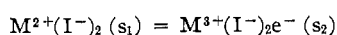


and useful observations regarding factors which appear important in determining whether a salt-like  $[M^{2+}(I^-)_2]$  or a "metallic"  $[M^{3+}(I^-)_2e^-]$  diiodide is to be formed if such a composition occurs at all. In this case the enthalpy change for the transformation



is  $-U_1 + I_3 + U_2$ . The metallic state presumably has the larger lattice energy because of the enhanced interactions of the higher-charged cation with both the anions and the delocalized electrons. To a first approximation it might be supposed that the rare earth metal diiodides should show relatively constant values for  $U_2 - U_1$ , or differences which change relatively smoothly. The fact that the change is resisted by  $I_3$  brings to mind two general guidelines which may be useful in assessing where and under what conditions such metal-like iodides may be encountered. First, it is evident that such will be favored by low values of  $I_3$ , and certainly the rare earth elements and a few neighbors in the periodic table are the most likely candidates to meet this requirement. Similarly, the apparently metallic  $Th^{4+}(I^-)_2(e^-)_2$ <sup>24</sup> results for that tetrapositive element which probably has the smallest value for ( $I_3 + I_4$ ), although we are obviously not prepared to explain why a metallic thorium triiodide did not form also or instead. Extension of this idea to normally dipositive metals would suggest that barium would present the most likely (practical) candidate for a  $M^{2+}I^-$  phase; however a recent, critical examination of the  $BaI_2$ -Ba system indicates that no such intermediate (or any other) is formed.<sup>25</sup>

(24) R. J. Clark and J. D. Corbett, *Inorg. Chem.*, **2**, 460 (1963).

(25) M. A. Bredig, private communication.

A second important condition, one which may actually supplant the first for heavy elements, can be placed on the electronic state of the reduced metal ion if a metal-like example is to occur. Obviously 4f orbitals, highly shielded and with small radial extension, are not likely candidates for the formation of the necessary conduction band. Hence the divalent ion derived from a  $M^{3+}$  ion with a  $4f^n$  configuration should probably be  $[Xe]4f^n5d^1$ , or not far removed from this, in order for the extra electron to be delocalized into a conduction band that probably has a substantial amount of 5d character.<sup>2,19,26</sup> This appears to be the case for La, Ce, Gd (and Th).<sup>21</sup> In this light  $NdI_2$  and the diiodides of Sm, Eu, Tm, and Yb are salt-like simply because the added electron is well buried in the 4f shell. The same consideration may also be pertinent with the salt-like  $UI_3$ <sup>27</sup> and in the conduction properties of  $MX_3$ -M melts.<sup>14,19</sup> The role of the iodide ion is less clear, although it is obviously important since "metallic" phases have not been found with either chloride or bromide.

Finally, the ferromagnetism observed for  $GdI_2$  is not particularly surprising since conduction electrons would provide a ready mechanism for coupling of  $4f^7$  cores, as in the metal. Magnetic orientation may also be present in  $CeI_2$  and  $PrI_2$ .

**Acknowledgment.**—The considerable assistance of J. D. Greiner, R. S. Lee, and F. J. Jelinek in providing the magnetic susceptibility data is gratefully acknowledged.

(26) This condition has also been noted by C. K. Jørgensen, *Mol. Phys.*, **7**, 420 (1964).

(27) J. D. Corbett, R. J. Clark, and T. F. Munday, *J. Inorg. Nucl. Chem.*, **25**, 1287 (1963).

CONTRIBUTION FROM THE DEPARTMENT OF INORGANIC CHEMISTRY,  
BRISTOL UNIVERSITY, BRISTOL, ENGLAND

## Chemistry of the Metal Carbonyls. XXVIII. Addition of Rhenium Pentacarbonyl Hydride to Fluoroolefins<sup>1,2</sup>

BY J. B. WILFORD<sup>3</sup> AND F. G. A. STONE

Received August 17, 1964

This paper describes the addition of rhenium pentacarbonyl hydride to the compounds  $CF_2=CF_2$ ,  $CF_2=CFCl$ ,  $CF_2=CCl_2$ , and  $CF_3C\equiv CCF_3$ , and the nature of the rhenium complexes obtained. The reaction between tetrafluoroethylene and methylrhenium pentacarbonyl is described and compared with that involving methylmanganese pentacarbonyl.

In previous papers we have described several fluorocarbon-transition metal complexes prepared by addition of the hydrides  $HMn(CO)_5$ ,  $\pi-C_5H_5Mo(CO)_3H$ , or  $\pi-C_5H_5W(CO)_3H$  to tetrafluoroethylene, by addition of  $HMn(CO)_5$  to chlorotrifluoroethylene, 1,1-dichloro-2,2-

difluoroethylene, or hexafluorobut-2-yne, and by addition of methylmanganese pentacarbonyl to tetrafluoroethylene or chlorotrifluoroethylene.<sup>4</sup> Continuing these studies we have investigated reactions between rhenium pentacarbonyl hydride and these unsaturated fluorocarbons. The addition of methylrhenium pentacarbonyl to tetrafluoroethylene is also described. The na-

(1) Previous paper in this series: J. B. Wilford and F. G. A. Stone, *J. Organometallic Chem.*, **2**, 371 (1964).

(2) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(3) Department of Scientific and Industrial Research predoctoral student.

(4) (a) For a summary of this work see P. M. Treichel and F. G. A. Stone, *Advan. Organometallic Chem.*, **1**, 143 (1964); (b) J. B. Wilford, P. M. Treichel, and F. G. A. Stone, *J. Organometallic Chem.*, **2**, 119 (1964).

TABLE I  
 SOME FLUOROCARBON DERIVATIVES OF RHENIUM<sup>a</sup>

Compound	M.p., °C.	Carbon, %		Hydrogen, %		Fluorine, %		Chlorine, %	
		Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
HCF <sub>2</sub> CF <sub>2</sub> Re(CO) <sub>5</sub> (I)	45-45.5	19.7	19.8	0.23	0.24	17.8	17.8	...	...
HCFClCF <sub>2</sub> Re(CO) <sub>5</sub> (II)	49-50	19.0	19.2	0.23	0.35	12.9	13.0	8.0	8.0
HCCl <sub>2</sub> CF <sub>2</sub> Re(CO) <sub>5</sub> (III)	90-91	18.3	18.4	0.22	0.28	8.3	8.2	15.4	15.5
CF <sub>3</sub> CH=C(CF <sub>3</sub> )Re(CO) <sub>5</sub> (IV)	27-27.5	22.1	22.3	0.21	0.36	23.3	23.5	...	...
CH <sub>3</sub> CF <sub>2</sub> CF <sub>2</sub> Re(CO) <sub>5</sub> (V)	60-60.5	21.8	21.8	0.70	0.78	17.2	17.0	...	...
CH <sub>3</sub> (CF <sub>2</sub> ) <sub>4</sub> Re(CO) <sub>5</sub> (VI)	35-36	22.2	22.2	0.55	0.35	28.1	27.5	...	...

<sup>a</sup> Microanalyses for C, H, F, and Cl were performed by the Alfred Bernhardt Mikroanalytisches Laboratorium, Max-Planck Institute für Kohlenforschung, Mulheim (Ruhr), West Germany.

ture of one of the products obtained from the latter reaction prompted further studies on the methylmanganese pentacarbonyl-tetrafluoroethylene reaction.

### Experimental

Methylrhenium pentacarbonyl and rhenium pentacarbonyl hydride were prepared by the method of Hieber and Braun.<sup>5</sup> Tetrafluoroethylene was obtained by slow pyrolysis of Fluon resin at 520°, and chlorotrifluoroethylene by dechlorination of 1,1,2-trichloro-1,2,2-trifluoroethane.<sup>6</sup> Fluorine and proton n.m.r. spectra were recorded with a Perkin-Elmer R-10 high resolution spectrometer. Line positions were measured from precalibrated charts and were the average of two or more traces. Infrared spectra were recorded using a Perkin-Elmer Model 237 grating spectrophotometer in conjunction with an auxiliary 9-in. recorder.

(1) Addition of Rhenium Pentacarbonyl Hydride to Unsaturated Fluorocarbons. (a) Tetrafluoroethylene.—In a representative experiment rhenium pentacarbonyl hydride (1.53 g., 4.70 mmoles) and tetrafluoroethylene (394 cc.,<sup>7</sup> 17.6 mmoles) were condensed into a 250-ml. Pyrex bulb attached to the vacuum system. The bulb was sealed off and held at 15° for 3 days, during which time a copious deposit of white, needle-like crystals formed. The reaction vessel was attached to the vacuum line, opened, and unreacted tetrafluoroethylene (282 cc., 12.6 mmoles) recovered. The solid in the bulb was washed out with pentane (40 ml.). Solvent was removed (-20°, 5 mm.) and the residue sublimed (12°, 0.1 mm.), affording 1.67 g. (84% yield based on HRe(CO)<sub>5</sub> taken) of white crystalline HCF<sub>2</sub>CF<sub>2</sub>Re(CO)<sub>5</sub> (I, Table I).

(b) Chlorotrifluoroethylene.—In view of earlier work<sup>4b</sup> which established that the direction of addition of manganese pentacarbonyl hydride across the double bond of chlorotrifluoroethylene depended both on the pressure and on the amount of the fluoroolefin taken for reaction, several reactions between rhenium pentacarbonyl hydride and chlorotrifluoroethylene were studied. Three typical experiments were as follows.

(i) Rhenium pentacarbonyl hydride (191.5 mg., 0.58 mmole) and chlorotrifluoroethylene (246 cc., 11.0 mmoles) were sealed together in a 250-ml. Pyrex bulb for 12 days at 15°. Although crystals appeared, reaction was obviously incomplete. Accordingly, the bulb was held at 38° for 7.5 hr. Subsequently, unreacted chlorotrifluoroethylene (233 cc., 10.4 mmoles) was recovered. Pentane extraction of the solid remaining in the bulb and sublimation (25°, 0.1 mm.) afforded 142.7 mg. of what proved to be white crystalline HCFClCF<sub>2</sub>Re(CO)<sub>5</sub> (II, Table I) in 55% yield based on the rhenium pentacarbonyl hydride taken for reaction.

(ii) In a similar experiment rhenium pentacarbonyl hydride (516 mg., 1.58 mmoles) and chlorotrifluoroethylene (490 cc., 21.8 mmoles) were held at 40° for 22 hr. On opening the reaction vessel, 453 cc. (20.2 mmoles) of chlorotrifluoroethylene

was recovered. Careful fractionation of the gas and examination of the infrared spectrum of various fractions failed to detect the presence of trifluoroethylene in the recovered chlorotrifluoroethylene. The solid in the bulb was purified in the usual way (see above) to give 568.5 mg. (81% yield) of II.

(iii) Rhenium pentacarbonyl hydride (457.6 mg., 1.4 mmoles) and chlorotrifluoroethylene (1468 cc., 65.5 mmoles) were distilled into a 150-ml. stainless steel Hoke bomb, which was allowed to stand at room temperature for 17 days. To ensure completion of the reaction, the bomb was then heated (40°, 19 hr.). On opening to the vacuum line, unreacted chlorotrifluoroethylene (1413 cc., 63.1 mmoles), identified by its infrared spectrum, was recovered. Pentane extraction of the solid in the bomb, followed by sublimation (25°, 0.1 mm.), afforded II (427 mg., 69% yield).

The products (II) obtained from reactions i-iii had identical infrared spectra in the 7-11 μ region and identical melting points. Had the isomer HCF<sub>2</sub>CFCRe(CO)<sub>5</sub> formed in reactions i or ii the spectrum of the products from these reactions would have shown additional bands to those in the spectrum of the product from reaction iii.<sup>4b</sup>

(c) 1,1-Dichloro-2,2-difluoroethylene.—In a reaction similar to that described in (a) above, rhenium pentacarbonyl hydride (530 mg., 1.62 mmoles) and 1,1-dichloro-2,2-difluoroethylene (246 cc., 11.0 mmoles) afforded after 5 hr. at 40° unreacted olefin (217 cc., 9.7 mmoles) and 567.5 mg. (76% yield based on HRe(CO)<sub>5</sub> taken) of HCCl<sub>2</sub>CF<sub>2</sub>Re(CO)<sub>5</sub> (III) (white crystals, Table I).

(d) Hexafluorobut-2-yne.—From the reaction between rhenium pentacarbonyl hydride (712 mg., 2.18 mmoles) and hexafluorobut-2-yne (419 cc., 21.9 mmoles) in a 250-ml. Pyrex bulb at 40° for 64 hr., CF<sub>3</sub>CH=C(CF<sub>3</sub>)Re(CO)<sub>5</sub> (IV, Table I) was obtained (887 mg., 83% yield) as pure white crystals. The hexafluorobut-2-yne recovered from this reaction amounted to 435 cc. (19.4 mmoles).

(2) Addition of Methylrhenium Pentacarbonyl to Tetrafluoroethylene. (a) At 2-3 Atm.—Methylrhenium pentacarbonyl (341 mg., 1.0 mmole) was weighed into a 250-ml. Pyrex bulb attached to the vacuum line. Tetrafluoroethylene (468 cc., 20.9 mmoles) was condensed into the bulb, which was sealed and heated at 130° for 4 hr. On cooling the reaction vessel and opening it to the vacuum system, carbon monoxide (2.2 mmoles) and tetrafluoroethylene (448 cc., 20.0 mmoles) were recovered, along with traces of perfluoropropene and perfluorocyclobutene (identified by their infrared spectra). Solid remaining in the bulb was extracted with pentane (40 ml.), and the combined extracts were evaporated (-20°, 10 mm.). Sublimation (17°, 0.01 mm.) of the residue afforded 66 mg. of a white solid which melted over the range 49-70°. The solid was dissolved in 1 ml. of pentane and placed on a 2 × 7.5 cm. Florisil column. Elution with pentane afforded a series of fractions (10 ml.) which were evaporated (-20°, 10 mm.) and the residues sublimed (17°, 0.01 mm.). The sublimes were identified as methylrhenium pentacarbonyl (20 mg.) and CH<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>Re(CO)<sub>5</sub> (V) (2 mg., 0.5% yield), by melting point and infrared spectroscopy. The Florisil column was finally washed with a 50% ether-pentane mixture. Evaporation of solvent afforded a trace of CH<sub>3</sub>(CF<sub>2</sub>)<sub>4</sub>Re(CO)<sub>5</sub> (VI) (see below), identified by its infrared spectrum.

(5) W. Hieber and G. Braun, *Z. Naturforsch.*, **14b**, 132 (1959).

(6) M. W. Buxton, D. W. Ingram, F. Smith, M. Stacey, and J. C. Tatlow, *J. Chem. Soc.*, 3830 (1952).

(7) Throughout this paper the abbreviation cc. refers to gases at standard conditions.

TABLE II  
 SOME F<sup>19</sup> AND H<sup>1</sup> CHEMICAL SHIFTS AND COUPLING CONSTANTS

Compound	$\delta(\alpha\text{-CF}_2)^a$ p.p.m.	$\delta(\beta\text{-CF}_2)^a$ p.p.m.	$\delta(\text{H})^a$ $\tau$	$J_{\text{F}\alpha\text{-H}}$ c.p.s.	$J_{\text{F}\beta\text{-H}}$ c.p.s.	$J_{\text{F}\alpha\text{-F}\beta}$ c.p.s.
HCF <sub>2</sub> CF <sub>2</sub> Re(CO) <sub>5</sub> (I)	98.4	42.5 <sup>b</sup>	4.87°	5.7	59.0	<1
HCFCICF <sub>2</sub> Re(CO) <sub>5</sub> (II)	116, 101 <sup>d</sup>	26.5 <sup>e</sup>	4.41 <sup>f</sup>	5.3, 11.8	52.5	g
HCCl <sub>2</sub> CF <sub>2</sub> Re(CO) <sub>5</sub> (III)	118.5 <sup>b</sup>	...	4.20 <sup>h</sup>	11.0	...	...
CH <sub>3</sub> CF <sub>2</sub> CF <sub>2</sub> Re(CO) <sub>5</sub> (V)	110.8 <sup>i</sup>	73.0 <sup>j</sup>	8.46°	2.5	20.0	4.5
CH <sub>3</sub> (CF <sub>2</sub> ) <sub>4</sub> Re(CO) <sub>5</sub> (VI)	92.2	82.8	g	g	g	g

<sup>a</sup> F<sup>19</sup> chemical shifts relative to C<sub>6</sub>F<sub>6</sub> (0.0 p.p.m.), increasing to low field. H<sup>1</sup> chemical shifts in  $\tau$  units. Solvent was CS<sub>2</sub>-acetone in all cases. <sup>b</sup> Doublet. <sup>c</sup> Triplet of triplets. <sup>d</sup> AB pattern. <sup>e</sup> Refers to F of  $\beta$ -CFClH group. <sup>f</sup> Two quartets, intensity 1:1:1:1 within each quartet. <sup>g</sup> Not measured. <sup>h</sup> Triplet. <sup>i</sup> Multiplet, 7 lines. <sup>j</sup> Quartet of triplets.

(b) At 20 Atm.—Methylrhenium pentacarbonyl (498 mg., 1.46 mmoles) was placed in a 150-ml. Hoke bomb which was sealed and evacuated. Tetrafluoroethylene (2277 cc., 101.7 mmoles) was distilled into the bomb, which was heated at 130° for 3 hr. On cooling and opening to the vacuum line, carbon monoxide and tetrafluoroethylene (2221 cc., 99.2 mmoles) were recovered. Pentane extraction of the residual solids afforded a sticky white solid (150 mg., 20% yield). An intractable brown material remained in the bomb.

In a similar experiment, methylrhenium pentacarbonyl (870.5 mg., 2.55 mmoles) and tetrafluoroethylene (1792 cc., 80.0 mmoles) were heated at 130° for 4 hr. On opening to the vacuum line carbon monoxide and tetrafluoroethylene (1744 cc., 77.8 mmoles) were recovered. Pentane extraction of the residual solids afforded a sticky white sublimate (100 mg., 10% yield).

Combined crude products from several such experiments were extracted with pentane (1 ml.) and placed on a short Florisil column, as in (a) above. In this way methylrhenium pentacarbonyl (60 mg.) and compounds V (72 mg.) and VI (16 mg.) (Table I) were eluted from the column. Analytical samples of V and VI were obtained by slow sublimation (17°, 0.01 mm.).

(3) Addition of Methylmanganese Pentacarbonyl to Tetrafluoroethylene at 20 Atm.<sup>8</sup>—In an experiment similar to (2b) above, methylmanganese pentacarbonyl (634 mg., 3.02 mmoles) and tetrafluoroethylene (2352 cc., 105.0 mmoles) were heated at 100° for 14 hr. On opening the bomb, tetrafluoroethylene (569 cc., 25.4 mmoles) was recovered. Pentane extraction of the residue afforded CH<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>Mn(CO)<sub>5</sub> (398 mg., 43% yield), identified by its melting point and infrared spectrum.<sup>4b</sup> A white residue in the bomb (2.3 g.) appeared to be polytetrafluoroethylene.<sup>9</sup>

In a repeat experiment, methylmanganese pentacarbonyl (466 mg., 2.22 mmoles) and tetrafluoroethylene (1135 cc., 50.7 mmoles) at 100° for 4 hr. afforded CH<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>Mn(CO)<sub>5</sub> (456 mg., 66% yield), unreacted C<sub>2</sub>F<sub>4</sub> (957 cc., 42.7 mmoles), and polymer (120 mg.). In neither experiment was a manganese analog of VI detected by infrared spectroscopy.

### Discussion

The new rhenium complexes obtained in this work are white volatile crystalline solids, and like many previously reported<sup>4</sup> fluorocarbon-transition metal complexes are apparently indefinitely stable in air when pure. Their n.m.r. and infrared spectra were recorded, and the results are summarized in Tables II and III. The spectra of compounds I-III and V show striking similarity to those of the analogous manganese compounds.<sup>4b,10</sup>

(8) Previous work<sup>4b</sup> involved reactions at 2-3 atm. Higher pressures of C<sub>2</sub>F<sub>4</sub> were used in the present work to determine whether CH<sub>3</sub>(CF<sub>2</sub>)<sub>4</sub>Mn(CO)<sub>5</sub> could be obtained, as well as CH<sub>3</sub>(CF<sub>2</sub>)<sub>2</sub>Mn(CO)<sub>5</sub>.

(9) In a control experiment it was found that when tetrafluoroethylene (105 mmoles) was heated (100°, 14 hr.) alone in the Hoke bomb an appreciable quantity (5.0 g.) of polymer was also obtained. Polymer formation under the experimental conditions is thus apparently independent of the addition of the organometallic across the double bond of the fluoroolefin.

(10) P. M. Treichel, E. Pitcher and F. G. A. Stone, *Inorg. Chem.*, **1**, 511 (1962).

As reported in the Experimental section, rhenium pentacarbonyl hydride adds to tetrafluoroethylene to give compound I in high yield. The reaction, however, was observed qualitatively to be much slower than with manganese pentacarbonyl hydride. Whereas manganese pentacarbonyl hydride adds to chlorotrifluoroethylene at ambient temperatures, it is necessary to warm the rhenium hydride with this fluoroolefin to effect complete reaction. Interestingly, the latter reaction affords HCFCICF<sub>2</sub>Re(CO)<sub>5</sub> as the only detectable rhenium complex. Under conditions similar to those described in the Experimental section under (1bii), manganese pentacarbonyl hydride and chlorotrifluoroethylene give a roughly equal mixture of the two isomers HCFCICF<sub>2</sub>Mn(CO)<sub>5</sub> and HCF<sub>2</sub>CFCIMn(CO)<sub>5</sub>.<sup>4b</sup>

The isomeric character of compound II is established by its n.m.r. and infrared spectra. The infrared spectrum is virtually identical with that of HCFCICF<sub>2</sub>Mn(CO)<sub>5</sub>. The F<sup>19</sup> spectrum consists of two groups of bands of intensity ratio 1:2, centered at 26.5 and 108.3 p.p.m., respectively, relative to hexafluorobenzene as standard. The chemical shift<sup>11</sup> of the latter resonance confirms that the CF<sub>2</sub> group is adjacent to rhenium. The multiplet has an AB pattern since the fluorine atoms of the  $\alpha$ -CF<sub>2</sub> group are not equivalent.<sup>10</sup> The bands at 26.5 p.p.m. consist of a pair of triplets arising from coupling between the  $\beta$ -CF group and the proton to give a doublet, which is split into two triplets by the fluorine atoms of the  $\alpha$ -CF<sub>2</sub> group.

It seemed possible that the absence of HCF<sub>2</sub>CFClRe(CO)<sub>5</sub> from among the products of reaction could have been due to its ready decomposition after initial formation. Previous work<sup>10</sup> suggests that if such a decomposition took place it would lead to formation of trifluoroethylene and rhenium pentacarbonyl chloride. Since these products were not found it appears that addition of rhenium pentacarbonyl chloride to chlorotrifluoroethylene is stereospecific. Again, contrasting with the corresponding manganese pentacarbonyl hydride reaction,<sup>13</sup> only one isomer was produced on reac-

(11) In the previous work<sup>4b,10</sup> on the F<sup>19</sup> n.m.r. spectra of HCF<sub>2</sub>CFCIMn(CO)<sub>5</sub> and HCFCICF<sub>2</sub>Mn(CO)<sub>5</sub>, trichlorofluoromethane was used as the standard. Chemical shift values obtained in the present study may be compared with those obtained earlier by subtracting them (Table II) from 163.7 p.p.m.<sup>12</sup> Thus for II we have  $\alpha$ -CF<sub>2</sub> at 55.4 p.p.m. and  $\beta$ -CF at 137.2 p.p.m.; to be compared with  $\alpha$ -CF<sub>2</sub> at 53.1 p.p.m. and  $\beta$ -CF at 138.4 p.p.m. for HCFCICF<sub>2</sub>Mn(CO)<sub>5</sub>.

(12) A. J. R. Bourn, D. G. Gillies, and E. W. Randall, *Proc. Chem. Soc.*, 200 (1963).

(13) J. B. Wilford, unpublished observations.

TABLE III  
 INFRARED SPECTRAL BANDS OF RHENIUM COMPOUNDS (cm.<sup>-1</sup>)

Compound	Carbonyl stretching frequencies <sup>a</sup>		Other bands <sup>b</sup>						
HCF <sub>2</sub> CF <sub>2</sub> Re(CO) <sub>5</sub> (I)	2148 w		2960 w	1355 m	1170 w	1090 s	1025 s	975 m	
	2039 vs	2012 s	945 w	640 m					
HCFClCF <sub>2</sub> Re(CO) <sub>5</sub> (II)	2147 w	2076 vw	2960 w	1318 s	1203 w	1130 m	1057 s	1015 s	
	2038 vs	2011 s	957 s	835 d, m	700 w				
HCCl <sub>2</sub> CF <sub>2</sub> Re(CO) <sub>5</sub> (III)	2148 w	2072 w	2910 w	1230 m	1210 w	1082 m	985 s	947 s	
	2038 vs	2035 vs	805 s	785 m	675 w				
CF <sub>3</sub> CH=C(CF <sub>3</sub> )Re(CO) <sub>5</sub> (IV)	2148 w		3020 w	2505 w <sup>c</sup>	2450 w <sup>c</sup>	1630 sh <sup>c</sup>	1617 s <sup>c</sup>	1345 m	
	2041 vs	2008 s	1290 s	1260 w	1230 vs	1200 w	1145 vs	1130 vs	1110 s
CH <sub>3</sub> CF <sub>2</sub> CF <sub>2</sub> Re(CO) <sub>5</sub> (V)			1020 w	950 w	905 w	855 sh	840 m	715 w	645 s
			3010 w						620 m
CH <sub>3</sub> (CF <sub>2</sub> ) <sub>4</sub> Re(CO) <sub>5</sub> (VI)	2148 w		2945 d, w	1385 m	1275 m	1205 s	1157 vs	1037 vs	
	2038 vs	2008 s		1000 vs	980 vs	940 s	845 s	635 m	
	2150 w		2925 w	2800 w	1310 s	1285 w	1185 d, s	1050 s	
	2040 vs	2015 s	1000 s	925 s	730 m				

<sup>a</sup> Cyclohexane solution, values from precalibrated charts using Kent recorder. <sup>b</sup> Carbon disulfide solution. <sup>c</sup> From spectrum of liquid film (at 30°) on NaCl plates.

tion of the rhenium hydride with 1,1-dichloro-2,2-difluoroethylene. Both the F<sup>19</sup> chemical shift and the small  $J_{F-H}$  are characteristic of a HCCl<sub>2</sub>CF<sub>2</sub>-M group.

The infrared spectrum of compound IV is very similar to that of the manganese complex *trans*-CF<sub>3</sub>-CH=C(CF<sub>3</sub>)Mn(CO)<sub>5</sub>.<sup>10</sup> The F<sup>19</sup> and H<sup>1</sup> n.m.r. spectra of IV are relatively simple, indicating that it is formed predominantly, if not only, as one isomer. As in the case of the manganese analog, the F<sup>19</sup> spectrum of IV establishes that the two CF<sub>3</sub> groups are *trans* to one another. The fluorine spectrum consists of two groups of peaks centered at 112.5 and 110.0 p.p.m. relative to hexafluorobenzene. The absorptions at 112.5 p.p.m. are a pair of quartets, arising from spin coupling of three fluorine atoms of a CF<sub>3</sub> group with a proton on the same carbon atom ( $J_{H-CF_3} = 9.1$  c.p.s.), and with the other CF<sub>3</sub> group ( $J_{CF_3-CF_3} = 2.5$  c.p.s.). The peaks at 110.0 p.p.m. are in the form of a quintuplet (intensity ratio 1:4:6:4:1) arising from two overlapping quartets ( $J_{CF_3-CF_3} = J_{H-CF_3} = 2.5$  c.p.s.). The proton spectrum shows four quartets, as does that of the manganese analog.<sup>10</sup> The small  $J_{CF_3-CF_3}$  coupling constant is characteristic of *trans*-CF<sub>3</sub> groups.<sup>10,14</sup> This assignment requires that the fluorine resonance centered at 110 p.p.m. is due to the CF<sub>3</sub> group *gem* to the Re(CO)<sub>5</sub> group.

As described in the Experimental section, a detailed study was made of the addition of methylrhenium pentacarbonyl to tetrafluoroethylene. In contrast to the other reactions reported in this paper the yield of the desired complex V was very low. Moreover, more than one organorhenium pentacarbonyl complex was formed in the reaction. This should be compared with

the addition of methylmanganese pentacarbonyl to tetrafluoroethylene, which affords the complex CH<sub>3</sub>-CF<sub>2</sub>CF<sub>2</sub>Mn(CO)<sub>5</sub> in about 60% yield.<sup>4b</sup>

It was found that the optimum conditions for producing V and VI were a reaction time of about 4 hr. at 130°<sup>15</sup> and approximately 20 atm. of tetrafluoroethylene. If shorter reaction times were used the methylrhenium pentacarbonyl remained largely unreacted. If longer reaction times were used, only a small amount of product was obtained due to thermal decomposition. Also, isolation of the organorhenium compounds was hindered by the presence of considerable amounts of polytetrafluoroethylene.

The infrared and F<sup>19</sup> and H<sup>1</sup> n.m.r. spectra of compound V conclusively demonstrated the presence of a CH<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>-metal group. Isolation and characterization of complex VI proved to be very difficult because it was obtained in small amounts. Formulation as CH<sub>3</sub>(CF<sub>2</sub>)<sub>4</sub>Re(CO)<sub>5</sub> is based on the following evidence. The presence of an Re(CO)<sub>5</sub> group and a fluorocarbon side chain was shown by infrared spectroscopy. The analysis (Table I) is consistent with a structure having eight fluorine atoms. The low but sharp melting point, high volatility, and behavior on chromatography are all consistent with the formulation. Melting points decrease in the series H(CF<sub>2</sub>)<sub>n</sub>Mn(CO)<sub>5</sub> as *n* increases,<sup>16</sup> so it is to be expected that VI would have a lower melting point than V. The F<sup>19</sup> n.m.r. spectrum of VI consists of two groups of peaks at 92.2 and 82.8 p.p.m. (relative to C<sub>6</sub>F<sub>6</sub>) with 1:3 intensity, respectively. This is in accord with an  $\alpha$ -CF<sub>2</sub> group and three other CF<sub>2</sub> groups having about equal chemical shift. Unfortunately, insufficient material was available to investigate the proton spectrum.

It was hoped to prepare the manganese analog of VI by addition of methylmanganese pentacarbonyl to tetrafluoroethylene at high pressures. However, under the conditions studied only the previously described CH<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>Mn(CO)<sub>5</sub> was obtained. The con-

(14) The assignments of the two  $J_{H-CF_3}$  coupling constants for IV are the reverse of those made previously for the two  $J_{H-CF_3}$  coupling constants for *trans*-CF<sub>3</sub>(H)C=C(CF<sub>3</sub>)Mn(CO)<sub>5</sub>.<sup>10</sup> That the proton-fluorine coupling constants of the manganese complex were incorrectly assigned by us<sup>10</sup> has been pointed out by Professor W. R. Cullen and by Dr. H. L. Gewanter. We are indebted to Professor Cullen and to Dr. Gewanter for providing us with n.m.r. data on the compounds *cis*- and *trans*-CF<sub>3</sub>(H)C=C(H)As(CH<sub>3</sub>)<sub>2</sub> and *cis*-CF<sub>3</sub>(H)C=C(CF<sub>3</sub>)R, prior to their publication of their respective results. The observed  $J_{H-CF_3}$  coupling constants in the compounds made by Cullen and Gewanter further confirm our deduction that compound IV is the *trans* isomer.

(15) Methylrhenium pentacarbonyl is known<sup>5</sup> to decompose at 140°.

(16) W. R. McClellan, *J. Am. Chem. Soc.*, **83**, 1598 (1961).

ditions employed were those at which the addition is known to take place rapidly.<sup>4b</sup> It was not practicable to attain rapidly the higher reaction temperatures found necessary to effect the addition of methylrhenium pentacarbonyl to tetrafluoroethylene. Apparently  $\text{CH}_3\text{CF}_2\text{CF}_2\text{Mn}(\text{CO})_5$  once formed does not react further with tetrafluoroethylene.

Attempts to effect the addition of methylrhenium

pentacarbonyl to tetrafluoroethylene in pentane using ultraviolet irradiation were not successful. This is in noticeable contrast to the behavior of methylmanganese pentacarbonyl, which undergoes essentially quantitative addition to tetrafluoroethylene on irradiation of mixtures.<sup>17</sup>

(17) J. B. Wilford, P. M. Treichel, and F. G. A. Stone, *Proc. Chem. Soc.*, 218 (1963).

CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, UNIVERSITY OF NORTH CAROLINA, CHAPEL HILL, NORTH CAROLINA, AND TULANE UNIVERSITY, NEW ORLEANS, LOUISIANA

## Substituted Pyridine N-Oxide Complexes of Copper(II) Halides

BY WILLIAM E. HATFIELD,<sup>1a</sup> Y. MUTO,<sup>1b</sup> H. B. JONASSEN,<sup>1b</sup> AND JOHN S. PASCHAL<sup>1a</sup>

Received August 3, 1964

The preparation and characterization of a number of 4-substituted pyridine N-oxide complexes of copper(II) halides are reported. Two series of compounds are formed; one with the general formula  $\text{CuLCl}_2$  and the second with the formula  $\text{CuL}_2\text{Cl}_2$ . Structural assignments are made on the basis of the similarity of the magnetic and spectral properties of these compounds with those of  $[\text{Cu}(\text{C}_5\text{H}_5\text{NO})\text{Cl}_2]_2$ .

### Introduction

In recent years a considerable interest in the donor properties of pyridine N-oxide has been evident. Quagliano, *et al.*,<sup>2</sup> and Carlin<sup>3</sup> have reported the preparation and characterization of a number of coordination compounds of this Lewis base with a wide variety of metal salts; Quagliano and co-workers<sup>4</sup> have studied the infrared spectra of the compounds reported earlier<sup>2</sup>; and Meek, Drago, and Piper<sup>5</sup> have measured the electronic spectra of complexes with nickel(II), chromium(III), and cobalt(II). Harris, *et al.*,<sup>6</sup> have confirmed the abnormally low magnetic moment reported by Quagliano, *et al.*,<sup>2</sup> for the complex with the empirical formula  $\text{CuCl}_2 \cdot \text{C}_5\text{H}_5\text{NO}$  in a study of the temperature dependence of the magnetic susceptibility. An independent study by Smith<sup>7</sup> is in accord with these results. We now wish to report the results of our magnetic and spectral studies on a series of copper(II) halide complexes with 4-substituted pyridine N-oxides. The results are interpreted in terms of the following structure which has been determined by a complete X-ray crystal structure examination<sup>8</sup> (Figure 1).

### Experimental

**Preparation of the Substituted Pyridine N-Oxides.**—Pyridine N-oxide and the 4-substituted pyridine N-oxides were prepared by the method reported by Ochiai<sup>9</sup> or were obtained commercially.

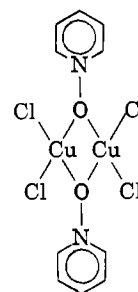


Figure 1.—The structure of  $[\text{Cu}(\text{C}_5\text{H}_5\text{NO})\text{Cl}_2]_2$ .

The melting points or boiling points of the compounds with a 4-substituent of  $-\text{H}$ ,  $-\text{Cl}$ ,  $-\text{OH}$ , and  $-\text{NO}_2$  were in good agreement with those given in Ochiai's paper.

**Preparation of the Coordination Compounds.**—The complexes were prepared by mixing a solution of the ligand in ethanol with a stoichiometric amount of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  in ethanol or  $\text{CuBr}_2$  in ethanol. The compounds listed in Table I either crystallized immediately or upon standing for a short time and were purified by recrystallization from ethanol.

**Magnetic Susceptibility Determinations.**—Equipment for the determination of magnetic susceptibilities by the Faraday method similar to that described earlier<sup>10</sup> has been assembled at Chapel Hill. Mercury(II) tetrathiocyanatocobaltate(II) was used as a magnetic susceptibility standard,<sup>11</sup> and the diamagnetic corrections were estimated from Pascal's constants.<sup>12</sup> In addition to the measurements by the Faraday method, measurements at room temperature by the Gouy method were made at Tulane.

**Spectral Studies.**—The infrared spectra of Nujol mulls of samples of the complexes were obtained using either a Perkin-Elmer 421 spectrophotometer which was calibrated with polystyrene or a Beckman IR 8 spectrophotometer. Spectra of the substituted pyridine N-oxides were obtained from  $\text{CS}_2$  solutions.

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