weaken as the metal-to-axial ligand bond strengthens. This idea is supported by the Mo–Mo stretching frequencies of $Mo_2(O_2CCF_3)_4$ in various solvents, given in Table VI. The frequencies decrease from the solid-state value in a manner roughly correlated with increasing donor strength of the solvent. The decrease for pyridine is by far the largest, and since the thermal stability of the crystalline pyridine adduct at room temperature is marginal, it seems doubtful that adducts containing weaker donors can be isolated under normal circumstances.

The frequency of the lowest energy electronic transition in $Mo_2(O_2CCF_3)_4$ appears to follow the same pattern as a function of solvent as the metal–metal stretching frequency (see Table VI). This observation has potential importance in the assignment of this transition, but we would not care to assess its significance without the aid of single-crystal polarized spectra. The two higher energy transitions[15] could not be studied as a function of solvent due to solvent absorption.

Molecular Structure. Comparison of the structure of $Mo_2(O_2CCF_3)_4(py)_2$ with the previous results for $Mo_2(O_2CCF_3)_4$[15] provides a quantitative measure of the decrease in Mo–Mo bond strength upon coordination of pyridine as an axial donor. The 2.129 (2) Å Mo–Mo bond length in the adduct is 0.039 (6) Å greater than the value of 2.090 (4) Å obtained for the parent compound. The difference is statistically significant but rather small from a chemical viewpoint. This coupled with the extremely long Mo–N bond of 2.548 (8) Å, 0.43 (1) Å longer than the average Mo–O distance, clearly indicates that the two molybdenum atoms energetically prefer to maintain their very strong metal–metal interaction rather than trade any significant amount thereof for a normal strength metal–ligand bond, *no matter how effective a donor the axial ligand L may be.* That is, the intrinsically strong Mo–Mo bond necessitates an intrinsically weak Mo–L bond. This "metal–metal *trans* effect" operates to some extent in the other dinuclear carboxylates. Thus, in $Cr_2(OAc)_4(H_2O)_2$[8] and $Cr_3O(OAc)_6(H_2O)_3^+$,[28] the average Cr–OAc distances of 2.018 (2) and 1.98 (1) Å are comparable to each other and to the Cr–OH_2 distance in the trimer, 2.02 (1) Å, but all are significantly shorter than the Cr–OH_2 distance in the dimer, 2.272 (3) Å. In the dimer, the water molecule is trans to the Cr–Cr bond; in the trimer, to the Cr–O bond. Again, the Rh–OH_2 distance of 2.310 (3) Å in $Rh_2(OAc)_4(H_2O)_2$ is substantially greater than the average Rh–OAc distance of 2.039 (2) Å. Nowhere is the trans effect more dramatically illustrated than in the molybdenum system, however; therefore, Mo(II) appears to have an intrinsically greater metal–metal bonding tendency in the carboxylate framework than do Cr(II) and Rh(II). This has long been suggested from theoretical considerations and the available X-ray data,[7] but never so conclusively demonstrated. One expects, then, that if good crystals of unsolvated $M_2(O_2CCF_3)_4$, M = Cr, Rh, could be obtained, which may not be possible, the Cr–Cr and Rh–Rh distances would definitely be longer than the Mo–Mo distance in $Mo_2(O_2CCF_3)_4$, allowing for differences in covalent radii. Moreover, if crystalline $M_2(O_2CCF_3)_4(py)_2$, M = Cr, Rh, could be obtained, which should be possible, the metal–nitrogen distances should definitely be shorter than in $Mo_2(O_2CCF_3)_4(py)_2$, again allowing for differences in covalent radii. The lengths found for metal-to-axial ligand bonds in the carboxylates thus provide valuable information about the implicit tendencies of the metals toward mutual attraction.

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Nuclear Magnetic Resonance Study of the Conformational Preferences of Some Substituted Ditertiary Arsine Chelate Complexes of Chromium Carbonyl[1,2]

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Abstract: The synthesis of some novel ditertiary arsine chelate complexes of chromium carbonyl are described. Detailed analyses of the nmr spectra of some of these substances were facilitated by heteronuclear double resonance experiments. The vicinal ^1H–^1H and ^{19}F–^1H couplings indicate that while some derivatives have a most marked conformational preference, others have several different conformations significantly populated.

It has been realized for many years that the five-membered rings of metal chelate complexes have the ligand in the gauche conformation.[3] The importance of nonbonded interactions in determining the favored conformations of such derivatives was first pointed out by Mathieu[4] and by Corey and Bailar,[5] and predic-

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(1) Preliminary communication: W. R. Cullen, L. D. Hall, and J. E. H. Ward, *Chem. Commun.*, 625 (1970).

(2) (a) This work is 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. (b) This paper may be regarded as part V of a series entitled, "The Conformations of Cyclic Compounds in Solution;" for part IV, see L. D. Hall and R. N. Johnson, to be published.

(3) A. M. Sargeson in "Transition Metal Chemistry," Vol. 3, R. L. Carlin, Ed., Marcel Dekker, New York, N. Y., 1966, p 303; J. H. Dunlop and R. D. Gillard, *Advan. Inorg. Chem. Radiochem.*, 9, 185 (1966).

(4) J. P. Mathieu, *Ann. Phys. (Paris)*, 19, 335 (1944).

(5) E. J. Corey and J. C. Bailar, *J. Amer. Chem. Soc.*, **81**, 2620 (1959).

tions of the relative stabilities of isomers based on these considerations have often been correct.[6] Recently, more sophisticated calculations of the conformations of chelate rings in simple[8] and complex[9,10] systems have been attempted. Calculations by Gollogly and Hawkins[8] on ethylenediamine type systems have indicated that a simple five-membered chelate ring is very flexible, having like cyclopentane[11] a wide range of conformations of essentially equivalent energy, including unsymmetric conformations not considered previously.[5]

Until quite recently experimental verification of the validity of the various theoretical models has been confined to X-ray crystallographic determinations, which suffer from the perturbing effects of intermolecular forces such as hydrogen bonding[12] and crystal packing.[10] Fortunately nuclear magnetic resonance spectroscopy now provides, at least in principle, an accurate method for evaluating the conformations of chelate rings *in solution*, and several groups of workers[3,7,13–20] have already described attempts to exploit this obvious potential. Only a few investigations yielded coupling constant information of conformational significance. The lack of general success can be ascribed to a number of causes, including the use of ligands which are basically unsuitable for nmr analysis. Beattie[14] has recently summarized the conformational investigations on tris(ethylenediamine) metal complexes.

In the present study we have deliberately chosen to use ligands which would give nmr spectra suitable for complete analysis. Since previous studies from this[21] and other laboratories[22] had demonstrated that ^{19}F nmr parameters are generally more sensitive than ^{1}H parameters to changes in stereochemical environment, several specifically fluorinated ligands were included. Serendipitously, this choice revealed a rather novel conformational preference for the fluorine substituents. For additional simplicity ditertiary arsine derivatives of chromium carbonyl were chosen for this initial study.

Experimental Section

Dimethylarsinic acid, chromium hexacarbonyl, and the various olefins were purchased commercially and were used without further purification. Tetramethyldiarsine was prepared by the reduction of dimethylarsinic acid in 2 *M* hydrochloric acid with hypophosphorous acid;[23] the diarsine was used without further purification.

All reactions were carried out in sealed Pyrex tubes. Air-sensitive reactants and products were handled either by syringe techniques in a nitrogen atmosphere or in a standard vacuum system. A Swagelok fitting equipped with an injection gasket[24] enabled the transfer of air-sensitive, involatile liquid samples 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 from an AEI MS-9 instrument with direct introduction of solid samples. All complexes produced peaks corresponding to their parent ion, followed by the stepwise loss of four carbonyl groups. Infrared spectra were measured in cyclohexane solution using a Perkin-Elmer Model 457 spectrometer and were calibrated against polystyrene and/or cyclohexane.

All nmr spectra were measured with an extensively modified Varian HA-100 spectrometer, operating in the locked, frequency-sweep mode. All ^{1}H chemical shifts were recorded with tetramethylsilane as the internal reference. For ^{19}F measurements the instrument was tuned to 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 described elsewhere.[25] Computer analyses of the nmr spectra used data obtained from carefully calibrated charts and were performed with a IBM 360–67 computer located at the University of British Columbia and the LAOCOON III Program, suitably modified by Mr. R. B. Malcolm of this laboratory.

A. **Preparation of 1,2-Bis(dimethylarsino)-1-fluoroethane (3).** A Carius tube (70-ml capacity) was evacuated, cooled in liquid nitrogen, and charged with tetramethyldiarsine (5.0 ml, 7.3 g, 35 mmol). Excess vinyl fluoride (29 g, 64 mmol) was condensed into the tube which was then sealed. The tube was irradiated for 48 hr with a 200-W Hanovia ultraviolet lamp placed at a distance of *ca.* 20 cm. The tube was continuously shaken and was cooled with a stream of air. When the reaction was completed, the tube was opened in a vacuum system and the volatile contents were removed, leaving a residue (7.2 g, 82%) of the colorless, air-sensitive liquid product.

B. **Preparation of 1,2-Bis(dimethylarsino)-1-fluoroethane(tetracarbonyl)chromium (9).** A Carius tube was charged with chromium carbonyl (1.0 g, 5 mmol), evacuated, and cooled in liquid nitrogen. The ligand **3** (1.0 g, 3.9 mmol) was added by syringe, followed by sodium dried benzene (5 ml). The tube was sealed, allowed to warm to room temperature, and then heated to 140° for 14 hr. The benzene was removed under reduced pressure and the oily residue was triturated with 5 ml of petroleum ether (bp 40–60°). The resulting yellow solid was treated with two more 5-ml portions of the same solvent, dried under reduced pressure, and then vacuum sublimed (120°, 10^{-3} mm). This produced a pure sample of **9** (0.75 g, 39%).

The above procedures are representative of those used for the preparation of the other ligands and complexes. Table I lists the ligands **1–6** and the complexes **7–12** synthesized. The reaction conditions and analytical data are summarized in Table II.

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[6] F. P. Dwyer, F. L. Garvan, and A. Shulman, *J. Amer. Chem. Soc.*, 81, 290 (1959); F. P. Dwyer, T. E. MacDermott, and A. M. Sargeson, *ibid.*, **85**, 2913 (1963); see also the discussion in ref 7.

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[11] J. E. Kilpatrick, K. S. Pitzer, and R. S. Spitzer, *ibid.*, 69, 2483 (1947); K. S. Pitzer and W. E. Doneath, *ibid.*, 81, 3213 (1959); J. B. Hendrickson, *ibid.*, 83, 4537 (1961).

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[14] J. K. Beattie, *Accounts Chem. Res.*, **4**, 253 (1971).

[15] J. K. Beattie and Sr. H. Elsbernd, *J. Amer. Chem. Soc.*, **92**, 1946 (1970); J. K. Beattie and L. H. Novak, *ibid.*, **93**, 620 (1971); J. K. Beattie, *Inorg. Chem.*, 10, 426 (1971).

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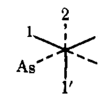
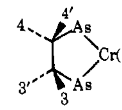
[25] R. Ernst, *J. Chem. Phys.*, **45**, 3845 (1966).

Table I. Ditertiary Arsine Ligands and Their Complexes Synthesized for Nmr Studies[a]

Ligands 	$(CH_3)_2AsC(1)(1')C(2)(2')As(CH_3)_2$ **1**, 1 = $Si(CH_3)_3$; 1', 2, and 2' = H **2**, 1 = $SiCl_3$; 1', 2, and 2' = H **3**, 1 = F; 1', 2, and 2' = H **4**, 1 = H; 1', 2, and 2' = F **5**, 1 = Cl; 1', 2, and 2' = H **6**, 1 = CN; 1', 2, and 2' = H
Complexes 	$(CH_3)_2AsC(3)(3')C(4)(4')As(CH_3)_2Cr(CO)_4$ **7**, 3 = $Si(CH_3)_3$; 3', 4, and 4' = H **8**, 3 = $SiCl_3$; 3', 4, and 4' = H **9**, 3' = F; 3, 4 and 4' = H **10**, 3 = H; 3', 4, and 4' = F **11**, 3 = Cl; 3', 4, and 4' = H **12**, 3 = CN; 3', 4, and 4' = H

[a] These diagrams are not intended to represent fixed rotamers or conformers in solution.

a first-order assignment and presents no problems beyond a decision as to which of the resonances are those of the geminal pair of protons. This decision was readily made by determining the relative signs of the three coupling constants, using the spin-tickling technique.[26] Irradiation of the *lowest* field transition of the H_4 quartet caused both of the *lower* field transitions of the $H_{4'}$ resonance to split into doublets, thus establishing that $J_{43'}$ and $J_{4'3'}$ have the same relative signs; hence H_4 and $H_{4'}$ must be the geminal pair of protons. An assignment for the trichlorosilyl derivative **8** was made similarly.

For the remaining derivatives **9**–**12** the lowest field resonance was intuitively assignable to the methine proton, this being the one which is deshielded most by the electronegative substituents at C_3.

Table II. Analytical and Preparative Data for Ligands and Their Complexes

Compound	Calcd, % C	Calcd, % H	Found, % C	Found, % H	Reaction time,[a] hr	Reaction temp, °C	Yield, %	Mp, °C
$(CH_3)_2AsCH_2CH(Si(CH_3)_3)As(CH_3)_2$	34.9	7.80	30.5	7.29	18		60	
$(CH_3)_2AsCH_2CH(SiCl_3)As(CH_3)_2$	19.4	4.07	19.3	4.36	15		86	
$(CH_3)_2AsCH_2CHFAs(CH_3)_2$	28.2	5.91	25.6	6.06	48		82	
$(CH_3)_2AsCF_2CFHAs(CH_3)_2$	24.7	4.49	24.6	4.35	24		90	
$(CH_3)_2AsCH_2CHClAs(CH_3)_2$	26.5	5.55	26.1	5.69	12		94	
$(CH_3)_2AsCH_2CHCNAs(CH_3)_2$	32.0	5.75	31.5	5.86	11		96	
$(CH_3)_2AsCH_2CH(Si(CH_3)_3)As(CH_3)_2Cr(CO)_4$	32.9	5.10	33.2	5.15	4	180	49	86–87
$(CH_3)_2AsCH_2CH(SiCl_3)As(CH_3)_2Cr(CO)_4$	22.4	2.82	22.3	2.79	5	140	74	135–138[b]
$(CH_3)_2AsCH_2CHFAs(CH_3)_2Cr(CO)_4$	28.6	3.60	28.4	3.45	14	140	39	160–162
$(CH_3)_2AsCFHCF_2As(CH_3)_2Cr(CO)_4$	26.3	2.87	26.5	2.90	6	150	65	194–195
$(CH_3)_2AsCH_2CHClAs(CH_3)_2Cr(CO)_4$[c]	27.5	3.46	27.5	3.43	4	140	38	164–165
$(CH_3)_2AsCH_2CHCNAs(CH_3)_2Cr(CO)_4$[d]	30.9	3.54	30.9	3.39	8	140	69	165–175[b]

[a] Ligands were prepared as described in experiment A and complexes as described in B. [b] Compound melts with decomposition. [c] Compound isolated by chromatography on Florisil by elution with benzene. [d] Compound purified by crystallization from a pentane-acetone mixture.

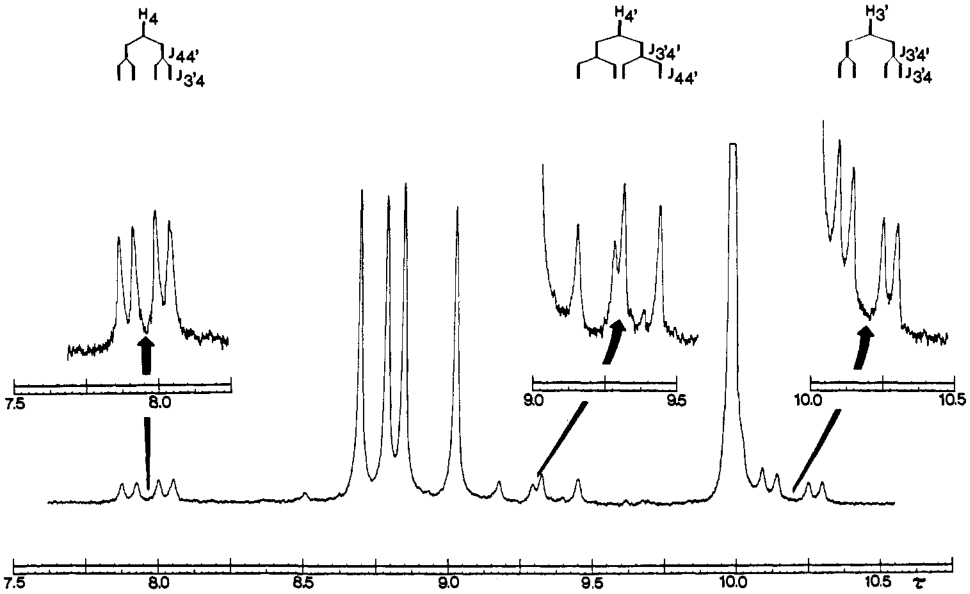


Figure 1. ^1H nmr spectrum (100 MHz) of 1,2-bis(dimethylarsino)-1-trimethylsilylethane(tetracarbonyl)chromium (7) in benzene-d_6 solution. A representation of the first-order assignment is given above the spectrum.

Results

The ^1H nmr spectrum of the trimethylsilyl derivative **7**, shown in Figure 1, is typical of those obtained for the chelates **7** and **8**. The spectrum is basically amenable to

The normal ^1H nmr spectrum of the monofluoro derivative **9**, shown in Figure 2, was complicated by the

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[26] *E.g.*, L. D. Hall and J. F. Manville, *Carbohyd. Res.*, **9**, 11 (1969), and references cited therein.

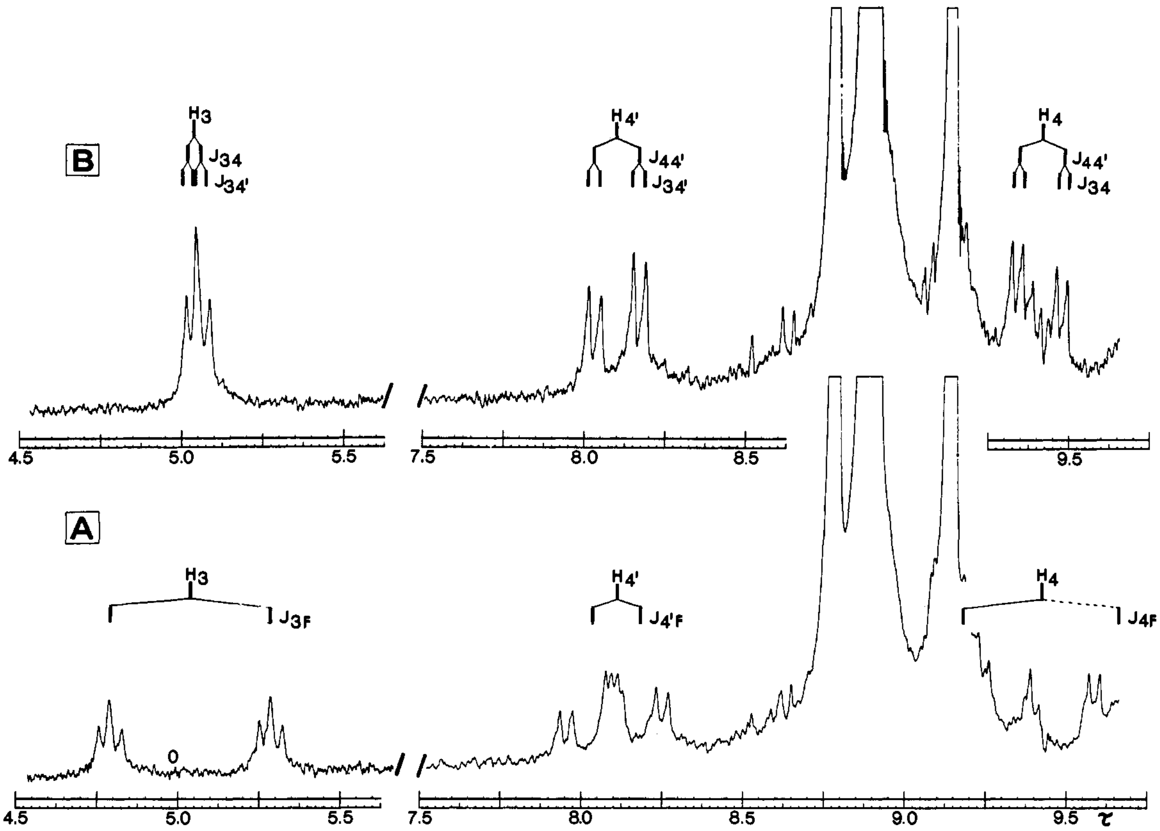

Figure 2. ^{1}H nmr spectra (100 MHz) of 1,2-bis(dimethylarsino)-1-fluoroethane(tetracarbonyl)chromium (**9**) in benzene-d_6 solution: A, the normal spectrum; B, the spectrum measured with simultaneous irradiation at the ^{19}F resonance frequency (94, 077, 949 Hz). Diagrammatic representations of the effect of the decoupling field and of the first-order assignement are also given.

additional spin coupling from the fluorine substituent and by the fact that one of the ring proton resonances was partially obscured by the methyl resonances and their attendant ^{13}C and spinning side bands. Fortunately it was an easy matter to simplify the spectrum by a ^{1}H-{^{19}F} heteronuclear decoupling experiment and this spectrum (Figure 2B), together with that of the ^{19}F resonance itself, provided adequate data for a full, iterative analysis. An expansion of the arsenic-methyl region of this spectrum is shown in Figure 3.

Analysis of the ^{19}F spectrum of the trifluoro derivative **10** proved to be straightforward. The determination of the signs of the ^{19}F-^{19}F couplings by selective ^{19}F-{^{19}F} double resonance experiments[27] was facilitated by the prior removal of all proton couplings from the ^{19}F spectrum by the noise-modulated, heteronuclear decoupling method.[25] Specifically it was found that irradiation of the *second highest* field component of the F_4 resonance caused the *lowest* field component of $F_{4'}$ to split into a doublet, thus establishing that $J_{43'}$ and $J_{4'3'}$ have the same relative signs. When the lowest field component of F_4 was irradiated, the *first* and *third highest* field components of $F_{3'}$ were split. Hence the relative signs of $J_{44'}$ and $J_{4'3'}$ are opposite and the vicinal ^{19}F-^{19}F couplings have negative signs.[27]

The chemical shifts and coupling constants obtained by iterative analysis of the spectra of complexes **7**-**12** are summarized in Tables III and IV, respectively. For reasons which are discussed later, each compound was studied in several different solvents.

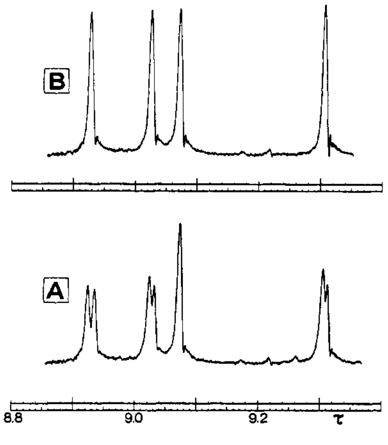

Figure 3. Expansion of the ^{1}H nmr resonances of the methyl groups of 1,2-bis(dimethylarsino)-1-fluoroethane(tetracarbonyl)-chromium (**9**): A, the normal resonances; B, with simultaneous irradiation at the ^{19}F resonance frequency (94, 077, 949 Hz).

Discussion

It is important to note at the outset that the energy barriers to conformational inversion of five-membered chelate ring systems are relatively small,[28] and hence *all conformations determined by the nmr method will be subject to some degree of time averaging.* Further, the ground-state energies of conformations which are close to one another on the pseudorotational cycle are likely

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(27) W. R. Cullen, L. D. Hall, and R. N. Johnson, to be published; L. D. Hall, R. N. Johnson, J. Adamson, and A. B. Foster, *Chem. Commun.*, 463 (1970), and references cited therein.

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

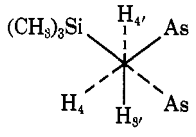
Table III. First-Order Chemical Shifts (τ and ϕ Values) for Complexes

Compound	Solvent[c]	3	3′	4	4′	Methyl groups			
7	C_6H_6		10.187	7.953	9.310	8.673	8.767	8.827	9.003
	$CHCl_3$		9.899	7.638	9.070	8.439	8.502	8.598	8.720
	CH_2Cl_2		9.869	7.612	9.052	8.448	8.518	8.608	8.721
	$(CD_3)_2CO$		9.85[d]	7.626	9.097	8.552	8.676	8.796	8.895
	$C_6H_5NO_2$		9.573	7.354	8.800	8.298	8.345	8.459	8.563
8	C_6H_6		9.718	7.964	9.183	8.633	8.695	8.967	9.215
	$CHCl_3$		9.164	7.434	8.810	8.226	8.371	8.417	8.612
	CH_2Cl_2		9.106	7.395	8.773	8.278	8.362	8.413	8.610
	$(CD_3)_2CO$[e]								
	$C_6H_5NO_2$[e]								
9	C_6H_6	5.503	193.00	8.103	9.435	8.838	8.933	8.974	9.205
	$CHCl_3$	4.400	193.17	7.500	8.734	8.439	8.486	8.520	8.650
	CH_2Cl_2	4.374	193.01	7.485	8.720	8.446	8.494	8.519	8.660
	$(CD_3)_2CO$	4.101	191.65	7.337	8.414	8.416	8.458	8.504	8.579
	$C_6H_5NO_2$	4.203	192.44	7.374	8.529	8.390	8.436	8.486	8.581
10	C_6H_6	4.265	220.84	120.17[a]	129.16[a]	*b*			
	$CHCl_3$	4.866	219.67	120.06	129.51	*b*			
	CH_2Cl_2	4.917	220.85	119.88	129.26	*b*			
	$C_6H_5NO_2$	5.204	220.41	120.10	128.51	*b*			
11	C_6H_6		6.492	8.930	8.544	8.883	8.938	9.082	9.111
	$CHCl_3$		7.283	9.696	9.375				
	CH_2Cl_2		5.672	8.134	7.789	8.448	8.448	8.521	8.565
	$C_6H_5NO_2$		5.522	8.042	7.711	8.425	8.425	8.477	8.528
12	C_6H_6[d]					8.932	9.008	9.082	9.244
	$CHCl_3$		7.736	7.765	*d*	8.376	8.396	8.427	8.539
	CH_2Cl_2		7.643	7.800	8.334	8.287	8.299	8.326	8.434
	$(CD_3)_2CO$		6.985	7.622	8.034	8.351	8.362	8.390	8.466
	$C_6H_5NO_2$		7.151	7.625	8.061	8.273	8.273	8.324	8.443

[a] The stereochemical assignment was made arbitrarily since the angular dependence of $^{19}F-^{19}F$ coupling is not well known. [b] Data not reported due to complexity of methyl resonances. [c] In order of increasing dielectric constant. [d] Proton resonance was obscured by the methyl resonances. [e] Sample decomposed in solution.

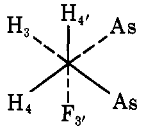
to be rather similar.[8] As a result, the present study and all like it are necessarily limited to an evaluation of which section of the pseudorotational cycle[8,29] is populated and, possibly, of the extent of that population. A single, specific conformation cannot be assigned, although it may be that in some instances one section of the pseudorotational cycle is extensively populated. In this paper we shall confine attention to defining the sense of rotation about the C–C bond of the ethane moiety. These limitations are made more pertinent by some recent structural studies on some hydrocarbon bridged ditertiary phosphine complexes. They reveal puckered unsymmetrical rings including conformations with both carbon atoms of the ethane bridging group lying below the P–M–P plane.[30]

It is convenient to start the discussion with the trimethylsilyl derivative **7**. It seemed likely that the ring conformation of this substance would be dictated by the steric requirements of the "bulky" trimethylsilyl group.[3–5,31] The vicinal $^1H-^1H$ coupling constants appear to agree with this anticipation, being *ca.* 16 and *ca.* 5 Hz in magnitude; the former value clearly indicates[32] a trans relationship between the two protons as indicated in A. A similar conclusion seems obvious for the related trichlorosilyl derivative **8**. In both instances the carbon–silicon bond projects toward the periphery of the molecule, as if it had an "equatorial" orientation.



A

The data for the monofluoro derivatives **9** indicate unequivocally that the fluorine substituent has a trans relationship with respect to a vicinal proton and hence that the C–F bond has an "axial" orientation as in B.



B

Thus the two vicinal $^1H-^1H$ coupling constants are both relatively small (*ca.* 3.5 Hz) while one of the vicinal $^{19}F-^1H$ coupling constants is approximately three times the magnitude of the other (*ca.* 49 and *ca.* 16 Hz).[21,33,34]

This marked conformational preference of the fluorine substituent had not been anticipated and in order to check its generality, the trifluoro derivative **10** was synthesized and studied. To our gratification its nmr parameters indicated a major preference for two of the C–F bonds to have the "axial" orientation, as in C.

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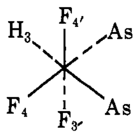
Table IV. First-Order Coupling Constants (Hz) for Complexes

Compound	Solvent[a]	$J_{33'}$	J_{34}	$J_{34'}$	$J_{3'4}$	$J_{3'4'}$	$J_{44'}$
7	C_6H_6				5.1	15.9	−12.7
	$CHCl_3$				5.2	16.1	−12.8
	CH_2Cl_2				5.3	15.9	−12.8
	$(CD_3)_2CO$				5.0	16.1	−12.8
	$C_6H_5NO_2$				5.2	15.9	−12.7
8	C_6H_6				4.8	15.5	−12.5
	$CHCl_3$				5.3	15.4	−12.8
	CH_2Cl_2				5.2	15.5	−12.9
9	C_6H_6	49.6	3.6	3.4	15.7	48.7	−13.9
	$CHCl_3$	49.7	3.6	3.4	15.5	48.3	−14.0
	CH_2Cl_2	49.7	3.6	3.4	15.8	48.8	−14.0
	$(CD_3)_2CO$	49.6	3.5	3.2	16.2	50.8	−14.3
	$C_6H_5NO_2$	49.6	3.4	3.3	15.9	49.6	−14.0
10	C_6H_6	49.0	5.5	15.1	−23.4	−15.8	266.9
	$CHCl_3$	49.1	5.3	14.8	−23.8	−15.9	267.9
	CH_2Cl_2	49.6	5.3	15.0	−23.6	−15.8	267.5
	$(CD_3)_2CO$	48.3	5.6	17.3	−21.6	−15.0	264.7
	$C_6H_5NO_2$	48.7	5.4	16.0	−22.6	−15.6	265.8
11	C_6H_6				5.2	7.5	−13.2
	$CHCl_3$				4.8	7.2	−13.4
	CH_2Cl_2				4.9	7.2	−13.6
	$(CD_3)_2CO$				4.8	6.5	−13.6
	$C_6H_5NO_2$				5.0	6.7	−13.5
12	C_6H_6[b]						
	$CHCl_3$				5.8	11.4	−12.4
	CH_2Cl_2				6.0	11.1	−13.1
	$(CD_3)_2CO$				6.1	10.2	−12.9
	$C_6H_5NO_2$				6.1	10.2	−13.0

[a] In order of increasing dielectric constant. [b] Proton resonance was obscured by the methyl resonances.



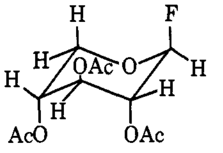
C

This conclusion is based primarily on the magnitudes of the vicinal $^{19}F-^{1}H$ coupling constants, although the vicinal $^{19}F-^{19}F$ coupling constants also appear to be in accord.[27]

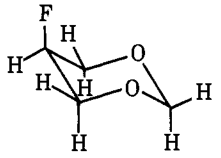
The chloro-**11** and cyano-**12** derivatives were next examined in order to determine whether other polar substituents exhibited the same strong preference as the fluorine substituent. Ignoring for the present the difference in electronegativity between the substituents of derivatives **7**, **9**, **11**, and **12**, the vicinal $^{1}H-^{1}H$ coupling constants indicate that neither the cyano nor the chloro substituent favors the "axial" orientation to the same extent as the fluoro substituent. Thus the trans $^{1}H-^{1}H$ couplings of **11** (*ca.* 7 Hz) and of **12** (*ca.* 10 Hz) are both significantly larger than that of the fluoro derivative **9** (*ca.* 3.5 Hz). In the 5-halo-1,3-dioxane system[26,35,36] the formally analogous observation has been made that a chloro substituent has a lower preference for an "axial" orientation than a fluoro substituent.

In an attempt to evaluate the possible influences of dipolar interactions on the above conformational preferences of derivatives **7**–**12**, their nmr parameters were determined in a number of solvents. It is well known that conformers (or rotamers) having the higher dipole moment are more favored by solvents of higher dielectric constant and we had hoped that some systematic changes might thereby be induced in the conformations and, hence, the nmr parameters of **7**–**12**. In any event, these experiments proved to be inconclusive and the changes in coupling constants which were observed are too small to justify detailed discussion.

Although we are unaware of any precedent for the marked conformational preference of the carbon–fluorine bond in organometallic systems, several instances are known in organic heterocycles. For example, the fluorine substituent of fluorinated carbohydrates such as **13**[37] has such a strong preference for the axial orientation that the compound favors the all-axial conformation shown. Similarly 5-fluoro-1,3-dioxane[2b] **14** and its derivatives[26,35,36] also show a marked preference for that conformer having the fluorine axially oriented.



13



14

While the precise source of these preferences is not not known, three different rationales have been proferred: one being based[38] on repulsive dipole–dipole interactions; a second on the preference for adjacent dipolar bonds to favor a "gauche" relationship;[39] and a

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Table V. Carbonyl Infrared Stretching Frequencies for the Complexes[a]

Compound				
7	2006	1915	1892	(1892)
8	2011	1923	1900	(1900)
9	2011	1923	1900	(1900)
10	2021	1931	1913	1907
11	2012	1923	1899	(1899)
12	2014	1928	1906	1903

[a] Measured in cm^{-1}, cyclohexane solution.

third[40] on p-p orbital overlap between fluorine p orbitals and those of some other suitably located atom. It is not obvious that any of these can be invoked here.

It will be noted that we have made no attempts to calculate dihedral angles from the vicinal coupling constants. This will not be warranted until such time that the effect of the arsenic and other substituents on the intrinsic magnitudes of the vicinal couplings are known.

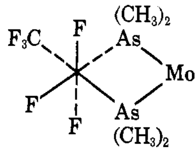
As can be seen from Table III four peaks corresponding to the four inequivalent arsenic–methyl groups are exhibited in the nmr spectra of the complexes. The monofluoro complex, Figure 3, shows coupling between the methyl groups and the fluorine atom, which is removed when the fluorine atom is decoupled (Figure 3B). The inequality of the couplings implies some stereospecificity in the methyl–fluorine interaction.

Table VI. First-Order Chemical Shifts (τ and ϕ Values) for Neat Ligands

Compound	1	1′	2	2′	Methyl groups			
1		9.383	8.517	8.438	9.156	9.186	9.198	9.226
2		8.502	8.330	8.107	8.841	8.885	9.027	9.040
3	188.33	4.939	7.988	8.171	*b*			
4	4.961	211.02	106.59[a]	108.36[a]	*b*			
5		5.152	7.923	7.999	*b*			
6		7.303	8.235	8.340	8.923	8.923	8.969	9.000

[a] See footnote *a*, Table III. [b] See footnote *b*, Table III.

Since we completed these nmr studies, Trotter and coworkers[41,42] have investigated the solid state structures of several fluorocarbon-bridged ditertiary phosphine and arsine derivatives of chromium and molybdenum carbonyls. Although the initial results indicated that their structures were abnormal,[42] it now seems that the solids are disordered and that the most chemically reasonable interpretation of the data requires each molecule to have normal geometries.[43] The results confirm that bulky groups such as the trifluoromethyl substituent in **15** occupies an "equatorial" position on a puckered five-membered chelate ring.[41,43] Furthermore the hydrogen atom on the bridge of **10** is in the "equatorial" position as expected from the nmr results.



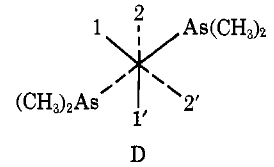
15

The infrared spectra of the complexes in the carbonyl stretching region have the three-to-four band pattern typical of complexes of the type chelate-$M(CO)_4$.[44] The frequencies of those bands are listed in Table V. Their values resemble those obtained from complexes of similar fluorocarbon- and hydrocarbon-bridged ligands such as $(C_6H_5)_2P\overline{C{=}CP(C_6H_5)_2CF_2C}F_2$ and $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$.[45] Thus it seems that the structures of the complexes are normal in solution. As usual there is a rough correlation between the frequencies and the "electronegativity" of the bridging groups, implying that the ligands become better π acceptors (or worse σ donors) as the bridge is progressively substituted by electronegative groups.

The nmr parameters of the free ligands **1–6** were also measured; the appropriate data are presented in Tables VI and VII. The vicinal $^1H-^1H$ coupling constants of all free ligands indicate that the favored rotamer is that having the two dimethylarsino substituents in an anti orientation, as in D. Thus it seems that the operation of the conformational preference of the fluorine substituent is only effective in the chelate ring system.

Table VII. First-Order Coupling Constants (Hz) for Neat Ligands

Compd	$J_{11'}$	J_{12}	$J_{12'}$	$J_{1'2}$	$J_{1'2'}$	$J_{22'}$
1				9.1	5.2	−12.9
2				7.0	6.8	−13.4
3	49.5	14.0	39.3	10.1	4.9	−13.2
4	47.5	13.1	21.5	−16.0	−23.7	265.6
5				10.1	5.7	−13.1
6				10.9	5.5	−12.8



D

Several extensions of the present study are obvious and will be explored in due course. Thus, the ligands **1–6** and their phosphorus analogs are likely to form stable chelate complexes with a wide variety of other metals which are of interest because of potentially different geometries. Furthermore the syntheses and study of other fluorine containing ligands would appear to be warranted since this might result in further

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insight concerning the conformational properties of the C–F bonds of organometallic substances.

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Kinetic Studies of the Reduction and Hydrogenation of Pentacyanocobaltate Complexes by Hexacyanochromate(II)[1a]

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Abstract: The reaction of $\mathrm{Cr(CN)_6^{4-}}$ with $\mathrm{Co(CN)_5Br^{3-}}$ in cyanide solution occurs in two stages. The first step forms $\mathrm{Cr(CN)_6^{3-}}$, $\mathrm{Co(CN)_5^{3-}}$, and $\mathrm{Br^-}$ in a second-order reaction with a rate constant of $1.14 \pm 0.08 \times 10^5\ M^{-1}\ \mathrm{sec}^{-1}$ (25.0°, $\mu = 1.00\ M$). The second reaction occurs between $\mathrm{Co(CN)_5^{3-}}$, a product of the first step, and $\mathrm{Cr(CN)_6^{4-}}$ and is an important process in the first reaction only if the latter reagent is in excess over $\mathrm{Co(CN)_5Br^{3-}}$. The reaction of $\mathrm{Co(CN)_5^{3-}}$ and $\mathrm{Cr(CN)_6^{4-}}$ produces $\mathrm{Co(CN)_5H^{3-}}$, $\mathrm{Cr(CN)_6^{3-}}$, and $\mathrm{OH^-}$ and occurs with a second-order rate constant of $2.4 \pm 0.1 \times 10^4\ M^{-1}\ \mathrm{sec}^{-1}$ (25.0°, $\mu = 1.00\ M$). Both reactions are independent of $[\mathrm{CN^-}]$ ($>0.2\ M$) and of $[\mathrm{OH^-}]$. The combination of the two reactions provides a means for carrying out the catalytic hydrogenation of α,β-unsaturated compounds without molecular hydrogen, $\mathrm{Cr(CN)_6^{4-}}$ serving as a reducing agent to liberate hydrogen from water *via* the intermediate hydrogenating agent $\mathrm{Co(CN)_5H^{3-}}$.

The strongly reducing and highly reactive complex $\mathrm{Cr(CN)_6^{4-}}$ is formed in solutions of Cr(II) containing excess cyanide ion.[2-5] In this work we wish to report on some kinetic studies carried out on the reactions of $\mathrm{Cr(CN)_6^{4-}}$ with $\mathrm{Co(CN)_5X^{3-}}$ complexes, work initially prompted by a desire to explore the rate patterns of outer-sphere reactions between anionic complexes. It became evident that a further unexpected reaction was occurring between the two strongly reducing species $\mathrm{Cr(CN)_6^{4-}}$ and $\mathrm{Co(CN)_5^{3-}}$. This latter reaction limited the number of different $\mathrm{Co(CN)_5X^{3-}}$ complexes whose reactions could usefully be studied, but it revealed a novel aspect of the chemistry of $\mathrm{Cr\ (CN)_6^{4-}}$, which resulted in the conversion of $\mathrm{Co(CN)_5^{3-}}$ to $\mathrm{Co(CN)_5H^{3-}}$ which is an active hydrogenation agent.

Experimental Section

Materials. Potassium hexacyanochromate(III) was prepared by the air oxidation of Cr(II) in solutions containing excess cyanide ion, precipitating $\mathrm{K_3Cr(CN)_6}$ by addition of ethanol.[6] The spectrum of the complex was in good agreement with that reported previously.[7] Salts of hexacyanochromate(II) were not isolated because of known difficulties with its high reactivity. Solutions of $\mathrm{K_3Cr(CN)_6}$ in excess cyanide were prepared just prior to each kinetic run and reduced with amalgamated zinc. In those rate runs where the reactant concentrations were comparable, the $\mathrm{Cr(CN)_6^{4-}}$ concentrations were analyzed by injecting an aliquot into an oxygen-free solution of ferricyanide, measuring the absorbance decrease at λ 420 nm ($\Delta\epsilon = 967\ M^{-1}\ \mathrm{cm}^{-1}$). The spectrum of $\mathrm{Cr(CN)_6^{4-}}$ shows absorption maxima at λ 327 nm (ε 8900) and 264 (6300) which agree favorably with the values established earlier, 327 (8700,[5a] 9000[5b]), 264 (5800[5a,5b]), and 227 (9700,[5a] 101,000[5b]).

The complex $\mathrm{K_3[Co(CN)_5Br]}$ was prepared by a procedure based upon the method of Adamson.[8] Solutions of $\mathrm{Co(CN)_5^{3-}}$ were prepared immediately prior to each run by injection of a $\mathrm{Co(ClO_4)_2}$ solution into an oxygen-free solution of sodium cyanide. The method of preparation of $\mathrm{Cs_2Na[Co(CN)_5H]}$ was that used by Banks and Pratt.[9] $\mathrm{NaClO_4}$ was recrystallized three times before use, whereas other inorganic chemicals not specifically referred to were used as the reagent grade materials. Conductivity water was used throughout.

The unsaturated organic substrates were purified by vacuum distillation just prior to use. Solutions of each in methanol were prepared on the basis of the densities of each reagent.

Kinetic Studies. An Atom-Mech stopped-flow apparatus[10-12] was used for the study of the reactions of $\mathrm{Cr(CN)_6^{4-}}$ with the $\mathrm{Co(CN)_5}$ complexes. Studies involving $\mathrm{Co(CN)_5^{3-}}$ were carried out at λ 970 nm where only this complex has an appreciable absorbance (ε ~300). Typically three or four repeat kinetic determinations were made on each set of reactant solutions.

A Cary-14 spectrophotometer was used for the study of the reactions[13] involving α,β-unsaturated organic substrates with $\mathrm{Co(CN)_5H^{3-}}$ which was used to confirm the production of the hydrido complex.

Results

Reaction between $\mathrm{Cr(CN)_4^{4-}}$ and $\mathrm{Co(CN)_5Br^{3-}}$. The stoichiometry of the main reaction is represented by the equation

$$\mathrm{Cr(CN)_6^{4-} + Co(CN)_5Br^{3-} = Co(CN)_5^{3-} + Cr(CN)_6^{3-} + Br^-} \qquad (1)$$

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