

$C_4F_6$  fragment (presumably hexafluorobutene-2) from  $C_4F_7FeC_5H_5^+$  to give  $C_5H_5FeF^+$  which can then undergo loss of a neutral hydrogen fluoride fragment to give  $C_5H_4Fe^+$ . The mass spectrum of the chromium derivative  $C_4F_7Cr(NO)_2C_5H_5$  (III,  $M = Cr$ ;  $L = NO$ ), as expected, exhibited many features similar to the mass spectrum of the isostructural and isoelectronic  $C_4F_7Fe(CO)_2C_5H_5$  (III,  $M = Fe$ ;  $L = CO$ ).

The mass spectra of the cobalt derivatives  $C_5H_5Co(CO)(R_f)(C_4F_7)$  (V) provide qualitative comparisons of the relative elimination tendencies of perfluoro-1-methylpropenyl and saturated perfluoroalkyl groups. In both cases (V,  $R_f = C_2F_5$  and  $CF_3CF_2CF_2$ ) the ion  $C_5H_5Co(CO)(C_4F_7)^+$  is over twice as abundant as the ion  $C_5H_5Co(CO)R_f^+$  ( $R_f = C_2F_5$  or  $CF_3CF_2CF_2$ ) suggesting that elimination of a saturated perfluoroalkyl group from the molecular ion  $C_5H_5Co(CO)(R_f)(C_4F_7)^+$  occurs significantly more readily than elimination of the unsaturated perfluoro-1-methylpropenyl group. This suggests that the bond of the cobalt atom to a saturated perfluoroalkyl group is weaker than the bond of the cobalt atom to the unsaturated perfluoro-1-methylpropenyl group. This effect can be rationalized by the availability of empty antibonding orbitals in the carbon-carbon double bond of the perfluoro-1-methyl-

propenyl group which can overlap with filled d orbitals of the cobalt atom to provide additional means to strengthen the metal-perfluoro-1-methylpropenyl bond by retrodonative bonding. However, arguments of this type based on mass spectra are necessarily imprecise since they rely on the assumption of similar further fragmentation tendencies of the ion  $C_5H_5Co(CO)(C_4F_7)^+$  and the saturated perfluoroalkyl ion  $C_5H_5Co(CO)R_f^+$ .

The mass spectra of the cobalt derivatives  $C_5H_5Co(CO)(R_f)(C_4F_7)$  (V,  $R_f = C_2F_5$  and  $CF_3CF_2CF_2$ ) also exhibited some features similar to those found in the mass spectra of the iron derivative  $C_4F_7Fe(CO)_2C_5H_5$  (III,  $M = Fe$ ;  $L = CO$ ) discussed above. Thus metastable ions were observed in the mass spectra of both cobalt compounds which correspond to the elimination of a neutral  $C_4F_6$  fragment from  $C_5H_5CoC_4F_7^+$  to give  $C_5H_5CoF^+$  and the elimination of a neutral HF fragment from  $C_5H_5CoF^+$  to give  $C_5H_4Co^+$ .

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CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF BRITISH COLUMBIA, VANCOUVER, BRITISH COLUMBIA, CANADA

## Reactions of Fluorocarbon-Bridged Di(tertiary phosphines and arsines) with Manganese and Rhenium Carbonyls

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Fluorocarbon-bridged di(tertiary arsines and phosphines) react with  $M_2(CO)_{10}$  ( $M = Mn, Re$ ) under a variety of conditions to give complexes of formula  $(L-L)M_2(CO)_8$  which are ligand bridged. The bridged complexes readily react with iodine with cleavage of the M-M bond and yield  $(L-L)[M(CO)_4I]_2$ . In the case where  $(L-L)$  is  $(CH_3)_2AsC=CA_s(CH_3)_2CF_2CF_2$  isomers of the bridged complexes can also be prepared. These have the structure  $(CO)_4M(CH_3)_2AsM(CO)_4(CH_3)_2AsC=CCF_2CF_2$  and are the result of a ligand rearrangement reaction.

### Introduction

Reactions of dirhenium and dimanganese decacarbonyls with various monodentate ligands have resulted in the replacement of one to four carbonyl groups with the formation of dinuclear compounds such as  $M_2(CO)_9L$ ,<sup>1-4</sup>  $[M(CO)_4L]_2$ ,<sup>2-11</sup>  $M_2(CO)_7L_3$ ,<sup>3-5</sup> and

$[M(CO)_3L_2]_2$  in which the metal-metal bond of the parent carbonyl is preserved. Bidentate ligands are reported to yield some chelated products of the types  $M(CO)_3(L-L)$ ,<sup>11,12</sup>  $M(CO)(L-L)_2$ ,<sup>11,12</sup>  $M_2(CO)_8(L-L)$ ,<sup>1,13</sup> and  $[M(CO)_3(L-L)]_2$ ,<sup>11,14</sup> in which the ligand replaces two or four carbonyl groups on a single metal atom.

In the course of a systematic study of the reactions of the versatile fluorocarbon-bridged ligands  $f_4fars$  and  $f_4fos$   $YC=CYCF_2CF_2$  ( $Y = (CH_3)_2As$  or  $(C_6H_5)_2P$ ) with metal carbonyls,<sup>15,16</sup> we have found that these ligands react with dimanganese and dirhenium decacarbonyls to

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produce dinuclear compounds of the type  $M_2(CO)_8$ -(L-L)<sup>17</sup> (M = Mn, Re) in which  $f_4fars$  and  $f_4fos$  are biligate and bimetallic acting as a bridge between the two metal atoms. In the present paper, we describe the preparation and reactions of these ligand-bridged metal carbonyl derivatives in detail. In addition we report two new mononuclear products of the type (L-L)M(CO)<sub>3</sub>Cl (M = Re, Mn) and two other interesting compounds formed by ligand rearrangement.

### Experimental Section

All reactions and chromatography were carried out under a nitrogen atmosphere using nitrogen-saturated solvents. The petroleum ether mentioned below is the 30–60° bp fraction. Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer, and nmr spectra on Varian T-60 and HA-100 instruments. Chemical shifts are given in ppm downfield from internal or external TMS and upfield from external CFC<sub>13</sub>. Microanalyses were performed by Mr. P. Borda of this department. The experimental details given in sections (1) and (2) have been selected from a number of related experiments and describe the conditions that have been found to result in the highest yields of the desired compounds. A 100-W source was used for ultraviolet irradiations. Rhenium and manganese carbonyls were purchased from Strem Chemicals Inc. and Pressure Chemical Co., respectively. The preparations of  $f_4fars$ <sup>18</sup> and  $f_4fos$ <sup>19</sup> have been described previously.

(1) Preparation of Bridged  $f_4farsM_2(CO)_8$  and  $f_4farsM(CO)_3Cl$ . (a)  $f_4farsMn_2(CO)_8$  (I) and  $f_4farsMn(CO)_3Cl$ .—Dimanganese decacarbonyl (1.1 g, 2.8 mmol) and  $f_4fars$  (1.2 g, 3.6 mmol) were sealed in a Carius tube in 20 ml of acetone and irradiated with ultraviolet light for 18 hr. The tube was opened and the acetone solvent was removed and the solid contents of the tube were chromatographed on Florisil. The first band which eluted in petroleum ether contained unreacted  $Mn_2(CO)_{10}$  (0.3 g). A second orange band was eluted with 95:5 petroleum ether-diethyl ether and gave, after crystallization from 1:1 hexane-acetone, orange crystals of  $f_4farsMn_2(CO)_8$  (I) (0.6 g, 44% based on  $Mn_2(CO)_{10}$  used). A third band eluted with 1:1 petroleum ether-diethyl ether gave yellow crystals of  $f_4farsMn(CO)_3Cl$  (0.05 g, 5%) after crystallization from cyclohexane.

(b)  $f_4farsRe_2(CO)_8$  (II) and  $f_4farsRe(CO)_3Cl$ .—Dirhenium decacarbonyl (5.0 g, 7.7 mmol) and  $f_4fars$  (5.0 g, 15 mmol) were refluxed in 50 ml of *m*-xylene (139°) for 5 hr. After removal of solvent under reduced pressure, the residue was chromatographed on a Florisil column. Unreacted  $Re_2(CO)_{10}$  (2.9 g) was eluted with petroleum ether. A second yellow band was eluted with 9:1 petroleum ether-diethyl ether and gave, after crystallization from acetone-hexane, yellow crystals of  $f_4farsRe_2(CO)_8$  (II) (1.77 g, 59% based on  $Re_2(CO)_{10}$  used). A third red band was eluted with diethyl ether. This product was concentrated and crystallized at Dry Ice temperature to yield 0.15 g of a mixture of  $f_4farsRe_2(CO)_8$  (II) and  $f_4farsRe(CO)_3Cl$ . Since only a small amount of  $f_4farsRe(CO)_3Cl$  was obtained even when using large quantities of  $Re_2(CO)_{10}$  and  $f_4fars$ , no further attempt to isolate this product was made. The <sup>1</sup>H nmr spectrum (CDCl<sub>3</sub> solution) of the mixture consisted of two singlets at 1.98 (area 2) and 2.02 ppm (area 1). Qualitative tests confirmed the presence of chlorine in the sample.

(2) Preparation of the Isomers of  $f_4farsM_2(CO)_8$ . (a) *i*- $f_4farsMn_2(CO)_8$  (III).—Dimanganese decacarbonyl (1.0 g, 2.6 mmol) and  $f_4fars$  (1.0 g, 3.0 mmol) were refluxed in *m*-xylene for 5 hr. After filtration of the precipitate and removal of the xylene at low pressure, repeated crystallization of the combined solids from dichloromethane-hexane yielded light yellow crystals of *i*- $f_4farsMn_2(CO)_8$  (III) (0.4 g, 29%). During this reaction (0.5 hr from start), 50% of the mixture consisted of bridged  $f_4farsMn_2(CO)_8$  (I) as shown by the infrared carbonyl spectrum. However, after 5 hr *i*- $f_4farsMn_2(CO)_8$  (III) was present as the major component (80%).

(b) *i*- $f_4farsRe_2(CO)_8$  (IV).—Dirhenium decacarbonyl (2.61 g, 4.0 mmol) and  $f_4fars$  (2.50 g, 7.5 mmol) in 40 ml of acetone were sealed in a Carius tube and irradiated with ultraviolet light for 24 hr. After opening the tube and concentrating the solution, the oily residue was chromatographed on a Florisil column. Petroleum ether and 9:1 petroleum ether-diethyl ether eluted 1.50 g of unreacted  $Re_2(CO)_{10}$  and 0.20 g of a mixed product, respectively. Crystallization of this mixed product from diethyl ether at Dry Ice temperature gave white crystals of *i*- $f_4farsRe_2(CO)_8$  (IV) (0.17 g, 11%, based on  $Re_2(CO)_{10}$  used). Evaporation of the mother liquor yielded yellow crystals of bridged  $f_4farsRe_2(CO)_8$  (II) (0.03 g, 2%), identified by its carbonyl infrared spectrum.

(3) Preparation of  $f_4fosMn_2(CO)_8$ .—Dimanganese decacarbonyl (1.0 g, 2.6 mmol) and  $f_4fos$  (1.3 g, 2.6 mmol) were refluxed in toluene for 2 hr. Work-up as in section (1a) (elution with 20:1 petroleum ether-diethyl ether followed by crystallization from acetone-hexane) gave yellow crystals of  $f_4fosMn_2(CO)_8$  (0.3 g, 14%).

(4) Preparation of Bridged  $f_4fosRe_2(CO)_8$ .—Dirhenium decacarbonyl (0.65 g, 1 mmol) and  $f_4fos$  (0.50 g, 1 mmol) were refluxed in 10 ml of *m*-xylene for 3 hr. Work-up as in section (1a) (elution with 1:1 diethyl ether-dichloromethane followed by recrystallization from diethyl ether-dichloromethane) yielded red crystals of  $f_4fosRe_2(CO)_8$  (0.22 g, 20%).

(5) Conversion of Bridged  $f_4farsM_2(CO)_8$  into the Isomeric *i*- $f_4farsM_2(CO)_8$ . (a) Conversion of Bridged  $f_4farsMn_2(CO)_8$  (I) into *i*- $f_4farsMn_2(CO)_8$  (III).—Bridged  $f_4farsMn_2(CO)_8$  (I) (0.5 g) was refluxed in *m*-xylene for 5 hr. Work-up as in section (2a) gave *i*- $f_4farsMn_2(CO)_8$  (III) (0.4 g, 80%).

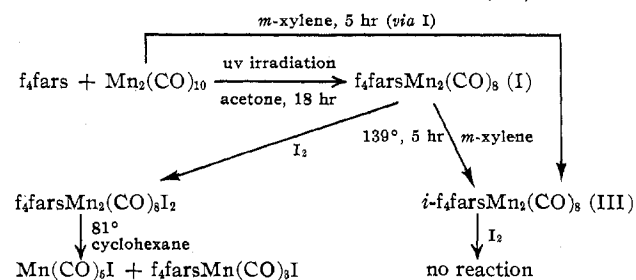
(b) Conversion of Bridged  $f_4farsRe_2(CO)_8$  (II) into *i*- $f_4farsRe_2(CO)_8$  (IV).—Bridged  $f_4farsRe_2(CO)_8$  (II) was refluxed in *m*-xylene. After 87 hr, the infrared carbonyl spectrum showed that ~90% of II had been converted to IV.

(6) Iodine Cleavage Reactions. (a)  $f_4farsMn_2(CO)_8$  (I).—Bridged  $f_4farsMn_2(CO)_8$  (I) (0.5 g, 7.5 mmol) was dissolved in 5 ml of dichloromethane. To this was added slowly, with vigorous stirring, a solution of iodine (0.2 g, 7.0 mmol) in 50 ml of dichloromethane. Crystallization of the product from hexane-dichloromethane yielded brown crystals of  $f_4farsMn_2(CO)_8I_2$  (0.6 g, 43%).

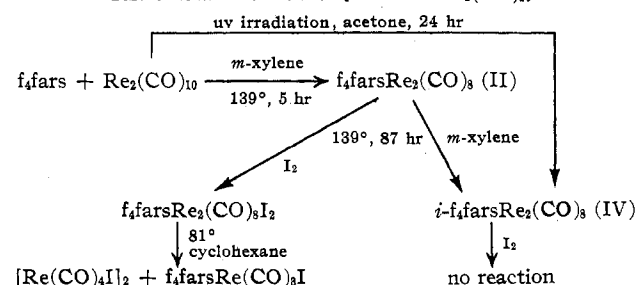
(b) When  $f_4farsMn_2(CO)_8I_2$  (0.5 g, 5.4 mmol) was refluxed in cyclohexane for 1 hr, a new solid was obtained. Crystallization from hexane yielded  $f_4farsMn(CO)_3I$  (0.1 g, 31%). The mother liquor contained  $Mn(CO)_5I$ , identified by its infrared carbonyl spectrum.

(c)  $f_4farsRe_2(CO)_8$  (II).—Bridged  $f_4farsRe_2(CO)_8$  (II) (0.15 g, 0.16 mmol) was dissolved in 10 ml of dichloromethane to which a solution of iodine (0.045 g, 0.18 mmol) in 15 ml of di-

#### SCHEME I REACTIONS INVOLVING $f_4fars$ AND $Mn_2(CO)_{10}$



#### SCHEME II REACTIONS INVOLVING $f_4fars$ AND $Re_2(CO)_{10}$



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TABLE I  
ANALYTICAL RESULTS FOR NEW COMPLEXES

Complex	% calcd				% found			
	C	H	F	Other	C	H	F	Other
f <sub>4</sub> farsMn <sub>2</sub> (CO) <sub>8</sub> (I)	28.8	1.8	11.4		28.9	1.8	11.1	
f <sub>4</sub> farsMn <sub>2</sub> (CO) <sub>8</sub> (III)	28.8	1.8	11.4		28.8	1.9	11.2	
f <sub>4</sub> fosMn <sub>2</sub> (CO) <sub>8</sub>	52.2	2.4	9.2		51.9	2.6	9.0	
f <sub>4</sub> farsMn <sub>2</sub> (CO) <sub>8</sub> I <sub>2</sub>	20.7	1.3		27.6 (I)	20.5	1.2		28.1 (I)
f <sub>4</sub> farsMn(CO) <sub>8</sub> I	22.0	2.0			21.8	2.0		
f <sub>4</sub> farsMn(CO) <sub>8</sub> Cl	25.9	2.3		7.0 (Cl)	25.8	2.2		7.0 (Cl)
f <sub>4</sub> farsCr(CO) <sub>4</sub>	28.9	2.4			28.8	2.2		
f <sub>4</sub> farsRe <sub>2</sub> (CO) <sub>8</sub> (II)	20.7	1.3	8.2		20.7	1.2	8.0	
f <sub>4</sub> farsRe <sub>2</sub> (CO) <sub>8</sub> (IV)	20.7	1.3	8.2		20.7	1.4	8.0	
f <sub>4</sub> fosRe <sub>2</sub> (CO) <sub>8</sub>	39.6	1.8	7.0		39.1	2.0	6.7	
f <sub>4</sub> farsRe <sub>2</sub> (CO) <sub>8</sub> I <sub>2</sub>	16.2	1.0		21.4 (I)	16.2	1.1		21.6 (I)

TABLE II  
INFRARED BANDS OF NEW COMPLEXES IN THE  
CARBONYL STRETCHING REGION<sup>a</sup>

Complex	Infrared Bands (cm <sup>-1</sup> )
f <sub>4</sub> farsMn <sub>2</sub> (CO) <sub>8</sub> (I)	2062 (5), 1994 (10), 1988 (10), 1944 (7), 1930 (9)
f <sub>4</sub> farsMn <sub>2</sub> (CO) <sub>8</sub> (III)	2080 (1), 2060 (7), 2006 (8), 1996 (10), 1974 (9), 1964 (7)
f <sub>4</sub> fosMn <sub>2</sub> (CO) <sub>8</sub>	2074 (4), 2034 (8), 2000 (7), 1982 (10), 1976 (8), 1960 (6), 1934 (6)
f <sub>4</sub> farsMn <sub>2</sub> (CO) <sub>8</sub> I <sub>2</sub>	2090 (6), 2026 (9), 2010 (10), 2006 (sh), 1972 (sh), 1963 (6)
f <sub>4</sub> farsMn(CO) <sub>8</sub> I	2036 (8), 1972 (9), 1924 (10)
f <sub>4</sub> farsMn(CO) <sub>8</sub> Cl	2040 (8), 1972 (8), 1922 (10)
f <sub>4</sub> farsCr(CO) <sub>4</sub>	2020 (4), 1930 (5), 1910 (10)
f <sub>4</sub> farsRe <sub>2</sub> (CO) <sub>8</sub> (II)	2076 (8), 2024 (9), 1985 (10), 1957 (9), 1953 (sh), 1937 (sh), 1932 (10)
f <sub>4</sub> farsRe <sub>2</sub> (CO) <sub>8</sub> (IV)	2102 (1), 2086 (6), 2003 (10), 1974 (9), 1963 (7)
f <sub>4</sub> fosRe <sub>2</sub> (CO) <sub>8</sub>	2079 (6), 2026 (6), 1990 (9), 1965 (6), 1957 (3), 1942 (sh), 1935 (10)
f <sub>4</sub> farsRe <sub>2</sub> (CO) <sub>8</sub> I <sub>2</sub>	2105 (4), 2026 (8), 2015 (10), 2010 (sh), 1965 (sh), 1955 (sh), 1952 (5)
f <sub>4</sub> farsRe(CO) <sub>8</sub> I	2047 (7), 1968 (10), 1917 (6)
f <sub>4</sub> farsRe(CO) <sub>8</sub> Cl	2048 (8), 1967 (9), 1916 (10)

<sup>a</sup> In cm<sup>-1</sup>; C<sub>6</sub>H<sub>12</sub> solution.

chloromethane was added slowly. Crystallization of the product from dichloromethane at Dry Ice temperature gave f<sub>4</sub>farsRe<sub>2</sub>(CO)<sub>8</sub>I<sub>2</sub> (0.16 g, 85%).

(d) When f<sub>4</sub>farsRe<sub>2</sub>(CO)<sub>8</sub>I<sub>2</sub> (0.27 g, 0.23 mmol) was refluxed in cyclohexane for 3 hr, a new product was obtained. Crystallization of the resulting solid from cyclohexane yielded 0.045 g of a mixture of f<sub>4</sub>farsRe(CO)<sub>8</sub>I and [Re(CO)<sub>4</sub>I]<sub>2</sub> as identified by their infrared and mass spectra.

(e) The Isomeric *i*-f<sub>4</sub>farsMn<sub>2</sub>(CO)<sub>8</sub> (III) and *i*-f<sub>4</sub>farsRe<sub>2</sub>(CO)<sub>8</sub> (IV).—No reaction was observed when III and IV were treated with iodine, using the same procedure as in section (8a).

(7) Preparation of f<sub>4</sub>farsCr(CO)<sub>4</sub>.—This compound was prepared in 80% yield by refluxing equimolar quantities of f<sub>4</sub>fars and norbornadienechromium tetracarbonyl in heptane. Purification was effected by crystallization from hexane.

### Results and Discussion

The reactions of the fluorocarbon-bridged ligands with dimanganese and dirhenium decacarbonyls were investigated under a variety of conditions because we wanted to increase the yields of desired products and also because our previous experience with iron<sup>15</sup> and ruthenium<sup>16</sup> carbonyls indicated that the products would be dependent upon the reaction conditions. This expectation has been found to be true since ultraviolet irradiation afforded f<sub>4</sub>farsMn<sub>2</sub>(CO)<sub>8</sub> (I) and *i*-f<sub>4</sub>farsRe<sub>2</sub>(CO)<sub>8</sub> (IV). f<sub>4</sub>farsRe<sub>2</sub>(CO)<sub>8</sub> (II) and *i*-f<sub>4</sub>farsMn<sub>2</sub>(CO)<sub>8</sub> (III) were obtained in thermal reactions (Schemes I and II). Both bridged compounds I and II are converted to their isomers III and IV by refluxing in *m*-xylene. This reaction is slower in the case of the

TABLE III  
NMR DATA FOR NEW COMPLEXES<sup>a</sup>

Complex	<sup>1</sup> H nmr in As-CH <sub>3</sub> region		<sup>19</sup> F nmr
	<sup>1</sup> H nmr in As-CH <sub>3</sub> region	<sup>19</sup> F nmr	
f <sub>4</sub> farsMn <sub>2</sub> (CO) <sub>8</sub> (I)	1.88 (s)	107.0 (s)	
f <sub>4</sub> farsMn <sub>2</sub> (CO) <sub>8</sub> (III)	1.86 (s), 1.92 (s)	Complex patterns centered at 103.0 and 106.8	
f <sub>4</sub> fosMn <sub>2</sub> (CO) <sub>8</sub>		Complex patterns centered at 106.5 and 110.1	
f <sub>4</sub> farsMn <sub>2</sub> (CO) <sub>8</sub> I <sub>2</sub>	2.02 (s)	No satisfactory solvent	
f <sub>4</sub> farsMn(CO) <sub>8</sub> I	1.88 (s), 2.06 (s)	110.5 (s)	
f <sub>4</sub> farsMn(CO) <sub>8</sub> Cl <sup>b</sup>	1.70 (s), 1.80 (s)	110.3 (s)	
f <sub>4</sub> farsCr(CO) <sub>4</sub>	1.74 (s)	110.0 (s)	
f <sub>4</sub> farsRe <sub>2</sub> (CO) <sub>8</sub> (II)	1.98 (s)	106.9 (s)	
f <sub>4</sub> farsRe <sub>2</sub> (CO) <sub>8</sub> (IV)	2.13 (s), 2.27 (s)	Complex patterns centered at 130.5 and 134.5	
f <sub>4</sub> fosRe <sub>2</sub> (CO) <sub>8</sub>		107.8 (s)	
f <sub>4</sub> farsRe <sub>2</sub> (CO) <sub>8</sub> I <sub>2</sub> <sup>c</sup>	1.22 (s)	104.8 (s)	
f <sub>4</sub> farsRe(CO) <sub>8</sub> Cl	1.98 (s), 2.02 (s)	No satisfactory solvent	

<sup>a</sup> In ppm; CDCl<sub>3</sub> solution unless otherwise specified. <sup>b</sup> CHCl<sub>3</sub> solution. <sup>c</sup> CCl<sub>4</sub> solution.

rhodium compound and allows the isolation of the bridged intermediate II. The thermal production of III also seems to involve initial formation of I.

The structures of I and II were deduced from analytical, mass spectral, and <sup>1</sup>H and <sup>19</sup>F nmr data. Analytical and spectroscopic data for these and other new complexes are given in Tables I–III. The analytical data for I and II indicate that they have the general formula f<sub>4</sub>farsM<sub>2</sub>(CO)<sub>8</sub> (M = Mn, Re). The mass spectra confirm this formulation and show peaks with an *m/e* ratio attributable to [molecular ion – *n*(CO)]<sup>+</sup> (*n* = 0, 3, 4, 5, 6, 7, 8) and also peaks attributable to f<sub>4</sub>farsM<sup>+</sup> and f<sub>4</sub>farsM<sub>2</sub><sup>+</sup>. Since the <sup>1</sup>H and <sup>19</sup>F nmr spectra show only a singlet, this suggests that f<sub>4</sub>fars is bonded symmetrically to the rest of the molecule and acts as a bridging ligand in these two complexes. This has been confirmed in the case of f<sub>4</sub>farsMn<sub>2</sub>(CO)<sub>8</sub>(I) by a crystal structure determination<sup>17</sup> which indicates a structure as shown in Figure 1.

These are the first examples of ligand-bridged derivatives containing metal carbonyl fragments otherwise held together only by metal-metal bonds. Previous examples of ligand-bridged products also contain bridging carbonyl groups as in f<sub>4</sub>farsCo<sub>2</sub>(CO)<sub>6</sub>,<sup>20</sup> bridging SR groups as in f<sub>4</sub>fars[Fe(CO)<sub>2</sub>SR]<sub>2</sub>,<sup>21</sup> or cluster systems as in f<sub>4</sub>farsFe<sub>3</sub>(CO)<sub>10</sub>,<sup>9,22</sup> f<sub>4</sub>farsRu<sub>3</sub>(CO)<sub>10</sub>,<sup>16,23</sup> and (f<sub>4</sub>fars)<sub>2</sub>Ru<sub>3</sub>(CO)<sub>8</sub>.<sup>16,24</sup> The structure shown in

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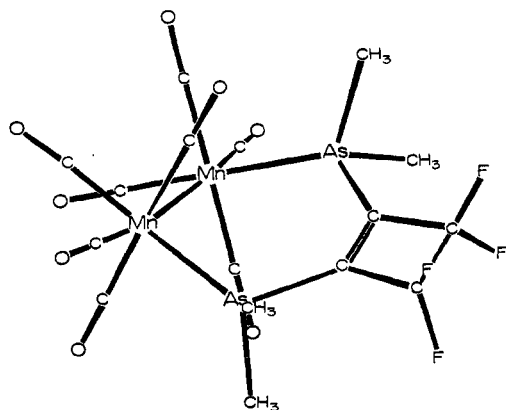
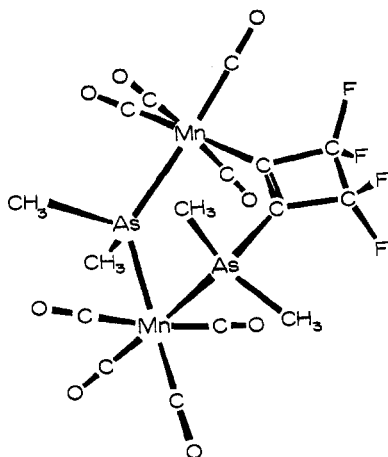
Figure 1.—The structure of  $f_4farsMn_2(CO)_8$  (I).Figure 2.—The structure of  $f_4farsMn_2(CO)_8$  (III). This compound is an isomer of that shown in Figure 1.

Figure 1 has staggered carbonyl groups which results in a nonplanar "cyclohexene" ring involving the bridging ligand. The nmr results, singlet As-CH<sub>3</sub> and <sup>19</sup>F resonances, suggest that the ring is planar in solution or, more likely, that the ring is involved in a conformational equilibrium so that an averaged spectrum is obtained.

Two other products, *i*- $f_4farsMn_2(CO)_8$  (III) and *i*- $f_4farsRe_2(CO)_8$  (IV), were obtained from the reactions of  $f_4fars$  with  $Mn_2(CO)_{10}$  and  $Re_2(CO)_{10}$  (Schemes I and II). Analytical and mass spectral data indicate that III and IV are isomers of I and II, respectively. However, the two singlets in the <sup>1</sup>H nmr spectra and the very complex pattern in the <sup>19</sup>F nmr spectra indicate that the molecules have lower symmetry than I and II. Initially, they were thought to have a structure where the ligand is chelated to one metal and represented by the formula  $f_4farsM(CO)_3M(CO)_5$  ( $M = Mn, Re$ ). Although this accounted for most of the spectroscopic properties, it did not explain the lack of reaction with iodine since the metal-metal bond in both I and II is readily cleaved by this reagent (*quod vide*). An X-ray crystallographic study<sup>25</sup> has found the structure of III is as shown in Figure 2. Here the metal-metal bond has been broken and one  $Mn(CO)_4$  moiety has inserted into one of the arsenic-carbon bonds. The formation of III and IV is interesting in that it involves

the breaking of a normally strong As-C bond and results in the formation of M-C and M-As  $\sigma$  bonds. It should be pointed out that the mass spectrum of III is identical with that of I so it is probable that I rearranges to III in the mass spectrometer. The rearrangement of  $f_4fars$  involved in the formation of III and IV is not unique. Other examples of such rearrangement are found in  $f_4farsFe_3(CO)_9$ <sup>15,26</sup> and  $f_4farsCo_3(CO)_9(?2H)$ .<sup>25</sup>

Two by-products of formula  $f_4farsM(CO)_3Cl$  ( $M = Mn, Re$ ) were also obtained in low yields from the reactions of  $f_4fars$  with  $Mn_2(CO)_{10}$  and  $Re_2(CO)_{10}$  when large quantities of reactants were used. Since they were not isolated in small-scale reactions, the source of the chlorine was probably a small amount of 1-chloro-2-dimethylarsinotetrafluorocyclobutene which was present in  $f_4fars$  as an impurity. The presence of this impurity is not unexpected since the preparation of  $f_4fars$  involves it as an intermediate product.<sup>18</sup>

The structure of  $f_4farsMn(CO)_3Cl$  was deduced from its spectroscopic properties. The three almost equally intense carbonyl stretching bands which are characteristic of compounds of the type *cis*- $Mn(CO)_3L_2X$ <sup>27</sup> indicate that all carbonyl groups are *cis* to each other in  $f_4farsMn(CO)_3Cl$ . The <sup>1</sup>H nmr spectrum shows two singlets as expected for this structure.

An analytically pure sample of  $f_4farsRe(CO)_3Cl$  could not be obtained and this compound was identified spectroscopically. The infrared spectrum shows three almost equally intense carbonyl bands in the same region as  $f_4farsMn(CO)_3Cl$ . Furthermore, the mass spectrum of a mixture of  $f_4farsRe(CO)_3Cl$  and  $f_4farsRe_2(CO)_8$  shows parent peaks for both  $f_4farsRe_2(CO)_8$  and  $f_4farsRe(CO)_3Cl$  followed by loss of eight and three carbonyl groups, respectively.

The formation of these two by-products provides rare examples of complexes in which the ligand  $f_4fars$  acts as a chelating ligand without also utilizing the double bond of the bridging fluorocarbon group as in  $f_4farsM_2(CO)_6$  ( $M = Ru$ ,<sup>16</sup>  $Fe$ <sup>28</sup>). Other examples in which  $f_4fars$  is chelated include  $f_4farsCr(CO)_4$  (prepared during this investigation) and  $f_4farsMo(CO)_4$ .<sup>29</sup> The related compounds  $f_4farsM(CO)_3I$  ( $M = Mn, Re$ ) will be described next.

Reactions of the bridged compounds I and II with iodine at room temperature simply result in the rupture of the metal-metal bonds to give the derivatives  $f_4fars[M(CO)_4I]_2$ . The proposed structure has been confirmed in the case of  $f_4fars[Mn(CO)_4I]_2$ <sup>17</sup> where the ligand bridges two  $M(CO)_4I$  moieties. The iodine atoms are *cis* to the arsenic atoms. These cleavage reactions also occur with the parent carbonyls  $M_2(CO)_{10}$  but apparently the rates are much slower<sup>30</sup> and it is difficult to understand why a bridging ligand should have this effect, although it is expected that substitution of carbonyl groups in  $M_2(CO)_{10}$  by poorer  $\pi$  ac-

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ceptors should decrease the M–M bond strength.<sup>31</sup> Certainly the Mn–Mn bond length in  $f_4farsMn_2(CO)_8$  (2.971 (3) Å) is longer than in  $Mn_2(CO)_{10}$  (2.923 (3) Å).<sup>17</sup> However, the mechanism of cleavage of  $Mn_2(CO)_{10}$  is probably different from that of  $Re_2(CO)_{10}$ .<sup>30</sup> The iodine complexes  $f_4fars[M(CO)_4I]_2$  are unstable and, on heating, give metal carbonyl iodides and the chelate complexes  $f_4farsM(CO)_8I$  (M = Mn, Re). This also is an unexpected result in view of the above-mentioned reluctance of  $f_4fars$  to form chelate complexes.<sup>32</sup>

The reactions of  $f_4fos$  with  $Mn_2(CO)_{10}$  and  $Re_2(CO)_{10}$

(31) C. E. Coffey, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 1741 (1964).

(32) A referee has pointed out that in view of the rather drastic rearrangements of groups involved in these thermal reactions structural assignments based on products of similar degradations may not be reliable. A case in point is the characterization of  $Mn_2(CO)_8(o\text{-phen})$  as  $(CO)_8MnMn(CO)_8(o\text{-phen})$  because of its photochemical decomposition to  $Mn_2(CO)_{10}$  and " $Mn(CO)_5(o\text{-phen})$ ": W. Hieber and W. Schropp, *Z. Naturforsch. B*, **15**, 271 (1960).

produce  $f_4fosMn_2(CO)_8$  and  $f_4fosRe_2(CO)_8$ , respectively. These were identified by elemental analysis and by mass spectrometry. In the case of the rhenium compound the calculated intensities for the parent multiplet, due to the two isotopes of rhenium, agreed very well with the observed spectrum. Since the  $^{19}F$  nmr spectrum of  $f_4fosRe_2(CO)_8$  consists of a singlet at 107.8 ppm, we propose a bridged structure similar to that in Figure 1 for it. The  $^{19}F$  nmr spectrum of  $f_4fosMn_2(CO)_8$ , however, shows two absorptions at 106.5 and 110.1 ppm, indicating that  $f_4fos$  does not act as a bridging ligand in this case. It is not certain whether it acts as a chelating ligand or it rearranges itself as in Figure 2 with the breaking of a phosphorus–carbon bond, although the former seems more likely.

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## A Nomenclature Symbolism for Chiral and Achiral Isomers of Bridged Inorganic Complexes

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A nomenclature symbolism for bridged inorganic complexes, characterized by an interplay of configurational and conformational chiralities, is described. The complexes are represented by two-dimensional projection formulas containing chirality descriptors ( $\Delta$ ,  $\Lambda$ ,  $\delta$ ,  $\lambda$ ) which make them three-dimensional as far as their manipulation and symmetry properties are concerned. The symbolism is applied to characterize and enumerate the isomers for dinuclear and tetranuclear skeletons known from X-ray crystallography.

### 1. Introduction

Many bridged inorganic complexes exist as different isomers caused by different configurations about the central ions combined with different conformations of chelate rings, including those rings involving the bridges. The present paper is concerned with giving account to the different isomers of the above type, in a systematic way, using symmetry considerations, and at the same time proposing a simple nomenclature symbolism, applicable to their classification and the unique specification of individual isomer species.

The number of structures, that one can think of, is immense, and this paper, therefore, does not attempt to cover the subject exhaustively. Rather, it takes as its starting point certain bridged complexes, which have been elucidated by structure analyses, and uses these to illustrate the way of going about the augmentation of the standard nomenclature for their skeletons.<sup>2</sup>

A recent IUPAC publication<sup>2b,3</sup> proposed the symbols  $\Delta$  and  $\Lambda$  for characterizing configurational chirality

and  $\delta$  and  $\lambda$  for conformational chirality. These proposals have been adhered to without exception.

In the present paper the basic idea is to represent a given complex by a kind of projection formula which is two dimensional, but which, by replacing the chiral components by the relevant  $\Delta$ ,  $\Lambda$ ,  $\delta$ ,  $\lambda$  symbols, becomes effectively three dimensional. Or, in other words, these symbols allow one to build a sterically correct model (from wire, *e.g.*) of the complex under consideration. It is important that this extended projection formula exhibits the same three-dimensional symmetry properties as the complex it represents.

### 2. Illustration of Principles

In order to clarify at the outset the interplay of configurational and conformational chiralities to give rise to diastereoisomerism we consider an example.

The tris(ethylenediamine)chromium(III) ion, which has the point group symmetry  $D_3-32$  (where the Schönflies and Hermann–Mauguin symbols have been given connected by a hyphen), exists in two configurational isomers,  $\Delta$  and  $\Lambda$  (Figure 1). In the  $\Delta$  form the edges covered by a pair of chelating ligands are skew lines defining a right-handed screw. By proper rotations the  $\Delta$  form remains  $\Delta$  and the  $\Lambda$  form  $\Lambda$ , but by improper rotations, *e.g.*, by inversion at the site of the

(1) (a) University of Braunschweig. (b) University of Copenhagen.

(2) (a) International Union of Pure and Applied Chemistry, "Nomenclature of Inorganic Chemistry," Butterworths, London, 1959; (b) 2nd ed. London, 1971.

(3) International Union of Pure and Applied Chemistry, Information Bulletin No. 33, 1968; *Inorg. Chem.*, **9**, 1 (1970).