Williams relationship. Very recently a straight-line correlation has also been observed[25] between the square of the metal–oxygen stretching frequencies and the first d–d band in the electronic and vibrational spectra of a series of oxymolybdenum(IV) complexes. Thus such correlations may be fairly general and undoubtedly merit further investigation.

Acknowledgments.—We are indebted to the Canada Council, the Consiglio Nazionale delle Ricerche (Rome, Italy), and the National Research Council (Ottawa, Canada) for financial support of this work.

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Symmetrically Disubstituted Ferrocenes. II. Complexes of Ferrocene-1,1′-bis(dimethylarsine) and Ferrocene-1,1′-bis(diphenylarsine) with Group VI Carbonyls[1]

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The reaction of the group VI carbonyls with stoichiometric amounts of the arsines ferrocene-1,1′-bis(dimethylarsine) (fdma) and ferrocene-1,1′-bis(diphenylarsine) (fdpa) gave the complexes (fdma)M$(CO)_4$ and (fdpa)M$(CO)_4$, M = Cr, Mo, and W. Prolonged reaction of excess fdma with $Mo(CO)_6$ led to the isolation of μ-fdma-[fdmaMo$(CO)_3$]$_2$ and (fdma)$_2$Mo$(CO)_3$. It is proposed that the former complex has a bridging diarsine and a facial arrangement of donor arsenic atoms in the molybdenum coordination sphere, while the latter complex has one unidentate and one bidentate diarsine with a meridional arrangement of the donor arsenic atoms about the molybdenum atom.

Introduction

We have undertaken a study of the chemistry of symmetrically 1,1′-disubstituted ferrocenes $(C_5H_4L)_2Fe$, where the substituents are potential donor groups. In the previous communication[1] we have described convenient syntheses of the potential ligands where L = PR_2, AsR_2, and S^- or SH. This work describes some complexes of the group VI metal carbonyls[3–7] with ferrocene-1,1′-bis(dimethylarsine) (fdma) and ferrocene-1,1′-bis(diphenylarsine) (fdpa).

Experimental Section

General Data.—Microanalyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Mülheim (Ruhr), West Germany; Galbraith Laboratories, Inc., Knoxville, Tenn.; Midwest Microlab, Inc., Indianapolis, Ind.; Spang Microanalytical Laboratory, Ann Arbor, Mich.; and at MIT by Dr. Stephen S. Nagy and Mrs. Nancy F. Alvord. Molecular weight determinations were carried out by Midwest Microlab, Inc.

All melting points are corrected and were determined using a Thomas-Hoover "Unimelt" melting point apparatus on samples sealed in evacuated capillaries.

Where sensitive materials were involved, manipulations were carried out in an atmosphere of prepurified nitrogen.

Infrared spectra were recorded on Perkin-Elmer 337 and 521 spectrophotometers. Nuclear magnetic resonance spectra were recorded on Varian Associates T-60, A-60, and HA-100 spectrometers with tetramethylsilane as an internal reference.

Materials.—Reagent grade solvents were used and, when required, were degassed *in vacuo*. Hydrocarbons were dried by refluxing over and distilling from calcium hydride under nitrogen. Diglyme was dried, as above, over lithium aluminum hydride. The arsines ferrocene-1,1′-bis(dimethylarsine) (fdma) and ferrocene-1,1′-bis(diphenylarsine) (fdpa) were prepared as described previously.[1] The technique of Werner and Coffield[8] was used to prepare molybdenum diglyme tricarbonyl. All other chemicals used were of commercial reagent grade and, unless stated below, were used without purification.

Preparations. Tetracarbonylferrocene-1,1′-bis(dimethylarsine)chromium(0).—A mixture of sublimed $Cr(CO)_6$ (2.21 g, 10.0 mmol) and fdmp (3.99 g, 10.1 mmol) in dry diglyme (40 ml) was stirred and brought slowly to reflux (*ca.* 2 hr). The $Cr(CO)_6$ which sublimed from the reaction mixture was returned to the flask periodically by swirling and by scraping the condenser with a nichrome wire spiral which passed through a serum cap such that the system remained closed at all times. The reaction mixture was kept at reflux for 5.0 hr and then evaporated to dryness (65° (0.1 mm)) and maintained under these conditions for 13 hr to remove the unreacted $Cr(CO)_6$. The dark orange residue was extracted, in one portion, with boiling heptane (270 ml). The extract was filtered hot through a bed of Celite. Cooling the filtrate gave fragile yellow needles which were collected, washed with heptane (two 10-ml portions), and dried *in vacuo*; yield 4.21 g (75%), mp 178–179°. *Anal.* Calcd for $C_{18}H_{20}As_2CrFeO_4$: C, 38.74; H, 3.61. Found: C, 38.94; H, 3.78.

The solid is stable to air but its solutions are rapidly decomposed by air. The complex dissolves readily in benzene, chloroform, and acetone.

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(1) Part I: J. J. Bishop, A. Davison, M. L. Katcher, D. W. Lichtenberg, R. E. Merrill, and J. C. Smart, submitted for publication.

(2) (a) Petroleum Research Fund Graduate Fellow, 1968–1969. (b) Fellow of the Alfred P. Sloan Foundation, 1967–1969. To whom correspondence should be addressed.

(3) Although no systematic studies have been described, brief reports of symmetrically disubstituted ferrocenes functioning as ligands have appeared.[4–7]

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Tetracarbonylferrocene-1,1′-bis(dimethylarsine)molybdenum(0).—This complex was obtained by a similar procedure except that the reflux period was 0.5 hr; yield 83%, long orange needles, mp 154–155.5°. *Anal.* Calcd for $C_{16}H_{20}As_2FeMoO_4$: C, 35.91; H, 3.35. Found: C, 35.87; H, 3.50.

Tetracarbonylferrocene-1,1′-bis(dimethylarsine)tungsten(0).—This complex was prepared as above with a reflux time of 7.0 hr; yield 82%, orange flakes, mp 157.5–159°. *Anal.* Calcd for $C_{16}H_{20}As_2FeWO_4$: C, 31.34; H, 2.92. Found: C, 31.56; H, 2.98.

The properties of the molybdenum and tungsten compounds are similar to those of (fdma)Cr(CO)$_4$.

Tetracarbonylferrocene-1,1′-bis(diphenylarsine)chromium(0).—A mixture of sublimed Cr(CO)$_6$ (0.80 g, 3.62 mmol) and fdpa (1.50 g, 2.34 mmol) in dry *n*-octane (50 ml) was stirred under reflux for 4 hr. During this time the solution became red-orange and deposited yellow crystals. The solvent and excess Cr(CO)$_6$ were removed (65°) (0.1 mm)) and the crude product was recrystallized from 175 ml of freshly distilled butanol, washed with heptane (two 10-ml portions), and dried *in vacuo*. The pure product, golden yellow flakes, weighed 1.65 g (88%), mp 246–248°. *Anal.* Calcd for $C_{38}H_{28}As_2FeCrO_4$: C, 56.60; H, 3.50. Found: C, 56.52; H, 3.73.

Tetracarbonylferrocene-1,1′-bis(diphenylarsine)molybdenum(0).—This complex was prepared similarly with a reflux period of 50 min, as golden yellow flakes, mp 251.5–254.5° dec; yield, 90%. A second recrystallization from butanol gave an analytically pure product, mp 252.5–256° dec. *Anal.* Calcd for $C_{38}H_{28}As_2FeMoO_4$: C, 53.68; H, 3.32. Found: C, 54.09; H, 3.53.

The complexes (fdpa)M(CO)$_4$ (M = Cr, Mo, W) are air stable as solids but give air-sensitive solutions in benzene, chloroform, acetone, and hot higher alcohols.

Tetracarbonylferrocene-1,1′-bis(diphenylarsine)tungsten(0).—A mixture of sublimed W(CO)$_6$ (1.42 g, 4.04 mmol) and fdpa (2.00 g, 3.11 mmol) was heated under reflux in dry diglyme (75 ml) for 2.0 hr. The hot solution was filtered and the crude product separated upon the addition of heptane (200 ml) to the cold filtrate. Recrystallization from boiling methylcyclohexane followed by drying *in vacuo* gave 1.93 g (66%) of fine yellow needles, mp 267–268.5°. *Anal.* Calcd for $C_{38}H_{28}As_2FeWO_4$: C, 48.65; H, 3.01. Found: C, 48.18; H, 3.31.

Tricarbonylbis[ferrocene-1,1′-bis(dimethylarsine)]molybdenum(0).—A mixture of Mo(fdma)(CO)$_4$ (1.50 g, 2.50 mmol), fdma (2.03 g, 5.15 mmol), and diglyme (10 ml) was magnetically stirred and maintained at 200° for 4 days. The volatile components of the reaction mixture were removed *in vacuo* (70° (0.1 mm)). The residue was treated with hot benzene and clarified by filtration through Celite. The combined filtrate and hot-benzene washes (two 10-ml portions) were evaporated to a red oil (70° (0.1 mm)). Trituration of this oil with two 20-ml portions of boiling heptane removed the unreacted ligand and Mo(fdma)(CO)$_4$. Recrystallization of the residual yellow solid from methylcyclohexane (225 ml) followed by washing with the same solvent (three 10-ml portions) and drying *in vacuo* gave the product as a fine yellow powder; yield 1.27 g (52%); mp 228.5–231.5° dec. *Anal.* Calcd for $C_{31}H_{40}As_4Fe_2MoO_3$: C, 38.47; H, 4.17; As, 30.96; Fe, 11.54; mol wt 968. Found: C, 39.25; H, 4.50; As, 31.40; Fe, 12.00; mol wt (HCCl$_3$) 780 and 800.

μ-Ferrocene-1,1′-bis(dimethylarsine)-bis[tricarbonylferrocene-1,1′-bis(dimethylarsine)molybdenum(0)].—A. A mixture of Mo(fdma)(CO)$_4$ (2.00 g, 3.33 mmol) and fdma (3.03 g, 7.7 mmol) was stirred and maintained at 200–215° for 50 hr. Some decomposition occurred during this period. The cooled reaction mixture was treated with 20 ml of hot toluene and then filtered through Celite to remove suspended black particles. The combined filtrate and hot toluene washes (three 10-ml portions) were evaporated to a red oil (50° (20.1 mm)). This oil was triturated with 50 ml of boiling heptane for 0.5 hr, which caused the crude product to solidify. The supernatant liquid was decanted and the product separated with two 20-ml portions of hot heptane. Recrystallization from toluene gave 0.59 g (23%) of air-stable orange needles, mp 251–251.5°. *Anal.* Calcd for $C_{48}H_{60}As_6Fe_3Mo_2O_6$: C, 37.39; H, 3.92; As, 29.15; Fe, 10.87; mol wt 1542. Found: C, 38.01; H, 4.02; As, 29.35; Fe, 11.42; mol wt (CHCl$_3$) 1340 and 1370.

B. (i) A greenish yellow slurry of tricarbonyl diglyme molybdenum (1.56 g, 4.98 mmol) and dry methylcyclohexane (100 ml) was treated dropwise with a solution of fdma (4.44 g, 11.3 mmol) in 20 ml of the same solvent. No gas evolution was observed during the addition. The reaction mixture was maintained at 50–55° with stirring. The reaction mixture was periodically monitored (ir) until the major species present was the reaction product (*ca.* 120 hr). The mixture was cooled to room temperature and filtered. The solid residue was mainly impure product and was purified as above to give 0.6 g of pure material.

(ii) The reaction was performed in an identical manner at 100°. The results were essentially the same as above except that the reaction was complete in 2 hr.

No tricarbonylbis[ferrocene-1,1′-bis(dimethylarsine)]molybdenum(0) was obtained in either (i) or (ii).

Additional Reactions.—A. A solution of Mo(CO)$_6$ (1.58 g, 6.0 mmol) and fdma (4.76 g, 12.0 mmol) in 20 ml of dry diglyme was brought to reflux during 1.3 hr. After 3.5 days the volatile components were removed (60° (0.1 mm)) and the orange residue was treated with boiling toluene. The mixture was filtered through a bed of Celite to remove suspended particles. The combined filtrate and hot toluene washings (three 10-ml portions) were evaporated (60° (0.1 mm)) to give orange crystals. These were extracted with hot methylcyclohexane (four 150-ml portions). The residue, 0.98 g (21%), mp 251–253.5°, was identified as μ-ferrocene-1,1′-bis(dimethylarsine)-bis[tricarbonylferrocene-1,1′-bis(dimethylarsine)molybdenum(0)] by its ir and nmr spectra. The combined extracts were filtered, while hot, and the solvent was removed by distillation at atmospheric pressure until the volume was *ca.* 275 ml. The solution was set aside at −15° for 24 hr. The product was collected and washed with heptane (10 ml) and dried *in vacuo*. The yield of tricarbonylbis[ferrocene-1,1′-bis(dimethylarsine)]molybdenum(0), as a fine yellow powder, was 3.24 g (56%), mp 229.0–232° dec.

B. The previous reaction was repeated but the reflux time was reduced to 32 hr. Utilizing the work-up procedure described under A the yields of μ-ferrocene-1,1′-bis(dimethylarsine)-bis[tricarbonylferrocene-1,1′-bis(dimethylarsine)molybdenum(0)] and tricarbonylbis[ferrocene-1,1′-bis(dimethylarsine)]molybdenum(0) were 47 and 21%, respectively.

C. A solution of Mo(fdma)(CO)$_4$ (2.0 g, 3.30 mmol) and fdma (2.91 g, 7.4 mmol) was heated under reflux in 25 ml of diglyme for 50 hr. The solvent and volatiles were removed (70° (0.1 mm)). The residue was treated with 20 ml of hot toluene and then filtered through Celite. The combined filtrate and hot toluene washes (three 10-ml portions) were evaporated to a red oil (70° (0.1 mm)). This oil was triturated with 50 ml of boiling heptane for 0.5 hr which caused the separation of a solid. The hot supernatant liquid was carefully decanted through a medium-porosity fritted funnel and set aside. This procedure was repeated with five further 20-ml portions of hot heptane. The orange solid, 1.72 g (67%), was identified as μ-ferrocene-1,1′-bis(dimethylarsine)-bis[tricarbonylferrocene-1,1′-bis(dimethylarsine)molybdenum(0)]. The combined heptane extracts yielded 0.4 g (11%) of tricarbonylbis[ferrocene-1,1′-bis(dimethylarsine)]molybdenum(0).

Nuclear Magnetic Resonance Spectra.—Data are given for the following compounds. Mo(fdma)(CO)$_4$: 6.08, singlet (2); 8.76, singlet (3) [C_6H_6]. Mo(fdpa)(CO)$_4$: 2.55, multiplet (5); 5.70, irregular triplet (1); 5.83, irregular triplet (1) [$DCCl_3$].

Results and Discussion

The group VI metal hexacarbonyls and the appropriate diarsine, in either refluxing *n*-octane or diglyme, give the tetracarbonyl complexes shown in Table I. These yellow air-stable complexes are readily soluble in hot aromatic solvents but are poorly soluble in

TABLE I

THE INFRARED SPECTRA OF DIARSINE COMPLEXES OF GROUP VI METAL CARBONYLS[a]

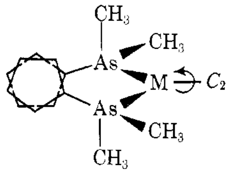
	A_1(trans)	A_1(cis)	B_1	B_2
Cr(fdma)$(CO)_4$	2003 s	1906 vs	1886 vs	1866 sh, s
Cr(fdpa)$(CO)_4$	2010 s	1917 s	1893 vs broad	
Mo(fdma)$(CO)_4$	2015 s	1913 vs	1898 vs	1871 sh, s
Mo(fdpa)$(CO)_4$	2023 s	1929 vs	1908 vs	1896 sh, s
W(fdma)$(CO)_4$	2007 s	1904 vs	1886 vs	1863 sh, s
W(fdpa)$(CO)_4$	2019 s	1918 vs	1896 vs	1876 sh, s

[a] The frequencies (cm^{-1}) are from spectra recorded in $CHCl_3$ solutions. The assignments are made according to those by Orgel[9] and Cotton.[10] Abbreviations: s, strong; sh, shoulder; v, very.

alkanes. Their infrared spectra (Table I) are characteristic[9,10] of *cis*-$L_2M(CO)_4$ complexes.

Because of the relatively large inter-ring distances in ferrocenes, *ca.* 3.30 Å, compared to C—C or C=C bond distances of 1.5 and 1.33 Å, respectively, complexes with L = $As(C_6H_5)_2$ or $As(CH_3)_2$ will possess greater steric hindrance around the metal atom than their benzene and ethane analogs *o*-phenylenebis(dimethylarsine) (diars) and 1,2-bis(diphenylarsino)ethane. The substituted ferrocene ligands are potentially quite flexible because, in addition to their low-energy barriers to torsional twisting of the cyclopentadienyl rings, their rings can also tilt from their parallel conformation without significant loss[11] in overlap energy.

The complexes in which the ferrocene ligand is bound to a metal, or other atom, can be viewed as [3]ferrocenophanes.[12] In principle, there are two limiting structures imposed upon these compounds by the steric requirements of the atoms in the bridge. They are related by the relative rotational orientation ω (in degrees) of the two five-membered rings. Structure I, for which ω is 36°, has a C_2 axis through the chelate ring and will be the preferred structure for those systems in which the bridging atoms are large. Structure II, a "stepped" conformation, with eclipsed rings (ω = 0°) and a mirror plane, will be preferred when the bridging atoms are small. Other factors which influence the preferred conformations I and II will be the inter-ring bond angles, As–M–As and C–As–M.



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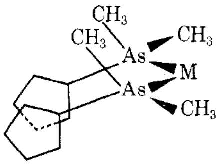

II

Neither of these limiting cases requires that the cyclopentadienyl rings be nonparallel. For both of these potentially nonrigid structures, inversions can be readily envisaged. An example of this type of inversion[13] has been recognized for the fluxional molecule 1,2,3-trithia[3]ferrocenophane. If it is required that the rings remain eclipsed and that the iron atom and the bridge atoms As and M remain coplanar, then it is also required that either the cyclopentadienyl rings must be tilted from their parallel orientation or the C–As–M bond angle must be increased. This conformation would be the energetically least favored mode of chelation. A further feature of stereochemical interest is important. For both the limiting cases I and II and also for intermediate cases ω = 0–36°, the alkyl and aryl substituents on the arsenic atoms fall into two nonequivalent quasi-axial and -equatorial sets. Further, the four protons on each cyclopentadienyl ring are nonequivalent and would be expected to give rise to an ABCD pattern in their proton magnetic resonance spectra. However, if rapid inversion takes place, the quasi-axial and -equatorial environments will become time averaged, as will the pairs of protons in the 2,5 and 3,4 positions on the cyclopentadienyl rings. This will result in an AA′BB′ pattern for the time-averaged spectra of the ring protons.

The nmr spectra of the molybdenum complexes are much simpler than those expected for static systems. They exhibit the cyclopentadienyl proton resonances as a pair of triplets, characteristic of an AA′BB′ pattern for which J_{AB} and $J_{A'B}$ (or $J_{AB'}$) are equal and smaller than the chemical shift between A and B. While we cannot, as yet, determine the limiting configuration of the chelate ring in the fluxional (arsine)M$(CO)_4$ complexes, a limiting structure containing I can invert to its optical antipode by a mechanism which rotates the relative orientation of the five-membered rings with respect to each other (*i.e.*, ω + 36° = −36°). A limiting structure containing II, which seems to be more favorable, at least for chromium, because of the *ca.* 90° As–M–As angle imposed by the requirements of octahedral coordination, can invert by a mechanism which effectively flips the $M(CO)_4$ group from one side of the $FeAs_2$ plane to the other. Both of these processes, as well as those for inversions of intermediate structures, occurring rapidly will account for the observed spectra. Attempts to obtain limiting low-temperature spectra were thwarted by the lack of solubility of the complexes in suitable solvents at very low temperatures.

The reaction of Mo(fdma)$(CO)_4$ with neat fdma at 200–215° for 50 hr gives a sparingly soluble orange complex, μ-fdma-$[(fdma)Mo(CO)_3]_2$. This complex can also be produced by the reaction of Mo(diglyme)$(CO)_3$ with fdma in methylcyclohexane.

The reaction of Mo(fdma)$(CO)_4$ and fdma in hot (*ca.* 200°) diglyme for 4 days gives a moderately soluble yellow complex, $(fdma)_2Mo(CO)_3$.

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[10] F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, **84**, 4432 (1962).

[11] C. J. Ballhausen and J. P. Dahl, *Acta Chem. Scand.*, **15**, 1333 (1961).

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[13] A. Davison and J. C. Smart, *J. Organometal. Chem.*, **19**, 7 (1969).

Mixtures of molybdenum hexacarbonyl and excess fdma, when refluxed for long periods of time (*ca.* 2–4 days), give mixtures of the two complexes which can be readily separated by extraction with hot methylcyclohexane. In this solvent, $(fdma)_2Mo(CO)_3$ is moderately soluble but μ-fdma-$[Mo(fdma)(CO)_3]_2$ is not.

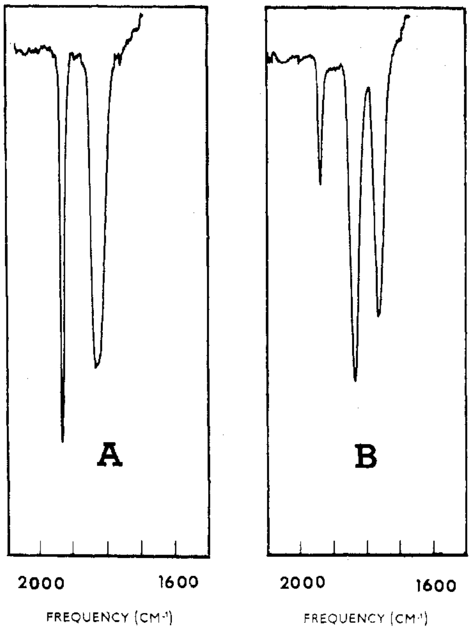

Figure 1.—The infrared spectra in the carbonyl stretching region of (A) μ-fdma-$[(fdma)Mo(CO)_3]_2$ and (B) $(fdma)_2Mo(CO)_3$ in chloroform solutions. The spectra were recorded with a Perkin-Elmer 337 grating spectrophotometer.

The infrared spectra (Figure 1) of both complexes in the carbonyl stretching region are quite simple. Both complexes are thought to contain $Mo(CO)_3$ moieties and the coordination number of each molybdenum is most reasonably 6. In such a situation the local symmetry for the $Mo(CO)_3$ group is C_{3v} for a cis or facial arrangement of the carbonyls and C_{2v} for a trans or meridional arrangement.

The spectrum of μ-fdma-$[(fdma)Mo(CO)_3]_2$ consists of two strong carbonyl stretching bands (1939 and 1835 cm^{-1}). The latter band is broad and was not split even when the spectrum was recorded on an instrument of higher resolution than that used to record the spectra shown. Two bands (A_1 and E) are expected for local C_{3v} symmetry.[9,10] The infrared spectrum is therefore in agreement with that of a diarsine-bridged structure which has a facial arrangement of carbonyl groups on the two equivalent noninteracting molybdenum atoms.

The spectrum of $(fdma)_2Mo(CO)_3$ consists of three carbonyl stretching bands (1925 (m), 1825 (vs), and 1763 cm^{-1} (s)). Three bands (A_1^1, B_1, and A_1^2) are expected for local C_{2v} symmetry. The spectrum of $(fdma)_2Mo(CO)_3$ is typical of that found in complexes[14] which have this local symmetry.[15] The infrared spectrum is in accord with a structure which has a meridional arrangement of the carbonyl groups about the molybdenum, with one of the two fdma groups functioning as a unidentate ligand.

The nmr spectra of these two complexes are shown in Figures 2 and 3 and are more complex than those discussed previously.

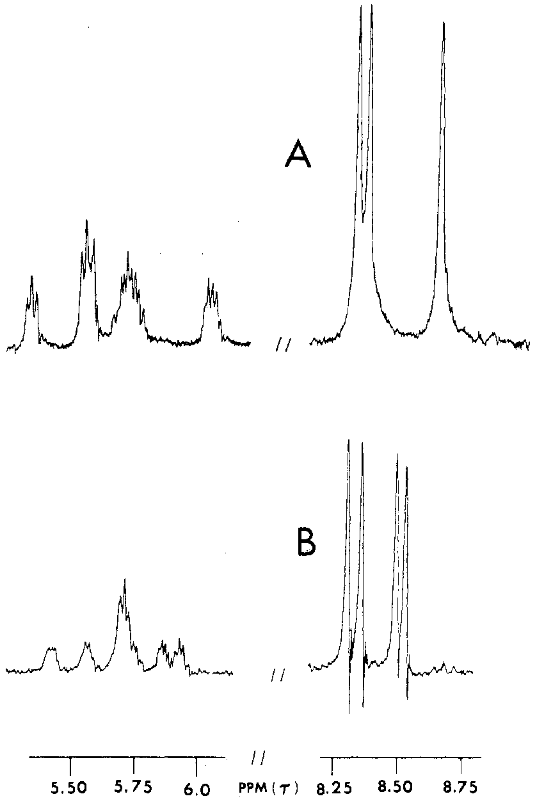

Figure 2.—The 100-MHz proton magnetic resonance spectra of (A) μ-fdma-$[(fdma)Mo(CO)_3]_2$ and (B) $(fdma)_2Mo(CO)_3$ in deuteriochloroform solutions.

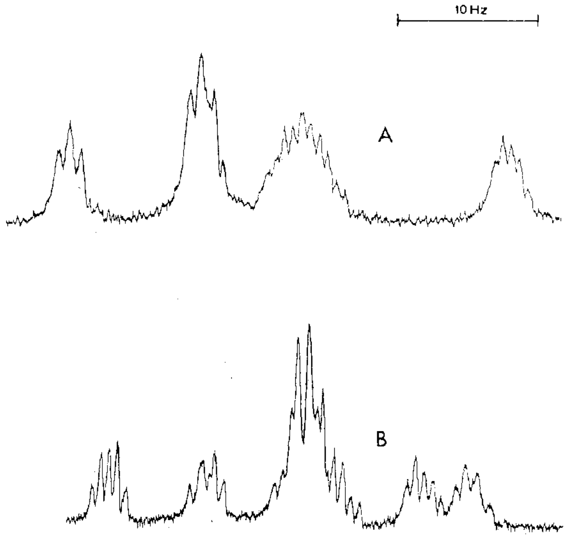

Figure 3.—The 100-MHz proton magnetic resonance spectra of the cyclopentadienyl ring protons of (A) μ-fdma-$[(fdma)Mo(CO)_3]_2$ and (B) $(fdma)_2Mo(CO)_3$ in deuteriochloroform solutions.

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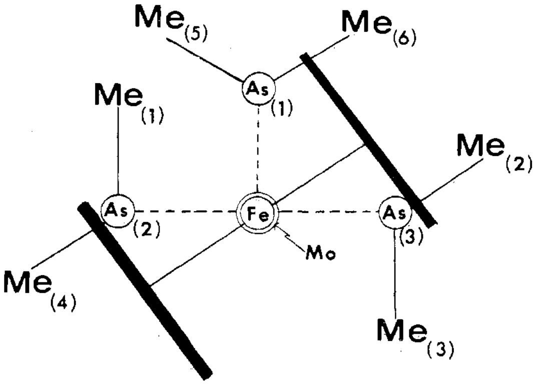
(14) J. D. Cotton, S. A. Knox, and F. G. A. Stone, *J. Chem. Soc. A*, 2758 (1968).

(15) S. F. Watkins, *ibid.*, 1552 (1969).

The spectrum of μ-fdma-[(fdma)Mo(CO)$_3$]$_2$ shows four sets of resonances in the cyclopentadienyl region, a triplet τ 5.42 (1) ($J \approx 1.5$ Hz), a triplet (broadened at the base) τ 5.60 (2) ($J \approx 1.4$ Hz), a multiplet τ 5.74 (2), and a multiplet τ 6.03 (1). Three singlets of equal intensity, τ 8.37 (3), 8.41 (3), and 8.67 (3), occur in the methyl region. The spectrum does not show any broadening when the sample in deuteriotoluene is heated to 200°. The analysis of the spectrum is quite straightforward. The resonance at τ 5.42 and part of the resonance at τ 5.60 form an AA′BB′ pattern found in symmetrically disubstituted ferrocenes and account for one-third of the total intensity of the cyclopentadienyl protons. This pattern is clearly due to the ring proton of the bridging arsine. The remaining resonances at τ 5.6, 5.74, and 6.03 comprise an ABCD pattern similar to that found[13] in 1,2,3-trithia[3]ferrocenophane and are assigned on the basis of their intensities to the ring protons of the chelating arsines. The nmr spectrum is in agreement with the proposed structure having a facial arrangement of carbonyl groups about each molybdenum atom.

Examination of molecular models for the *fac*-As$_3$Mo(CO)$_3$ arrangement with the two limiting conformations I and II of the chelated arsine is instructive.

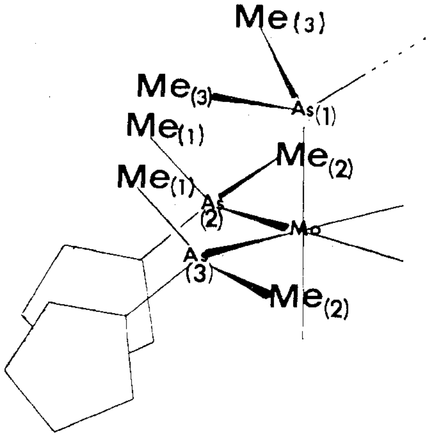
If the chelated arsine adopts the chiral configuration (I) in a static structure (III) shown schematically in Figure 4, the nmr spectrum would be more complex than that observed. This structure will have four nonequivalent methyl groups for the chelated arsines. Two of them, CH$_{3(1)}$ and CH$_{3(2)}$, occur on the side of the plane that is defined by the molybdenum atom, the chelating arsenic atoms As$_{(2)}$ and As$_{(3)}$, and the iron atom of the chelating ligand. These methyl groups are the closest ones to the bridging arsenic atom As$_{(1)}$. The other two methyl groups of the chelating ligand CH$_{3(3)}$ and CH$_{3(4)}$ occur on the opposite side of this plane. The bridging arsine will have two nonequivalent methyl groups, CH$_{3(5)}$ and CH$_{3(6)}$. The two cyclopentadienyl groups of the chelating ligand because of the presence of As$_{(1)}$ are also nonequivalent. Each of these rings has four magnetically distinct proton environments. A twist mechanism which converts the chelate to the opposite chirality will average the environments of CH$_{3(1)}$ with CH$_{3(2)}$, CH$_{3(3)}$ with CH$_{3(4)}$, CH$_{3(5)}$ with CH$_{3(6)}$, and the two cyclopentadienyl rings of the chelating ligand. The time-averaged nmr spectra of III rapidly undergoing such a twist would exhibit three methyl resonances of equal intensity and a single ABCD pattern for the chelating ligand's ring protons. The observed spectrum is that expected in the fast-exchange limit for a fluxional process of this type.



(III)

Figure 4.—Schematic representation of the chiral configuration (ω = 36°) of *fac*-μ-fdma-[(fdma)Mo(CO)$_3$]$_2$ as viewed along an axis which passes through the iron atom of the chelating diarsine and the molybdenum atom and bisects the angle formed by the molybdenum atom and the chelating arsenic atoms.

If the chelate adopts the stepped configuration (IV) shown in Figure 5, the molecule cannot invert through the MoAs$_{(2)}$As$_{(3)}$ plane because of extremely severe steric hindrance from the methyl groups on As$_{(1)}$. The static structure shown has three methyl environments and two magnetically differing cyclopentadienyl arrangements. One of these arrangements would give an ABCD pattern of cyclopentadienyl proton resonances of relative intensity 2, and the other will give an AA′BB′ pattern of relative intensity 10. Thus this static structure is also in accord with the observed spectra. It is at present impossible to distinguish between these two cases. The compound's insolubility in suitable solvents has precluded low-temperature nmr studies. These studies would, in principle, permit structures III and IV to be distinguished.

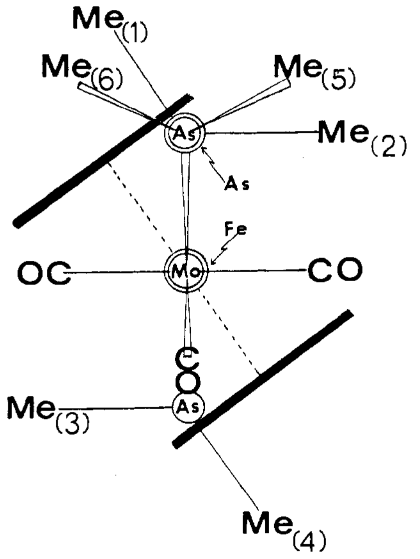


(IV)

Figure 5.—Schematic representation of the "stepped" configuration (ω = 0°) of *fac*-μ-fdma-[(fdma)Mo(CO)$_3$]$_2$.

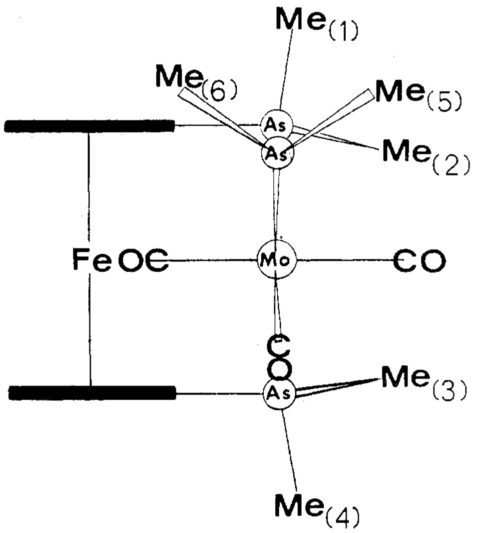
The spectrum of (fdma)$_2$Mo(CO)$_3$ shows five complex sets of resonances in the cyclopentadienyl region, τ 5.48 (1), 5.58 (1), 5.72 (4), 5.87 (1), and 5.94 (1). Four singlets of equal intensity, τ 8.30 (3), 8.37 (3), 8.50 (3), and 8.67 (3), occur in the methyl region. The spectrum does not show any broadening at temperatures up to +130° in deuteriotoluene. The analysis of this spectrum is less straightforward than in the previous case. The bands at τ 5.48, 5.58, 5.87, and 5.94, which account for half of the total intensity of ring protons, clearly form an ABCD pattern,[13] while the complex band at τ 5.72 is due to the remaining cyclopentadienyl protons.

The ir spectrum strongly suggests that this complex has a *mer*-$Mo(CO)_3$ group. The two limiting static structures based on configurations I and II are shown schematically as V and VI in Figures 6 and 7, respectively. The views chosen are along the planes about which ferrocene ring inversion processes will take place. It is readily apparent that for both structures V and VI, a more complex nmr spectrum is expected than that which is found; *i.e.*, four sets of ABCD patterns and eight methyl resonances are expected. However, in each case, a rapid inversion about a plane perpendicular to the *mer*-$Mo(CO)_3$ group will average $CH_{3(1)}$ with $CH_{3(2)}$, $CH_{3(3)}$ with $CH_{3(4)}$, $CH_{3(5)}$ with $CH_{3(6)}$, and $CH_{3(7)}$ with $CH_{3(8)}$ (not shown) to give a spectrum which has four methyl resonances. This process will also average the cyclopentadienyl protons in each ring to give four sets of AA′BB′ resonances. This latter expectation *is clearly not in accord with the experimental observations.* At present, no explanation exists for this result. It is, however, interesting to note that the nmr spectrum has precisely those features that one would expect for the facial isomer. However, this configuration, as far as the local environment about the molybdenum atom is concerned, is almost identical with that proposed for the μ-fdma-[*fac*-(fdma)$Mo(CO)_3$]$_2$. In the latter structure no interaction between the two $Mo(CO)_3$ groups is expected, and if both complexes had the same $Mo(CO)_3$ configuration, identical ir spectra in the carbonyl stretching region should be observed.



(V)

Figure 6.—Schematic representation of the chiral configuration (ω = 36°) of *mer*-$(fdma)_2Mo(CO)_3$ as viewed along an axis which passes through the molybdenum atom and the iron atom of the chelating diarsine and bisects the angle formed by the molybdenum atom and the chelating arsenic atoms.



(VI)

Figure 7.—Schematic representation of the stepped configuration (ω = 0°) of *mer*-$(fdma)_2Mo(CO)_3$ as viewed along an axis which passes through the molybdenum atom and bisects the angle formed by the molybdenum atom and chelating arsenic atoms.

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