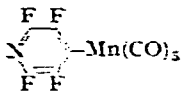
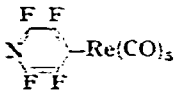
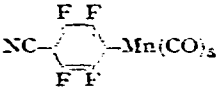
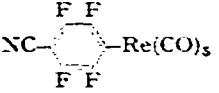


## Reactions of metal carbonyl anions with pentafluoropyridine and pentafluorobenzonitrile

The ready reaction of nucleophiles with pentafluoropyridine<sup>1</sup> to give mono-substituted compounds of the type  $\text{XC}_5\text{F}_4\text{N}$  ( $\text{X} = \text{NH}_2$ ,  $\text{NR}_2$ ,  $\text{NH}\cdot\text{NH}_2$ ,  $\text{H}$ ,  $\text{OH}$ ,  $\text{OMe}$ ,  $\text{CH}:\text{CHMe}$ ,<sup>2</sup> or  $\text{Ph}$ <sup>3</sup>), and the similar, though less-thoroughly investigated, ease of nucleophilic attack on pentafluorobenzonitrile<sup>4</sup>, suggested that pentafluoropyridine and pentafluorobenzonitrile might be good traps for metal carbonyl anions. Reactions involving the anions  $[\text{Mn}(\text{CO})_5]^-$  and  $[\text{Re}(\text{CO})_5]^-$ , now reported, occurred readily at room temperature in tetrahydrofuran, and the white crystalline, sublimable products, purified by chromatography then recrystallised, are shown in Table 1.

TABLE 1  
INFRARED SPECTRA

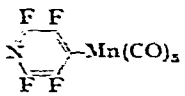
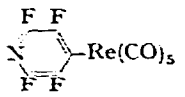
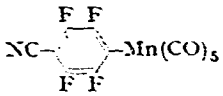
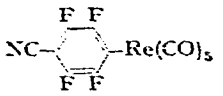
Compound	M.p. (°C)	Yield (%)	Carbonyl stretching frequencies ( $\text{cm}^{-1}$ )			
			$A_1^{1b}$	$E$	$A_1^{1a}$	
	96-97	46	2137 m	2075 w, sh	2045 vs	2016 s <sup>a</sup>
	117-118	60	2150 m	2075 w	2046 vs	2017 s <sup>a</sup>
	134-135 (dec.)	56	2143 m	2088 w, sh	2054 vs	2031 s <sup>b</sup>
	152-153 (dec.)	52	2155 m	2095 w, sh	2050 vs	2036 s <sup>b</sup>

<sup>a</sup>  $\text{CaF}_2$  optics, solution in  $\text{CCl}_4$ . <sup>b</sup>  $\text{CaF}_2$  optics, solution in  $\text{CHCl}_3$ .

The compounds are stable in air for several hours, both in the solid state and in solution, and their <sup>19</sup>F spectra (Table 2) all show characteristic symmetrical AA'XX' patterns which can only arise if substitution has occurred in the 4-position, in agreement with previously reported spectra of tetrafluoropyridine derivatives<sup>5</sup>. Calculation of the coupling constants was not possible due to inadequate resolution. The infrared spectra in the metal carbonyl region (Table 1) show the expected pattern<sup>6</sup> for  $C_{4v}$  symmetry of a medium  $A_1^{1b}$  band and strong  $E$  and  $A_1^{1a}$  bands. The presence of a weak shoulder in the 2070-2095  $\text{cm}^{-1}$  region in these compounds may be due to the  $B_1$  stretching mode normally inactive in the infrared region. This may indicate some degree of asymmetry<sup>7</sup>, but no splitting of the intense  $E$  band was observed.

Further support for the structure of  $\text{C}_5\text{F}_4\text{N}\cdot\text{Mn}(\text{CO})_5$  was obtained by the formation of 2,3,5,6-tetrafluoropyridine on reaction with an excess of hydrogen chloride at 100°.

TABLE 2  
 $^{19}\text{F}$  NMR SPECTRA<sup>a</sup>

Compound	$\delta$ (ppm)	
	2-F	3-F
	17.5	31.5
	18.0	30.0
	23.4	58.0
	21.1	57.7

<sup>a</sup> 35% w/v solution in  $\text{CHCl}_3$ ; figures quoted in ppm upfield from  $\text{CF}_3\text{-CO}_2\text{H}$  external reference.

We have yet to establish whether the attack of the manganese or rhenium anions on pentafluoropyridine or pentafluorobenzonitrile is more ready than the reaction of these anions with tetrafluoroethylene, hexafluoropropene or perfluorocyclohexene, although it is noteworthy that tetrafluoroethylene does not react with  $[\text{Mn}(\text{CO})_5]^-$  (Ref. 8). King and Bisnette<sup>9</sup> showed that the salt  $\text{NaMn}(\text{CO})_5$  did not react with hexafluorobenzene in refluxing tetrahydrofuran.

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