0.3 Hz in the vicinal ¹H–¹⁹F coupling constants.

(11) W. R. Cullen, L. D. Hall, and J. E. H. Ward, *J. Amer. Chem. Soc.*, in press.

(12) R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **39**, 216 (1961).

(13) J. N. Shoolery and B. Crawford, *J. Mol. Spectrosc.*, **1**, 270 (1957).

The ¹H nmr spectrum of (CH₃)₂AsCF₂CF₂As(CH₃)₂ (3) exhibits peaks attributable to two isomers, both having AA'XX' type spectra. The spectrum of the major component, the racemic form, was easily solved, yielding all the vicinal and geminal coupling constants. However, the peaks of the minor component were partially obscured and its spectrum was not analyzed.

Tables III and IV contain the chemical shifts and the coupling constants derived from the ¹H and ¹⁹F nmr spectra of the neat ligands 1–3.

The nmr spectra of the trimethylsilyl 4 and 5, fluoro 6, trifluoroarsenic 7 and 8, trifluorophosphorus 9 and 10, and cyano 14 and 15 complexes are similar to those obtained for their chromium analogs.² The relative signs of the coupling constants for the compounds discussed in the present work were assigned on the basis of

Table V. Chemical Shifts (τ and ϕ Values) for the Chelate Complexes 4–17

| Compd | Solvent ^a | | | | | Methyl groups | | | |
|-------|---|--------|--------|---------------------|---------------------|---------------|-------|-------|-------|
| | | 3 | 3' | 4 | 4' | | | | |
| 4 | C ₆ H ₆ | | 10.176 | 8.041 | 9.299 | 8.723 | 8.848 | 8.872 | 9.064 |
| | CHCl ₃ | | 9.838 | 7.677 | 9.017 | 8.424 | 8.509 | 8.577 | 8.700 |
| | (CD ₃) ₂ CO | | 9.529 | 7.481 | 8.831 | 9.002 | 9.097 | 9.154 | 9.264 |
| 5 | C ₆ H ₆ | | 10.196 | 8.137 | 9.330 | 8.630 | 8.774 | 8.774 | 8.984 |
| | CHCl ₃ | | 9.828 | 7.732 | 9.019 | 8.316 | 8.406 | 8.465 | 8.587 |
| | (CH ₃) ₂ CO | | 9.467 | 7.501 | 8.797 | 8.259 | 8.365 | 8.407 | 8.520 |
| 6 | CHCl ₃ | 4.467 | 193.47 | 7.528 | 8.667 | 8.448 | 8.495 | 8.519 | 8.653 |
| | (CD ₃) ₂ CO | 4.176 | 192.95 | 7.374 | <i>b</i> | | | | |
| 7 | CHCl ₃ | 5.106 | 219.29 | 119.69 ^d | 128.42 ^d | <i>c</i> | | | |
| | (CD ₃) ₂ CO | 4.449 | 222.49 | 120.50 | 126.77 | | | | |
| 8 | CHCl ₃ | 5.158 | 219.31 | 119.90 ^d | 130.51 ^d | <i>c</i> | | | |
| | (CD ₃) ₂ CO | 4.472 | 222.45 | 120.80 | 128.84 | | | | |
| 9 | CHCl ₃ | 5.218 | 219.49 | 122.40 ^d | 127.99 ^d | <i>c</i> | | | |
| | (CD ₃) ₂ CO | 4.495 | 222.10 | 122.47 | 127.49 | | | | |
| 10 | CHCl ₃ | 5.191 | 219.39 | 122.06 ^d | 127.50 ^d | <i>c</i> | | | |
| | (CD ₃) ₂ CO | 4.493 | 222.36 | 122.48 | 126.70 | | | | |
| 11 | C ₆ H ₆ ^e | 9.22 | 9.22 | 105.8 | 105.8 | 9.42 | 9.42 | 9.52 | 9.52 |
| 12 | C ₆ H ₆ ^e | 9.17 | 9.17 | | | 9.43 | 9.43 | 9.55 | 9.55 |
| 13 | C ₆ H ₆ ^e | 9.28 | 9.28 | | | 9.42 | 9.42 | 9.51 | 9.51 |
| 14 | CHCl ₃ | | 7.644 | 7.832 | 8.334 | 8.386 | 8.400 | 8.430 | 8.538 |
| | (CD ₃) ₂ CO | | 6.930 | 7.670 | 7.993 | 8.334 | 8.334 | 8.373 | 8.444 |
| 15 | CHCl ₃ | | 7.683 | 7.867 | <i>b</i> | 8.258 | 8.270 | 8.309 | 8.419 |
| | (CD ₃) ₂ CO | | 6.853 | 7.679 | <i>b</i> | 8.218 | 8.218 | 8.265 | 8.329 |
| 16 | CHCl ₃ | 212.10 | 4.565 | 212.10 | 4.565 | 8.459 | 8.459 | 8.495 | 8.495 |
| | (CD ₃) ₂ CO | 212.05 | 4.159 | 212.05 | 4.159 | 8.423 | 8.423 | 8.442 | 8.442 |
| 17 | CHCl ₃ | 211.96 | 4.602 | 211.96 | 4.602 | 8.433 | 8.433 | 8.445 | 8.445 |
| | (CD ₃) ₂ CO | 212.22 | 4.191 | 212.22 | 4.191 | 8.426 | 8.426 | 8.433 | 8.433 |
| | C ₆ H ₅ NO ₂ | 207.61 | 4.233 | 207.61 | 4.233 | 8.428 | 8.428 | 8.449 | 8.449 |

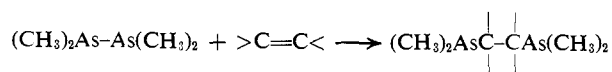
^a In order of increasing dielectric constant. ^b Proton resonance was obscured by the methyl resonances. ^c Data are not reported due to complexity of methyl resonances. ^d The stereochemical assignment was made arbitrarily since the angular dependence of vicinal ¹⁹F–¹⁹F coupling constants is not well known. ^e External TMS.

the sign determinations on the spectra of the related chromium chelate complexes. A sample spectrum of a chelate complex considered in this paper is shown in Figure 2, which illustrates the effect of phosphorus decoupling of the ¹H nmr spectrum on the chromium derivative (CH₃)₂PCHFCH₂P(CH₃)₂Cr(CO)₄ (9).

The nmr spectra of the complexes (CH₃)₂AsCH₂CF₂As(CH₃)₂M(CO)₄ 11–13 (M = Cr, Mo, W) were not subjected to computer analysis since the spectra of the methylene protons showed no fine structure in the anticipated triplet. Analysis of the ¹H nmr spectra of the (CH₃)₂AsCHFCH₂As(CH₃)₂M(CO)₄ 16 and 17 (M = Cr, Mo) complexes presented no problems, while the ¹⁹F nmr spectra of the hexafluoropropane derivatives did not warrant detailed analyses, since the uncertainty of the angular relationships of vicinal ¹⁹F–¹⁹F coupling constants¹⁴ precludes conformational interpretation. Tables V–VII contain the chemical shifts and coupling constants derived from the nmr spectra of the chelate complexes 4–17.

Discussion

Characterization. All the analytical data obtained for the new ditertiary arsines and their chelate complexes are satisfactory and indicate that the products are formulated correctly. The yields of the ligands are probably a fairly accurate measure of the ease of the addition reaction



On the other hand, yields of the chelate complexes vary considerably. At the high reaction temperatures used,

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

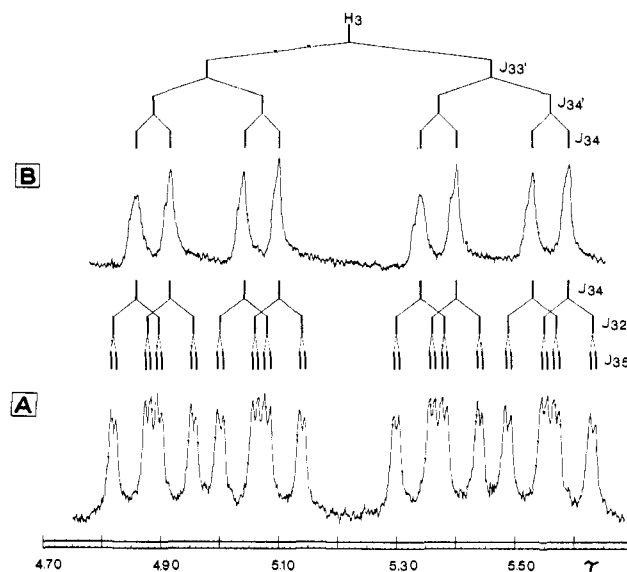


Figure 2. Partial ¹H nmr spectra (100 MHz) of (CH₃)₂PCHFCH₂P(CH₃)₂Cr(CO)₄ in chloroform solution. A is the normal spectrum. B was measured with simultaneous irradiation at the ³¹P resonance (40.4840000 MHz). Representations of the first-order assignment for the spectra are also shown.

some of these products decomposed. The yields of the complexes were also reduced in some cases by the reluctance of the ligand to chelate with the transition metal. Frequently the major products obtained were M(CO)₃ derivatives (identified by infrared spectroscopy), in which only one of the donor atoms of the ligand was bonded to the metal atom. For these reasons the tungsten analogs of (CH₃)₂AsCHFCH₂As(CH₃)₂Mo(CO)₄ (6) and (CH₃)₂AsCHFCH₂As(CH₃)₂M(CO)₄ 16 and 17 (M = Cr, Mo) were not prepared.

Table VI. Coupling Constants (Hz) for the Chelate Complexes 4-17

| Compd | Solvent ^a | $J_{33'}$ | J_{34} | $J_{34'}$ | $J_{3'4}$ | $J_{3'4'}$ | $J_{44'}$ |
|-----------------|---|-----------|----------|-----------|-----------|-------------------|--------------------|
| 4 | C ₆ H ₆ | | | | 4.5 | 15.7 | -13.0 |
| | CHCl ₃ | | | | 4.5 | 15.9 | -13.0 |
| | (CD ₃) ₂ CO | | | | 4.4 | 16.0 | -12.9 |
| 5 | C ₆ H ₆ | | | | 4.5 | 15.9 | -13.0 |
| | CHCl ₃ | | | | 4.6 | 16.0 | -12.9 |
| | (CD ₃) ₂ CO | | | | 4.5 | 16.0 | -13.1 |
| 6 | CHCl ₃ | 49.1 | 4.5 | 2.9 | 14.0 | 48.2 | -14.0 |
| | (CD ₃) ₂ CO | 49.4 | 4.1 | 2.9 | 14.2 | 49.2 ^b | -14.4 |
| 7 | CHCl ₃ | 48.9 | 4.7 | 16.1 | -23.2 | -16.3 | 268.4 |
| | (CD ₃) ₂ CO | 48.5 | 5.3 | 19.1 | -20.0 | -15.0 | 264.2 |
| 8 | CHCl ₃ | 48.7 | 4.5 | 15.1 | -23.6 | -16.4 | 269.9 |
| | (CD ₃) ₂ CO | 48.0 | 5.0 | 18.0 | -20.9 | -15.2 | 265.9 |
| 9 ^c | CHCl ₃ | 48.4 | 6.0 | 18.5 | -17.6 | -15.5 | 269.5 ^d |
| | (CD ₃) ₂ CO | 47.4 | 6.2 | 20.8 | -16.3 | -14.6 | 266.0 |
| 10 ^c | CHCl ₃ | 48.0 | 5.2 | 19.7 | -16.8 | -15.4 | 269.8 |
| | (CD ₃) ₂ CO | 47.0 | 5.3 | 21.9 | -14.9 | -14.7 | 266.1 |
| 11 ^e | C ₆ H ₆ | | | | | | |
| 12 ^e | C ₆ H ₆ | | | | | | |
| 13 ^e | C ₆ H ₆ | | | | | | |
| 14 | CHCl ₃ | | | | 5.4 | 10.1 | -13.0 |
| | (CD ₃) ₂ CO | | | | 5.4 | 10.1 | -13.3 |
| 15 | CHCl ₃ | | | | 5.4 | 11.8 | -13.6 |
| | (CD ₃) ₂ CO | | | | 5.7 | 9.8 | -13.2 |
| 16 | CHCl ₃ | 49.9 | -27.9 | 11.1 | 11.1 | 7.1 | 49.9 |
| | (CD ₃) ₂ CO | 50.0 | -25.1 | 12.1 | 12.1 | 7.7 | 50.0 |
| 17 | CHCl ₃ | 50.1 | -26.3 | 10.4 | 10.4 | 7.4 | 50.1 |
| | (CD ₃) ₂ CO | 50.4 | -23.0 | 11.6 | 11.6 | 8.4 | 50.4 |
| | C ₆ H ₅ NO ₂ | 50.1 | -25.5 | 10.6 | 10.6 | 7.6 | 50.1 |

^a In order of increasing dielectric constant. ^b Proton resonance was obscured by the methyl resonances. ^c See Table VII for ³¹P-¹⁹F and ³¹P-¹H coupling constants. ^d Values are approximate since the iteration proceeded only to 0.7 RMS error. ^e Sums of all vicinal coupling constants are 72, 73, and 72 Hz for **11**, **12**, and **13**, respectively.

Table VII. Phosphorus Coupling Constants (Hz) for the Chelate Complexes 9 and 10

| Compd | Solvent | $ \begin{array}{c} \begin{array}{c} 3 \quad 4 \\ \quad \\ (\text{CH}_3)_2\text{P}^1 - \text{C} - \text{C} - \text{P}^{11}(\text{CH}_3)_2\text{M}(\text{CO})_4^a \\ \quad \\ 3' \quad 4' \end{array} \end{array} $ | | | | | | | |
|-------|------------------------------------|---|---------------------------|--------------------------|---------------------------|-------------------------------|------------------------------|------------------------------|---------------------------|
| | | $J_{\text{P}^1\text{3}}$ | $J_{\text{P}^1\text{3}'}$ | $J_{\text{P}^1\text{4}}$ | $J_{\text{P}^1\text{4}'}$ | $J_{\text{P}^1\text{P}^{11}}$ | $J_{\text{3}'\text{P}^{11}}$ | $J_{\text{4}'\text{P}^{11}}$ | $J_{\text{4}'\text{P}^1}$ |
| 9 | CHCl ₃ | 7.9 | 35.0 ^b | 9.9 | 2.1 | 0.8 | 2.0 ^b | 34.2 | 35.6 |
| | (CD ₃) ₂ CO | 6.2 | 31.0 | 11.8 | 1.3 | 1.2 | 2.8 | 32.0 | 38.8 |
| 10 | CHCl ₃ | 7.3 | 36.5 | 8.1 | 1.5 | 1.0 | 1.2 | 36.5 | 38.7 |
| | (CD ₃) ₂ CO | 6.1 | 33.8 | 9.9 | 0.8 | 1.3 | 1.9 | 34.0 | 42.5 |

^a ${}^2J_{\text{PF}}{}^2J_{\text{PH}}$ coupling constants are assumed to be larger than their respective ${}^3J_{\text{PF}}$ and ${}^3J_{\text{PH}}$ values. ^b This value is estimated at ± 1 Hz.

Mass spectra of the molybdenum and tungsten chelate complexes of those ditertiary arsine ligands described previously² showed peaks corresponding to the loss of four carbonyl groups from the parent ion. Other peaks encountered frequently in these spectra could be attributed to the loss of a methyl group from the parent ion or from the parent ion less one to four carbonyl groups. All the mass spectra exhibited peaks corresponding to the fragments $[(\text{CH}_3)_4\text{As}_2]^+$ and $[(\text{CH}_3)_3\text{As}_2]^+$.

The infrared absorption frequencies for the carbonyl groups of the chelate complexes 4-20 are summarized in Table VIII. The complexes typically exhibit three or four absorptions in the carbonyl-stretching region of the infrared spectrum. In general, carbonyl group absorptions shift to higher energy as the total electronegativity of the substituents bonded to a transition metal increases. The data in Table VIII bear this prediction out. For example, the carbonyl groups of the trifluoro derivative **7** absorb at higher frequencies than those of the fluoro **6** or cyano **14** derivatives. For a given set of ditertiary arsine or phosphine derivatives,

Table VIII. Carbonyl Infrared Stretching Frequencies (± 2 cm⁻¹) for the Chelate Complexes 4-20^a

| Complex | Frequencies, cm ⁻¹ | | | |
|---------|-------------------------------|------|------|--------|
| | | | | |
| 4 | 2020 | 1925 | 1906 | 1902 |
| 5 | 2016 | 1918 | 1896 | (1896) |
| 6 | 2018 | 1933 | 1913 | (1913) |
| 7 | 2036 | 1937 | 1924 | 1917 |
| 8 | 2030 | 1934 | 1916 | 1913 |
| 9 | 2021 | 1936 | 1913 | 1909 |
| 10 | 2032 | 1943 | 1922 | 1920 |
| 11 | 2016 | 1927 | 1903 | (1903) |
| 12 | 2032 | 1935 | 1917 | 1912 |
| 13 | 2024 | 1927 | 1906 | (1906) |
| 14 | 2025 | 1935 | 1914 | (1914) |
| 15 | 2021 | 1928 | 1906 | (1906) |
| 16 | 2017 | 1926 | 1909 | 1903 |
| 17 | 2030 | 1937 | 1916 | (1916) |
| 18 | 2020 | 1933 | 1912 | (1912) |
| 19 | 2040 | 1942 | 1929 | 1921 |
| 20 | 2025 | 1935 | 1915 | (1915) |

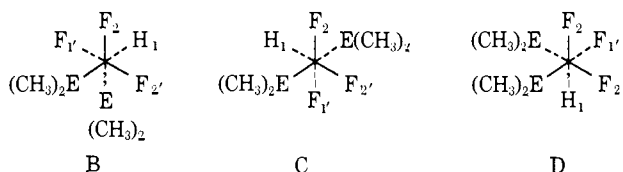
^a Cyclohexane solvent, 0.1- and 0.5-mm KBr cells.

the carbonyl-stretching frequencies follow the trend Mo \geq Cr > W. A similar relationship has been ob-

served and rationalized in the parent group VI transition metal hexacarbonyls by King.¹⁵

In contrast, it is interesting to note that these carbonyl absorptions are fairly insensitive to changes from arsenic to phosphorus donor atoms. Thus, there is little difference between the carbonyl-stretching frequencies of $(\text{CH}_3)_2\text{AsCHF}_2\text{CF}_2\text{As}(\text{CH}_3)_2\text{Mo}(\text{CO})_4$ (**7**) and $(\text{CH}_3)_2\text{PCHF}_2\text{CF}_2\text{P}(\text{CH}_3)_2\text{Mo}(\text{CO})_4$ (**10**).

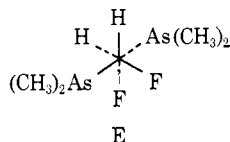
Ditertiary Arsines and Phosphines. The vicinal ^1H - ^{19}F coupling constants (*ca.* 17 and 14 Hz) of the trifluorophosphorus ligand **1** indicate a significant population of the rotamer having the proton gauche to two fluorine atoms as in **B**.¹⁶ This contrasts with the behavior of many of the ligands we discussed previously,² which seem to prefer rotamers where the dimethylarsino substituents exist trans to one another as in **C**. The arsenic analog of this trifluorophosphorus ligand may also exist in forms **B** and **C** as well as **D**.



In **C** and **D** a proton and fluorine are trans to one another and significant populations of these rotamers could be indicated by the large $^3J_{\text{HF}}$ value of *ca.* 22 Hz. It seems likely that both of these trifluoro compounds have significant populations of all the three rotational isomers **B**-**D**, and in these ligands the preferences of the fluorine substituents as well as the steric requirements of the "bulky" $(\text{CH}_3)_2\text{E}$ substituents may be important.

The vicinal ^1H - ^{19}F coupling constants determined from the nmr spectrum of the difluoro compound **2**, two large and two small $^3J_{\text{HF}}$ values (*ca.* 31 and 13 Hz), indicate that the rotamer with both protons trans to fluorine atoms, the rotamer with the dimethylarsino groups trans to each other, is a major component.

A similar conclusion applies to the difluoro ligand **3**. Vicinal ^1H - ^{19}F ¹⁶ and ^1H - ^1H ¹⁷ coupling constants indicate mutually gauche protons and protons trans to fluorine atoms ($^3J_{\text{HH}} = 4.6$ Hz, $^3J_{\text{HF}} = 35.9$ Hz). Thus the preferred rotamer is that having the dimethylarsino substituents trans to one another. The data also indicate that the more abundant isomer is the racemic form of 1,2-bis(dimethylarsino)-1,2-difluoroethane, as in **E**. This particular rotamer represents the



only way in which any of the possible rotational isomers of the meso or racemic forms of this compound can exist with both protons trans to fluorine atoms.

Chelate Ring Conformations. At this point it is worth-

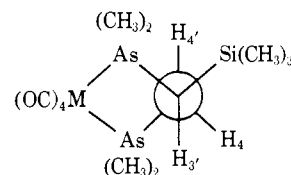
(15) R. B. King, *Inorg. Nucl. Chem. Lett.*, **5**, 905 (1969).

(16) (a) A. M. Ihrig and S. L. Smith, *J. Amer. Chem. Soc.*, **92**, 759 (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).

(17) (a) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); (b) M. Karplus, *J. Amer. Chem. Soc.*, **85**, 2870 (1963); (c) E. B. Whipple, *J. Magn. Resonance*, **5**, 163 (1971).

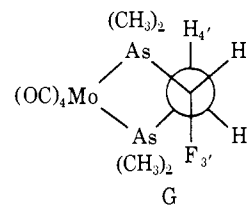
while to summarize the limitations inherent in the conformational studies of five-membered chelate rings. The energy barriers to the conformational inversion of five-membered chelate rings are relatively small.¹⁸ Thus the conformations determined by nmr will be time averaged to some extent. A single, specific conformation cannot be assigned, although one particular conformation may be very highly populated. In this work we confine the discussion to those conformers which involve rotation about the carbon-carbon bond of the ethane bridge.

(a) Vicinal Coupling Constants. The vicinal ^1H - ^1H coupling constants of the trimethylsilyl derivatives **4** and **5** are very similar to those values obtained from their chromium analog² for a given solvent. For example, in chloroform solution, these $^3J_{\text{HH}}$ values are 15.9 and 4.5 Hz for the molybdenum complex **4** and 16.0 and 4.6 Hz for the tungsten chelate compound. These trans coupling constants are only *ca.* 0.1 Hz smaller than that of the chromium complex, while the corresponding gauche ^1H - ^1H coupling constants are *ca.* 0.6 Hz smaller. It appears that all the group V chelate complexes of the trimethylsilyl ditertiary arsine have conformations in which the trimethylsilyl group adopts an "equatorial" position on the five-membered chelate ring, as in **F**.



F, M = Cr, Mo, W

Data for the monofluoro derivative **6** seem to indicate that the fluorine substituent has a trans relationship with respect to a vicinal proton. Thus the carbon-fluorine bond has an "axial" orientation as in **G**, similar



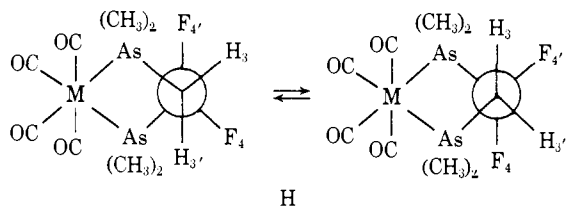
to the conformation determined for its chromium analog.² The vicinal ^1H - ^1H coupling constants are both relatively small (*ca.* 4 and 3 Hz) and one of the vicinal ^1H - ^{19}F coupling constants is approximately three times the magnitude of the other (*ca.* 48 and 14 Hz), consistent with this interpretation.

The trifluoroarsenic **7** and **8** and trifluorophosphorus **9** and **10** complexes yielded nmr parameters similar to those derived for their related chromium chelate complex $(\text{CH}_3)_2\text{AsCF}_2\text{CF}_2\text{As}(\text{CH}_3)_2\text{Cr}(\text{CO})_4$.² The vicinal coupling constants determined for the compounds reported in this work indicate that their preferred conformations include the proton in an "equatorial" position on the five-membered chelate ring, while two fluorine substituents adopt the "axial" orientation. Data for the phosphorus derivatives differ significantly from those obtained from the arsenic analogs, but it is

(18) J. R. Gollgoly, C. J. Hawkins, and J. K. Beattie, *Inorg. Chem.*, **10**, 317 (1971).

difficult to determine the exact source of these differences at this time.

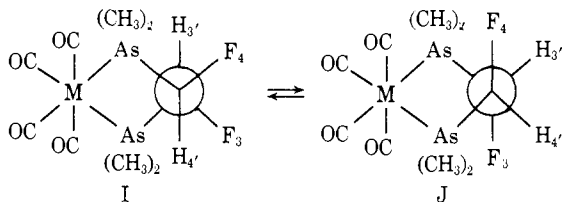
We take the nmr parameters of the difluoro chelates **11**–**13** to indicate that conformational equilibrium occurs rapidly on the nmr time scale, as in H. This



accounts for the complete averaging of the vicinal ^1H – ^{19}F coupling constants.

The cyano derivatives **14** and **15** were next examined and their nmr parameters proved to be very similar to those obtained for the related chromium chelate complex.² Apparently a cyano substituent in all the group VI complexes favors an “equatorial” orientation on the chelate ring, but not so markedly as a trimethylsilyl group, assuming that the electronegativity differences between these two types of substituents are not responsible for the lowering of $J_{3'4'}$. For a given solvent, the vicinal ^1H – ^1H coupling constants of the cyano derivatives are almost identical (*ca.* 11 and 6 Hz).

The chromium and molybdenum chelate complexes of the new ditertiary arsine $(\text{CH}_3)_2\text{AsCHFCHFA}(\text{CH}_3)_2$ (**3**) which is obtained mainly in the racemic form (see above) were the final complexes considered. The ^1H and ^{19}F nmr parameters indicate that the chelate rings slightly favor conformations in which the two fluorine substituents adopt “equatorial” positions and, hence, exist *gauche* to one another, as in I. Thus the



^1H – ^1H coupling constants are *ca.* 7 Hz while the ^1H – ^{19}F vicinal coupling constants are *ca.* 10–12 Hz. However, the relatively small values of the trans ^1H – ^1H coupling constants appear to indicate that the populations of the conformers with two fluorine atoms in the “axial” position on the chelate ring, as in J, may be substantial.

(b) **Chemical Shifts.** The chemical shift data for the ethane bridge substituents of the chelate complexes **4**–**17** corroborate the interpretations based on the dihedral angle dependences of the vicinal coupling constants. In complexes which have substituents predominantly preferred in an “axial” or “equatorial” orientation on the chelate ring, the chemical shift of an “axial” methylene proton is significantly higher than that of the “equatorial” methylene proton. For example, the “axial” geminal proton $\text{H}_{4'}$ in the trimethylsilyl derivative **4** in benzene solution absorbs at τ 9.3, while the “equatorial” proton H_3 absorbs at τ 8.0. Similar results have been obtained for 1,2-propylenediamine chelate complexes of several transition metals.^{19,20} The methylene protons in the monofluoro

(19) S. Yanyo, H. Ito, Y. Koike, J. Fujita, and K. Saito, *Bull. Chem. Soc. Jap.*, **42**, 5184 (1969).

6 and cyano **14** and **15** complexes behave in a similar manner.

(c) **Solvent Effects.** By varying the solvents in which the spectra of the chelate complexes were taken, it was hoped to induce systematic changes in the conformations and thus the nmr parameters of **4**–**17**. As in our previous study,² these experiments seemed inconclusive. In almost all cases the solvent variability of coupling constants could be accounted for in terms of those changes expected for the J values of rigid molecules.²¹ The vicinal ^1H – ^1H coupling constants for those complexes thought to have one conformation highly populated vary in a range of *ca.* 0.3 Hz. However, the ^1H – ^1H coupling constants in the cyano **14** and **15** and difluoro **16** and **17** derivatives vary by as much as 2 Hz, probably because of the alterations in conformer populations with the changes in solvent polarity. The vicinal ^1H – ^{19}F and ^{19}F – ^{19}F coupling constants also vary as anticipated for rigid molecules²¹ sometimes by as much as *ca.* 3 Hz, as in the trifluoro chelate complexes **7** and **8**.

(d) **Transition Metal Variations.** It seemed possible that by varying the size of the metal atom in the five-membered chelate ring, subsequent conformational changes would occur in the rest of the ring, and these would be reflected in the nmr parameters of the chelate derivatives. For a given solvent only small changes in the coupling constants and chemical shifts occur for chromium, molybdenum, and tungsten analogs, and thus the conformations of the chelate rings of a given set of group VI derivatives are approximately the same. The following describes our attempts to estimate the geometrical changes in the five-membered chelate rings induced by transition metal variations.

Hawkins and coworkers^{18,22} have demonstrated that for diamine systems a variety of theoretical chelate ring geometries are energetically similar, lying within 0.2 kcal/mol of each other. According to their investigations, ring strain caused by increasing the M–N bond lengths can be alleviated by (a) reducing the N–M–N bond angle, (b) increasing the dihedral angle about the two carbon bridge, and/or (c) increasing the N–C–C or C–C–N bond angles. The last was shown to be the least energetically favorable alternative. Thus, in the present work, we will consider the changes in M–As bond lengths and As–M–As bond angles to be the significant parameters having a bearing on the magnitude of the changes of the dihedral angle about the C–C bond.

Some of their calculations involved changing the M–N bond lengths from 2.0 to 2.3 Å, which caused average variations in the dihedral angle about the C–C bond from 57.5 to 65°. Thus the expected alteration in the dihedral angle for a bond length increase of 14% [$100\% \times (2 \times 0.3)/(2.0 + 2.3)$]²³ would be the difference between these angles, 65° – 57.5° = 7.5°. It has also been shown²² that a decrease in the N–M–N angle of an ethylenediamine chelate ring from 88 to 86° (by 2°) results in a decrease in the dihedral angle by 1°.

Typical Cr–As and Mo–As bond lengths, 2.43 and

(20) S. Yanyo, Y. Koike, J. Fujita, and K. Sato, *Chem Commun.*, 460 (1969).

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

(22) J. R. Golligly and C. J. Hawkins, *Inorg. Chem.*, **8**, 1168 (1969).

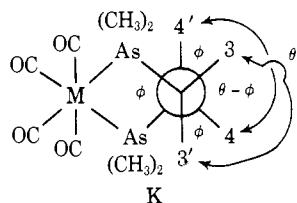
(23) The two bond lengths are averaged in order to avoid discrepancies caused by large relative bond length alterations.

2.58 Å, have been determined by Trotter and co-workers²⁴ for a number of chelate complexes, including the trifluoroarsenic and -phosphorus derivatives **7** and **10** as well as the difluoro complex **11**. These values do not seem to vary appreciably from complex to complex. The corresponding W-As bond length is not known, but we anticipate that it will be close to those found for the molybdenum arsenic compounds, since the atomic radii of molybdenum and tungsten are almost identical.¹⁵

The X-ray examination of these compounds also revealed that, for a given ligand, the As-M-As angle decreases from *ca.* 84° for the chromium chelate complexes to *ca.* 82° for the molybdenum analogs. The same angular decrease was noted in two trifluoro-chromium derivatives **7** and **10**, when the arsenic donor atoms were replaced by phosphorus atoms.

For the substitution of chromium by molybdenum, the M-As bond length varies from 2.3 to 2.58 Å, that is, by *ca.* 6% [$100\% \times (2 \times 0.15)/(2.43 + 2.58)$]. The variation in dihedral angle for this bond length change might be expected to be an increase of $6\%/14\% \times 7.5^\circ \simeq 3^\circ$. This would likely be offset by a *ca.* 1° decrease in the dihedral angle resulting from the 2° reduction in the As-M-As angle. Hence, the combined effects of the changes in M-As bond length and As-M-As bond angle would be to increase the dihedral angle by *ca.* 2° for a substitution of a chromium atom by a molybdenum atom.

In order to use Karplus relationships to calculate dihedral angles, it is always necessary to make some assumptions concerning the geminal angles. Our initial calculations were based on the model system shown in **K**, where θ is the in-plane projection of two identical



“tetrahedral” angles about the ring carbon atoms. Although this latter is not a totally satisfactory assumption, the introduction of any further variables makes the whole analysis underdetermined.

The following equations (1–3)^{16a,b,25} are expressions for the vicinal coupling constants in the chelate ring, where ϕ is the dihedral angle as in **K**.

$$J_{3'4 \text{ or } 34'} = A \cos^2 \phi \quad (1)$$

$$J_{34} = A \cos^2 (\theta - \phi) \quad (2)$$

$$J_{3'4'} = B \cos^2 (\theta + \phi) \quad (3)$$

For vicinal ¹H-¹H coupling constants we have chosen (A/B) \simeq $9/10$,²⁶ while for ¹H-¹⁹F J values we have selected (A/B) \simeq $2/3$.^{16c} In principle the equations can be solved using an approach similar to that of Slessor and coworkers,^{26,27} except that the stereochemical assignment of the vicinal atoms is made before the dihedral

angle calculations. Usually, with only two coupling constants available to define the dihedral angle ϕ , it is not possible to solve for the value of θ , and it is necessary to estimate the size of this angle, normally 120°, as have other workers.^{28,29}

The coupling constant ratios, their types, the calculated dihedral angles, ϕ , and the Karplus coefficients A and B are reported in Table IX. The calculations assume that all the complexes highly favor a particular conformation, although it may be true in several instances that the chelate complexes have significant proportions of other conformers in solution.

The data obtained for the trimethylsilyl derivatives are consistent with those values of ϕ , A , and B which we had anticipated. The dihedral angles vary from 53.5 to 56°, a range similar to that found for many ethylenediamine and propylenediamine chelate complexes.^{22,28b} For a given solvent, the increase in dihedral angle on substituting the chromium metal atom by molybdenum is *ca.* 2°, as previously predicted. The Karplus coefficients are also in accordance with our expectations, being *ca.* $1/3$ higher than those values determined for carbocyclic compounds.^{17a,b} This increase is likely due to the inverse proportionality of the Karplus coefficients to the electronegativity of the substituents.³⁰ It is also interesting to note that the Karplus coefficients are virtually independent of the transition metal and solvent used. Thus, the vicinal coupling constants in this group of chelate complexes seem to be independent of the *electronic* nature of the transition metal and can be accounted for simply in terms of its actual size. The small variations in A and B fall within the range of experimental error introduced by solvent variations.²¹ Finally, we wish to point out that the parameters derived for the tungsten analog are, to all intents and purposes, identical with those of the molybdenum trimethylsilyl chelate complex **4**. This corroborates our claim that the alterations in chelate ring geometry caused by transition metal variations in a given group are mainly a function of metal atom size, since the atomic radii of tungsten and molybdenum are thought to be almost the same.¹⁵

The data derived for the trichlorosilyl derivative are similar to those obtained for the related trimethylsilyl compounds **4** and **5**. The lower values of the Karplus coefficients, 14.2 and 15.6 Hz (in CHCl₃), compared with those of the trimethylsilyl chromium derivative, 14.7 and 16.2 Hz, are likely a reflection of the greater electronegativity of a trichlorosilyl group.

The monofluoro complexes are considered next. The values of the dihedral angles calculated independently from the vicinal ¹H-¹H and ¹H-¹⁹F coupling constants differ by *ca.* 12–13°. Moreover, the Karplus coefficients in the case of the ¹H-¹H solution seem slightly *high* since we would expect that the extremely electronegative fluorine atom would cause a more pronounced lowering of A and B . The ¹H-¹⁹F A and B values are approximately the same as those reported in fluorinated carbocyclic systems^{16c} and are *less* than expected. Nevertheless, for both ¹H-¹H and ¹H-¹⁹F sets

(24) I. W. Nowell, S. Rettig, and J. Trotter, *J. Chem. Soc., Dalton Trans.*, 2381 (1972).

(25) W. A. Thomas, *Annu. Rev. NMR Spectrosc.*, **1**, 72 (1968).

(26) K. N. Slessor and A. S. Tracey, *Can. J. Chem.*, **49**, 2874 (1971).

(27) L. D. Hall, S. A. Black, K. N. Slessor, and A. S. Tracey, *Can. J. Chem.*, **50**, 1912 (1972).

(28) (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).

(29) R. E. Cramer, *Inorg. Chem.*, **11**, 1019 (1972).

(30) K. L. Williamson, *J. Amer. Chem. Soc.*, **85**, 516 (1963).

Table IX. Calculated Dihedral Angles (ϕ) and Karplus Deficients (A and B) for Some Chelate Complexes

| Compd | Metal | Solvent | Ratio type | Coupling constant ratio | ϕ , deg | A , Hz | B , Hz |
|--|----------------------------|----------------------------|--------------------|-------------------------|--------------|----------|----------|
| $(\text{CH}_3)_2\text{AsCH}(\text{Si}(\text{CH}_3)_3)\text{CH}_2\text{As}(\text{CH}_3)_2\text{M}(\text{CO})_4$ | Cr | CHCl_3 | $J_{3'4}/J_{3'4}$ | 3.10 | 53.5 | 14.7 | 16.2 |
| | | $(\text{CD}_3)_2\text{CO}$ | | 3.22 | 54.25 | 14.6 | 16.1 |
| | Mo | CHCl_3 | $J_{3'4'}/J_{3'4}$ | 3.53 | 56.0 | 14.4 | 15.8 |
| | | $(\text{CD}_3)_2\text{CO}$ | | 3.64 | 56.5 | 14.5 | 15.9 |
| | W | CHCl_3 | $J_{3'4'}/J_{3'4}$ | 3.48 | 55.75 | 14.5 | 15.9 |
| | | $(\text{CD}_3)_2\text{CO}$ | | 3.56 | 56.0 | 14.5 | 15.9 |
| $(\text{CH}_3)_2\text{AsCH}(\text{SiCl}_3)\text{CH}_2\text{As}(\text{CH}_3)_2\text{M}(\text{CO})_4$ | Cr | CHCl_3 | $J_{3'4'}/J_{3'4}$ | 2.91 | 52.25 | 14.2 | 15.6 |
| | Cr ^a | CHCl_3 | $J_{34}/J_{34'}$ | 1.06 | 60.5 | 14.0 | 15.4 |
| | | $(\text{CD}_3)_2\text{CO}$ | | 1.09 | 60.75 | 13.4 | 14.7 |
| | Mo ^a | CHCl_3 | $J_{34}/J_{34'}$ | 1.55 | 63.5 | 14.7 | 16.2 |
| | | $(\text{CD}_3)_2\text{CO}$ | | 1.41 | 62.75 | 13.9 | 15.3 |
| | Cr ^b | CHCl_3 | $J_{3'4'}/J_{3'4}$ | 3.12 | 47.5 | 33.9 | 50.9 |
| $(\text{CD}_3)_2\text{CO}$ | | | 3.14 | 47.5 | 35.7 | 53.5 | |
| $(\text{CH}_3)_2\text{AsCHFCF}_2\text{As}(\text{CH}_3)_2\text{M}(\text{CO})_4$ | Cr | CHCl_3 | $J_{34}/J_{34'}$ | 3.44 | 49.5 | 33.4 | 50.1 |
| | | $(\text{CD}_3)_2\text{CO}$ | | 3.46 | 49.75 | 34.0 | 51.1 |
| | Mo | CHCl_3 | $J_{34}/J_{34'}$ | 0.36 | 51.75 | 38.6 | 57.9 |
| | | $(\text{CD}_3)_2\text{CO}$ | | 0.32 | 51.0 | 43.7 | 65.5 |
| | W | CHCl_3 | $J_{34}/J_{34'}$ | 0.29 | 50.25 | 39.3 | 59.0 |
| | | $(\text{CD}_3)_2\text{CO}$ | | 0.28 | 50.0 | 45.9 | 68.4 |
| $(\text{CH}_3)_2\text{PCHFCF}_2\text{P}(\text{CH}_3)_2\text{M}(\text{CO})_4$ | Cr | CHCl_3 | $J_{34}/J_{34'}$ | 0.30 | 50.5 | 37.1 | 55.7 |
| | | $(\text{CD}_3)_2\text{CO}$ | | 0.28 | 50.0 | 45.9 | 68.4 |
| | Cr | CHCl_3 | $J_{34'}/J_{34''}$ | 2.79 | 68.25 | 38.6 | 57.9 |
| | | $(\text{CD}_3)_2\text{CO}$ | | 3.09 | 69.0 | 43.7 | 65.5 |
| | Mo | CHCl_3 | $J_{34'}/J_{34''}$ | 3.42 | 69.75 | 39.3 | 59.0 |
| | | $(\text{CD}_3)_2\text{CO}$ | | 3.60 | 70.25 | 45.9 | 68.9 |
| W | CHCl_3 | $J_{34'}/J_{34''}$ | 3.36 | 69.75 | 37.1 | 55.7 | |
| | $(\text{CD}_3)_2\text{CO}$ | | 3.60 | 70.25 | 45.9 | 68.9 | |
| $(\text{CH}_3)_2\text{PCHFCF}_2\text{P}(\text{CH}_3)_2\text{M}(\text{CO})_4$ | Cr | CHCl_3 | $J_{34}/J_{34'}$ | 0.32 | 51.0 | 46.7 | 70.0 |
| | | $(\text{CD}_3)_2\text{CO}$ | | 0.30 | 50.5 | 51.2 | 76.7 |
| | Mo | CHCl_3 | $J_{34}/J_{34'}$ | 0.26 | 49.5 | 46.7 | 70.1 |
| | | $(\text{CD}_3)_2\text{CO}$ | | 0.24 | 49.0 | 50.6 | 76.0 |
| | Cr | CHCl_3 | $J_{34'}/J_{34''}$ | 3.08 | 69.0 | 46.7 | 70.0 |
| | | $(\text{CD}_3)_2\text{CO}$ | | 3.35 | 69.75 | 51.2 | 76.7 |
| $(\text{CH}_3)_2\text{AsCH}(\text{CN})\text{CH}_2\text{As}(\text{CH}_3)_2\text{M}(\text{CO})_4$ | Cr | CHCl_3 | $J_{3'4'}/J_{3'4}$ | 3.79 | 70.5 | 46.7 | 70.1 |
| | | $(\text{CD}_3)_2\text{CO}$ | | 4.13 | 71.0 | 50.6 | 76.0 |
| | Mo | CHCl_3 | $J_{3'4'}/J_{3'4}$ | 1.96 | 43.75 | 11.1 | 12.2 |
| | | $(\text{CD}_3)_2\text{CO}$ | | 1.67 | 40.0 | 10.4 | 11.4 |
| | W | CHCl_3 | $J_{3'4'}/J_{3'4}$ | 2.06 | 44.75 | 10.7 | 11.8 |
| | | $(\text{CD}_3)_2\text{CO}$ | | 1.87 | 42.75 | 10.0 | 11.0 |
| W | CHCl_3 | $J_{3'4'}/J_{3'4}$ | 2.18 | 46.25 | 11.3 | 12.4 | |
| | $(\text{CD}_3)_2\text{CO}$ | | 1.72 | 40.75 | 9.9 | 10.9 | |

^a ^1H - ^1H . ^b ^1H - ^{19}F .

of calculations, there occurs an increase of *ca.* 2 for substitution of the chromium atom by molybdenum. It is possible that distortions from "tetrahedral" dispositions at the bridge carbons are the cause of these seemingly anomalous results.

The trifluoroarsenic and trifluorophosphorus chelate complexes also presented several problems. While the calculated dihedral angles seem to fall in the expected range, they decrease by 1° , rather than increase by 2° , upon substitution of chromium by molybdenum. Moreover, the Karplus coefficients fluctuate considerably with the solvent in which the spectra were taken. The latter phenomenon may be a reflection of the solvent dependency of ^1H - ^{19}F coupling constants and, perhaps, of the conformational preferences in these chelate systems, although it has been suggested that the Karplus coefficients themselves may take on solvent-dependent values.²⁶ Since we could not unambiguously assign the two geminal fluorine atoms to specific positions on the chelate rings,² we performed calculations on the complexes in which the assignments of F_4 and F_4' are interchanged. This yields anomalously high dihedral angles, *ca.* 70° , and at the present, it seems that the assignment which leads to dihedral angles of *ca.* 51° is the more acceptable.

Finally, we examined the cyano chelate complexes. We have previously suggested² that the chromium derivative undergoes some degree of conformational inversion. In the present work, our calculations give rise to seemingly low and solvent-dependent dihedral angles (*ca.* $43 \pm 3^\circ$). In addition, the Karplus coefficients also vary significantly, although they fall in the range we would expect. Since we have demonstrated that the Karplus coefficients for the trimethylsilyl derivatives are essentially independent of the solvent medium, the deviations of A and B are likely to be due to the changes in conformer populations induced by solvent alterations. These data amply illustrate the pitfalls to be encountered in calculating geometrical parameters from systems undergoing conformational inversion.

Thus it appears that such simple ϕ , A , and B calculations for our fluorinated chelate complexes do not yield consistent results. On the other hand, the parameters derived from the silyl derivatives seem well behaved, and in the latter cases, the ϕ , A , and B values we have derived may be approximate, but we anticipate that the trends we have observed would still be evident if minor fluctuations in ϕ and A/B occurred.

Donor Atom Variations. A geometrical treatment

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 $^{31}\text{P}-^1\text{H}^{31}$ couplings and it is our purpose to comment further on this in future publications.

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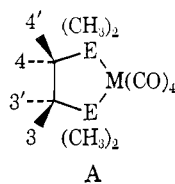
A Nuclear Magnetic Resonance Study of the Conformational Preferences of Some Manganese Carbonyl Halide Chelate Complexes of Di(tertiary arsines)

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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 ($\text{M} = \text{Cr}, \text{Mo}$,



W; $3 = \text{Si}(\text{CH}_3)_3$, SiCl_3 , F , Cl , and CN and $3'$, 4 and $4' = \text{H}$; 3 and $3' = \text{H}$ and 4 and $4' = \text{F}$; 3 and $4 = \text{F}$ and $3'$ and $4' = \text{H}$; and $3' = \text{H}$ and 3 , 4 , and $4' = \text{F}$), 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 atoms³ 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 fulfillment of the requirements for the Ph.D. degree in Chemistry, University of British Columbia.

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