

SOME NMR STUDIES ON SIX-MEMBERED CHELATE RINGS IN FLUOROCARBON-BRIDGED DITERTIARY ARSINE METAL CARBONYL COMPLEXES

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SUMMARY

Dimethylarsine reacts with $(\text{CH}_3)_2\text{AsCF}_2\text{CCl}=\text{CF}_2$ to give the novel ligand 1,3-bis(dimethylarsino)-2-chloro-1,1,3,3-tetrafluoropropane, (I). This ditertiary arsine affords the complexes $(\text{L-L})\text{M}(\text{CO})_4$ and $(\text{L-L})\text{Mn}(\text{CO})_3\text{I}$, ($\text{M} = \text{Cr}, \text{Mo}$; $\text{L-L} = (\text{I})$), which contain six-membered chelate rings. The ^1H and ^{19}F NMR spectra have been studied in an attempt to obtain conformational information from the derived coupling constants. The ^{19}F spectra of the chromium and molybdenum complexes have been solved using spin "tickling" techniques.

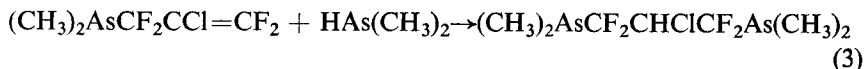
INTRODUCTION

Studies on the conformation of five-membered chelate rings in ditertiary arsine complexes such as $(\text{L-L})\text{M}(\text{CO})_4$ ($\text{M} = \text{Cr}, \text{Mo}$; $\text{L-L} = (\text{CH}_3)_2\text{AsCHFCH}_2\text{-As}(\text{CH}_3)_2$) show an unexpected preference for the fluorine atom to occupy axial positions in the puckered ring¹⁻³. In view of this and the current interest in the conformations of six-membered diamine chelate rings⁴⁻¹⁰, it seemed desirable to study metal carbonyl complexes of ditertiary arsines with a three-carbon bridging group.

The present paper is concerned with the synthesis of such a ligand with a fluorocarbon bridge, $(\text{CH}_3)_2\text{AsCF}_2\text{CHClCF}_2\text{As}(\text{CH}_3)_2$, (I), and an NMR investigation of its chelate complexes $(\text{L-L})\text{M}(\text{CO})_4$ and $(\text{L-L})\text{Mn}(\text{CO})_3\text{I}$ ($\text{M} = \text{Cr}, \text{Mo}$; $\text{L-L} = (\text{I})$).

EXPERIMENTAL

Volatile reactants and products were manipulated in a conventional vacuum system. Non-volatile, air-sensitive liquids were handled using syringes. Infrared spectra were recorded on a Perkin-Elmer 457 instrument and NMR spectra on an



Confirmation of this structure comes from the isolation and complete characterization of complexes of the ligand with metal carbonyls as will be described next.

When the ligand (I) is reacted with chromium or molybdenum hexacarbonyl, or pentacarbonylmanganese iodide, two carbonyl groups are displaced and the chelate complexes (II) shown in Figure 1 are obtained. The chromium and molybdenum compounds are also obtained when (I) reacts with the appropriate norbornadiene metal carbonyl derivatives. Analytical data for the new complexes are given in Table 1. The infrared spectrum of the manganese complex indicates that the ligand is *cis* to the iodine atom as shown in Figure 1*.

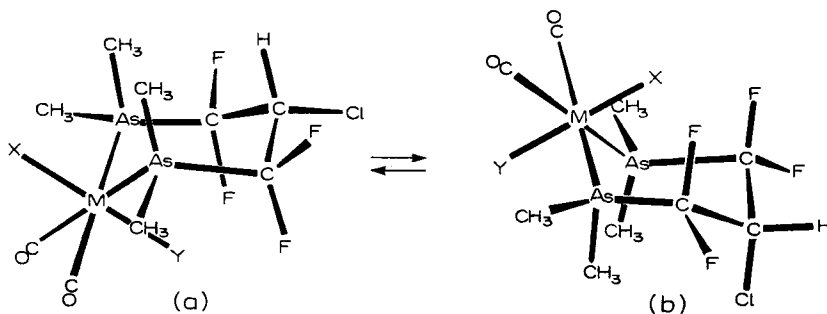


Fig. 1. The conformational equilibrium proposed for the complexes (II) in solution. (M = Cr, Mo; X = Y = CO; M = Mn; X = CO, Y = I or X = I, Y = CO).

TABLE 1

ANALYTICAL DATA AND CARBONYL INFRARED SPECTRA OF NEW COMPOUNDS

Compound ^a	Analysis: Calcd. %		Found %		Infrared spectra, $\nu(\text{CO})^b$	M.p. ^c (°C)
	C	H	C	H		
(L-L)Cr(CO) ₄	25.29	2.51	25.58	2.60	2023, 1931, 1916, 1907	164-166
(L-L)Mo(CO) ₄	23.32	2.31	23.20	2.15	2036, 1940, 1928, 1917	162-164
(L-L)Mn(CO) ₃ I	19.24	2.10	19.03	2.08	2033, 1974, 1931	darkens at ca. 200

^a (L-L) is the ligand (I).

^b Cyclohexane solution; all bands are strong.

^c With decomposition.

* The pattern of bands is characteristic of *cis* substitution and is identical with that obtained from $\text{Cl}(\text{CO})_3\text{Mn}(\text{CH}_3)_2\text{AsCH}_2\text{CH}_2\text{CH}_2\text{As}(\text{CH}_3)_2$ which has the expected solid-state structure¹⁷.

Previous results from the solid-state structures of diamine and ditertiary phosphine complexes indicated that the ligand would be in the chair conformation in (II)^{4,9,10,14}. Furthermore, the NMR studies on diamine systems⁷⁻⁹ indicate that in solution (II) would be involved in a conformational equilibrium between the two possible chair forms. An X-ray investigation of the chromium complex (II) has confirmed that in the solid state the chelate ring is in the chair conformation with the hydrogen atom occupying the axial position¹⁵. This structure shows no sign of the disorder problems which have plagued the solid-state investigation of related ditertiary arsine and phosphine complexes of chromium and molybdenum carbonyls containing a five-membered chelate ring^{16,17}.

The proton-decoupled ¹⁹F NMR spectra of the chromium and molybdenum compounds (II) were of the AA'BB' type; a sample spectrum, that of the chromium compound, is shown in Figure 2. The analysis of such a system is not straightforward. For six of the 12 expected transitions in each half of the symmetrical spectrum (disregarding weak combination lines), no explicit algebraic expressions can be obtained for either the transition energies or their relative intensities. The most successful and general methods for analyzing AA'BB' systems have involved the construction of an energy-level diagram (ELD) from which all the parameters $\delta(AB)$, $N = J(AB) + J(AB')$, $L = J(AB) - J(AB')$, $M = J(AA') - J(BB')$ and the elusive $K = J(AA') + J(BB')$ are obtainable^{18,19}. The construction of a complete and unique ELD is accomplished most easily using the weak double-irradiation ("tickling") method, as detailed by Lustig and co-workers²⁰, and this is the method used for the following analyses.

The lines in the downfield half of the spectrum of the chromium complex were "tickled" and the resulting splittings are recorded in Table 2. Since the line pairs $\bar{3}$, $\bar{4}$ and $\bar{9}$, $\bar{10}$ are individually only 3.2 Hz and 2.0 Hz apart respectively, each could not be singly irradiated, but as will be seen this does not hinder the final analysis.

From the fact that "tickling" each of the lines $\bar{1}$, $(\bar{3} + \bar{4})$, $\bar{6}$, $\bar{7}$, $(\bar{9} + \bar{10})$ and $\bar{12}$ splittings occurred at lines 1, 3, 6, 7, 10 and 12 respectively, the latter are classified as being $0-|1|$ transitions of the α group. Two of these lines, using energy levels 0_1 and 0_4 are expected to produce splittings in a total of four lines each, while the remaining four, using energy levels 0_2 and 0_3 are expected to cause splittings in six other lines each when irradiated. From Table 2, lines 3 and 10 are therefore seen to be 0_1 and 0_4 transitions, while lines 1, 6, 7 and 12 are 0_2 and 0_3 transitions. "Tickling" lines $\bar{1}$, $\bar{6}$, $\bar{7}$ and $\bar{12}$ caused, apart from splittings in other $0-|1|$ transitions, splittings in lines 4 and 9, which are therefore $2-1$ transitions. By elimination, lines 2, 5, 8 and 11 are the \mathcal{L} group transitions. This is substantiated by the result that tickling line \bar{i} produces splittings only in lines $|k|$, $i \neq k$ where i or $k = |2|$, $|5|$, $|8|$, or $|11|$.

From the above arguments and a further consideration of the results in Table 2, the completed ELD in Figure 3 may be constructed. The sum relationships

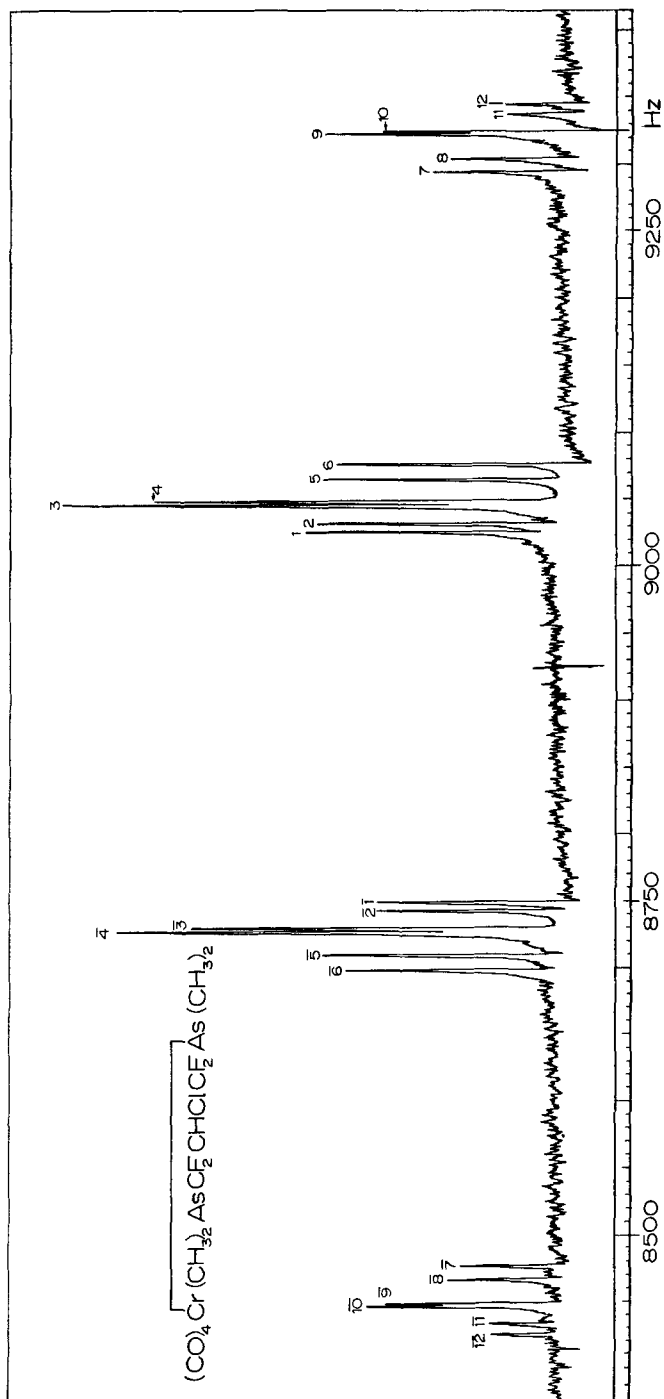


Fig. 2. The ^{19}F NMR spectrum of the chromium complex (II) with proton decoupling.

TABLE 2

RESULTS OF "TICKLING" EXPERIMENTS ON THE COMPOUND $(L-L)Cr(CO)_4$ ^a

		"Tickle"											
		$\bar{1}$	$\bar{2}$	$\bar{3}$	$\bar{4}$	$\bar{5}$	$\bar{6}$	$\bar{7}$	$\bar{8}$	$\bar{9}$	$\bar{10}$	$\bar{11}$	$\bar{12}$
Observe	$\bar{1}$							X					X
	$\bar{2}$								X			X	
	$\bar{3}$												
	$\bar{4}$												
	$\bar{5}$								X			X	
	$\bar{6}$							X					X
	$\bar{7}$	X											
	$\bar{8}$		X			X							
	$\bar{9}$												
	$\bar{10}$												
	$\bar{11}$		X			X							
	$\bar{12}$	X						X					
	1	X								X			X
	2					X			X				
	3			X									X
	4									X			X
	5		X									X	
	6			X				X					
	7							X		X			
	8		X									X	
	9	X		X				?					
	10	X						?		X			
	11					X			X				
	12			X									X

^a Lines in the downfield half of the spectrum, Figure 2, were "tickled" and the perturbed lines are indicated with an X.

$\nu_1 + \nu_{12} = \nu_6 + \nu_7$; $\nu_4 + \nu_6 = \nu_7 + \nu_9$; and $\nu_2 + \nu_{11} = \nu_5 + \nu_8$, which are expected from the ELD, were found to be valid to 0.1 Hz. This ELD also rationalizes the somewhat surprising result that tickling the line pairs $(\bar{3} + \bar{4})$ and $(\bar{9} + \bar{10})$ caused splittings in only four other lines, all of which were in the upfield half of the spectrum.

Following the method of Whitman¹⁹, the energy levels also given in Figure 3 were calculated, and from these the five parameters $\delta(AB) = 535.6$, $N = +277.3$, $L = +273.2$, $M = +38.0$ and $K = +56.6$ describing the ¹⁹F system were obtained. The derived coupling constants were refined using a modified version of the LAØCØØN III program and are given, along with the ¹H NMR parameters, in Table 3 for both the chromium and molybdenum complexes. Although the sign of K relative to N is not directly evident from either the spectra or the ELD, calculated spectra using equal and opposite signs indicated that K , as well as N , is positive. (The fluorine spectrum of the manganese complex (II) was unfortunately too broad for any meaningful assignments to be made.)

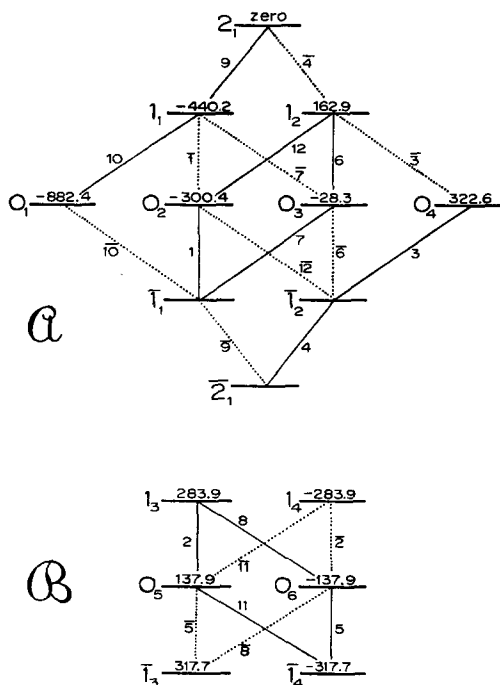


Fig. 3. The energy-level diagram for the chromium complex (II). The numbers associated with the transitions correspond with those of the absorptions in Figure 2.

In all compounds, the resonance of the single proton in the six-membered ring was split by the fluorine atoms into a triplet of triplets. Although the crystal-structure determination of the chromium complex indicated that the chlorine atom occupied the equatorial position, it is probable that these complexes undergo conformational inversion in solution, as shown in Figure 1. Since the effect of the arsenic substituent on the ³ $J(\text{H-F})$ and ⁴ $J(\text{F-F})$ values is not well understood, only *qualitative* discussion about the relative population of the two conformers will be presented.

The conformers with the chloro substituents locked in the axial position would most likely yield roughly equal $^3J(\text{H-F})$ values less than *ca.* 8 Hz in magnitude²¹. The data in Table 3 seem to exclude this possibility. They also indicate that these conformers are not *very* predominant in solution.

TABLE 3
NMR DATA FOR NEW COMPLEXES^a

Compound	$\delta_{\text{A}}^{\text{b}}$	$\delta_{\text{B}}^{\text{b}}$	$J(\text{AB})$	$J(\text{AB}')$	$J(\text{AA}')^{\text{c}}$	$J(\text{BB}')^{\text{c}}$	$\delta_{\text{H}}^{\text{d}}$	$J(\text{HF})$
(L-L)Cr(CO) ₄	91.58	97.27	+275.2	+2.0	+9.3	+47.2	4.45	5.6, 15.2
(L-L)Mo(CO) ₄	90.29	97.34	+276.9	+2.0	+8.3	+49.1	4.52	6.0, 15.8
(L-L)Mn(CO) ₃ I	—	—	—	—	—	—	5.05	4.0, 21.2

^a CDCl₃ solution.

^b Upfield from internal CFCl₃.

^c See text.

^d Downfield from internal TMS.

Locked conformers (II)(a) would be expected to have *trans* $^1\text{H-}^{19}\text{F}$ (axial-axial) coupling constants several times larger than their *gauche* (axial-equatorial) couplings²¹. If the *trans* $^1\text{H-}^{19}\text{F}$ couplings of the locked conformers (II)(a) were relatively small, for example 25 Hz, the data could be taken to infer that the complexes exist in solution as an equilibrium mixture of (II)(a) and (II)(b). If, however, this *trans* $^3J(\text{H-F})$ value were larger, say 40 Hz, the equilibrium population of (II)(a) would be much lower. Thus, even a qualitative interpretation of the relative populations of the conformers is dependent upon knowledge of the $^3J(\text{H-F})$ couplings for the locked conformers (II)(a) and (II)(b).

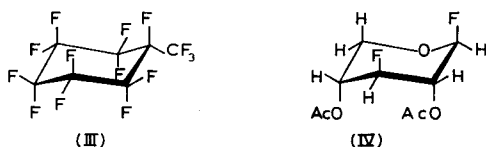
A slight axial chlorine preference⁹ has been reported as the result of measurements on some six-membered diamine chelate complexes. In "normal" cyclohexanes, chlorine has a small equatorial preference²⁵. The diamine chelates probably show a slight axial preference because of hydrogen bonding with the $>\text{NH}_2$ moieties.

Since the *trans* $^1\text{H-}^{19}\text{F}$ coupling constant for the manganese complex is *ca.* 5 Hz larger than those obtained for the chromium and molybdenum derivatives, it is possible that this difference indicates a greater population of conformer (II)(a). As is shown in Figure 2, there are two geometric isomers for the manganese complex having the proton and chlorine atoms in a specific configuration. (This may account for the broadened ^{19}F spectrum.) Thus, even if the ring were known to be locked, the position of the iodine atom relative to the ring cannot be assigned. A similar trend has been observed²⁴ in the Cr(CO)₄ and Mn(CO)₃I complexes of the ligand (CH₃)₂AsCD₂CH₂CH₂As(CH₃)₂, where the $^3J(\text{H-H})$ couplings suggest that one conformation in the chelate ring of the manganese compound is highly

avored. However, until further information about the electronic and steric effect of changing the metal atom and its substituents is obtained, it is unwise to attribute *all* these coupling changes to purely conformational alterations.

It must be mentioned at this stage that the mathematical solution of an AA'BB' system does not allow one to differentiate between δ_A or δ_B , or between $J(A-A')$ and $J(B-B')$. Because F₃ and F₄ are involved in axial-axial and equatorial-equatorial interactions with the proton, the assumption can be made that the greater H-F coupling in the chromium and molybdenum compounds is associated with these fluorine atoms. The atoms F₁ and F₂ are only involved in *gauche* (axial-equatorial) interactions, so that their coupling constants should be less. Examination of the undecoupled spectrum reveals that it is the downfield half which must be assigned to F₃ and F₄. But even with this information the calculated coupling constants from *K* and *M* can still not be assigned uniquely to $J(A-A')$ and $J(B-B')$.

With regard to $^4J(F-F)$ couplings, if there is no strong conformational preference in solution $J(A-A')$ and $J(B-B')$ should be the average of axial-axial and equatorial-equatorial couplings. The value of *ca.* 9 Hz is in line with the published values of both Abraham²² ($J(ax.-ax.) = +26$, $J(ax.-eq.) = 0$ and $J(eq.-eq.) = -10$) and Hall and co-workers²³ ($J(ax.-ax.) = 10.4$, $J(ax.-eq.) = 0$ and $J(eq.-eq.) = -3$) who studied molecules such as (III) and (IV).



The very different value of *ca.* 43 Hz, however, is irreconcilable with these previously published constants. It appears that the chlorine atom in one of its positions greatly affects these $^4J(F-F)$ couplings, making them both significantly more positive.

On the other hand, if it is assumed that the equilibrium (in solution) is weighted in favor of (II)(a), the X-ray determined structure, then the F₃-F₄ coupling would be predominantly axial-axial and $J(F_1-F_2)$ predominantly equatorial-equatorial. The assignment of $J(F_3-F_4)$ to the larger coupling of 48 Hz and $J(F_1-F_2)$ to the lower-valued coupling of *ca.* 9 Hz would mean that both axial-axial and equatorial-equatorial couplings are, in these complexes, significantly more positive than the published values. The reverse assignment would again explain the smaller coupling, leaving the larger one at least 50 Hz higher than the published negative values.

Further studies now in progress on ditertiary arsine complexes containing fewer fluorine atoms should clarify some of the problems that have arisen in the present investigation.

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REFERENCES

- 1 W. R. CULLEN, L. D. HALL AND J. E. H. WARD, *Chem. Comm.*, (1970) 625.
- 2 W. R. CULLEN, L. D. HALL AND J. E. H. WARD, *J. Amer. Chem. Soc.*, in press.
- 3 W. R. CULLEN, L. D. HALL AND J. E. H. WARD, unpublished results.
- 4 C. J. HAWKINS, *Absolute Configuration of Metal Complexes*, Wiley-Interscience, New York, 1971.
- 5 R. J. GEUE AND M. R. SNOW, *J. Chem. Soc. (A)*, (1971), 2981.
- 6 P. G. BEDDOE, M. J. HARDING, S. F. MASON AND B. J. PEART, *Chem. Comm.*, (1971) 1283.
- 7 T. G. APPLETON AND J. R. HALL, *Inorg. Chem.*, 9 (1970) 1807.
- 8 T. G. APPLETON AND J. R. HALL, *Inorg. Chem.*, 10 (1971) 1717.
- 9 T. G. APPLETON AND J. R. HALL, *Inorg. Chem.*, 11 (1972) 117.
- 10 J. R. GOLLOGLY AND C. J. HAWKINS, *Inorg. Chem.*, 11 (1972) 156.
- 11 R. BURTON AND L. D. HALL, *Canad. J. Chem.*, 48 (1970) 59.
- 12 H. GOLDWHITE, D. G. ROWSELL AND C. VALDEZ, *J. Organometallic Chem.*, 12 (1968) 133.
- 13 W. R. CULLEN, *Adv. Organometallic Chem.*, 4 (1966) 145.
- 14 G. R. CLARK AND G. J. PALENIK, *Inorg. Chem.*, 9 (1970) 2754.
- 15 I. W. NOWELL AND J. TROTTER, personal communication.
- 16 W. R. CULLEN, I. W. NOWELL, P. J. ROBERTS, J. TROTTER AND J. E. H. WARD, *Chem. Comm.*, (1971) 560.
- 17 J. TROTTER, personal communication.
- 18 B. DISCHLER, *Z. Naturforsch.*, 20a (1965) 888.
- 19 D. R. WHITMAN, *J. Chem. Phys.*, 36 (1962) 2085.
- 20 E. LUSTIG, E. P. RAGELIS, N. DUY AND J. A. FERRETTI, *J. Amer. Chem. Soc.*, 89 (1967) 3953.
- 21 A. M. IHRIG AND S. L. SMITH, *J. Amer. Chem. Soc.*, 92 (1970) 759; K. L. WILLIAMSON, Y.-F. L. HSU, F. H. HALL, S. SWAGER AND M. S. COULTER, *ibid.*, 90 (1968) 6717.
- 22 R. J. ABRAHAM, *J. Chem. Soc. (B)*, (1969) 1022.
- 23 L. D. HALL, R. N. JOHNSON, A. B. FOSTER AND J. H. WESTWOOD, *Canad. J. Chem.*, 49 (1971) 236.
- 24 W. R. CULLEN, H. K. SPENDJIAN AND L. D. HALL, unpublished results.
- 25 E. L. ELIEL, N. L. ALLINGER, S. J. ANGYAL AND G. A. MORRISON, *Conformational Analysis*, Wiley-Interscience, New York, 1965.