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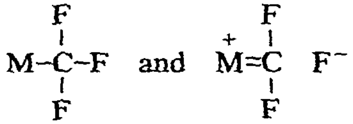
SHORT COMMUNICATIONS

Bonding in fluorinated organometallic compounds

Within the past year, several workers have discussed the bonding of perfluoroalkyl groups to transition metals, in order to explain the great thermal and aerobic stability of perfluoroalkyl-metallic compounds. The crystal structures of π-$C_5H_5Rh(CO)(C_2F_5)I$[1] and $K_3[Co(CN)_5CF_2CF_2H]$[2] are reported to provide persuasive evidence of the shortening and hence strengthening of the M–C bond of the perfluoroalkyl group. Some unusual features of the infrared spectra of perfluoroalkyl derivatives have likewise been examined by Wilford and Stone[3], and Cotton and McCleverty[4]. Theoretical descriptions have been given in the following terms: (*a*) a stabilization of the metal–perfluoroalkyl bond because of metal-orbital contraction due to the high electronegativity of the perfluoroalkyl group (*i.e.* an electrostatic model); (*b*) a valence bond approach[3] based on the contribution of canonical structures such as



$$M-\overset{F}{\underset{F}{C}}-F \quad \text{and} \quad \overset{+}{M}=\overset{F}{\underset{F}{C}} \quad F^-$$

(*c*) the π-acceptor capacity of the perfluoroalkyl group[4], requiring a drift of $d\pi$ electrons from the metal into C–F anti-bonding orbitals. Models (*b*) and (*c*) are very approximately equivalent in that both should increase the bond order and reduce the length of the M–C bond, and conversely decrease the bond order and increase the length of the C–F bonds. The compound *cis*-$CFH{=}CFMn(CO)_5$ provides the first evidence of the latter effect, and the structure, infrared and ^{19}F NMR spectra can be related, at least qualitatively.

Considering infrared data first, Cotton and McCleverty[4] have pointed out the lowering by about 100 cm^{-1} of the C–F stretching frequencies of $CF_3Mn(CO)_5$ from those of CF_3X ($X = Cl$, Br, or I). Such a frequency change indicates a drop of about 10% in the C–F force constant, and this was attributed to the use of the C–F

TABLE 1
INFRARED DATA FOR TRIFLUOROMETHYL COMPOUNDS

Compound	*C–F frequencies* (cm^{-1})	*Ref.*
$(CH_3)_3GeCF_3$	1194, 1098	5
$(CH_3)_3SnCF_3$	1158, 1071	6
$(CH_3)_3PbCF_3$	~1140, ~1070	7
$(CH_3)_2PCF_3$	1175, 1125, 1118	8
CF_3X ($X = Cl$, Br, or I)	1177–1217, 1058–1104	quoted in ref. 4
$CF_3Mn(CO)_5$	1053, 1018	quoted in ref. 4

anti-bonding orbitals according to model (*c*) above. This comparison can be extended to trifluoromethyl derivatives of main group metals as shown in Table 1. Applying Cotton and McCleverty's argument, we can conclude that in general the degree of $M{-}CF_3$ π-interaction in $(CH_3)_nMCF_3$ ($M = Ge, Sn, Pb$, or P; $n = 3$ or 2) is comparable to that in CF_3X ($X = Cl, Br$, or I) and certainly less than in $CF_3Mn(CO)_5$. It must however, be pointed out that participation of the canonical form $[(CH_3)_3Sn^+{=}CF_2]F^-$ might be invoked as a possible explanation of the ready pyrolysis of $(CH_3)_3SnCF_3$ to $(CH_3)_3SnF$ and difluorocarbene[6].

The best illustration to date of the unusual bonding features of a fluoroorganometallic compound is provided by *cis*-$CFH{=}CFMn(CO)_5$, for which both spectroscopic[9] and structural[10] data are now available. The C–F stretching frequencies are 1045 and 968 cm^{-1} (nujol mull). A comparison with the corresponding frequencies (liquid film) for $(CH_3)_3SnCF{=}CFH$ [1086, 1058 and 1038 (doublet) cm^{-1}][11] and with the spectra of perfluorovinyl–metal compounds[12] shows that in *cis*-$CFH{=}CFMn(CO)_5$ the C–F stretching frequencies are appreciably lowered. If this is due to involvement of the C–F anti-bonding orbitals, one might hope to see both a shortened Mn–C(F) distance, and an elongation of the C–F bonds. The crystal data[10] show the latter to occur, the C–F distances being $C\alpha{-}F = 1.46 \pm 0.03$ Å, and $C\beta{-}F = 1.50 \pm 0.03$ Å, compared with the expected 1.33 Å. It is particularly interesting *both* C–F bonds are long, suggesting that the π-interaction from Mn to the $-CF{=}CFH$ group extends through the $>C{=}C<$ bond system to affect the two fluorine atoms equally. Moreover, the unusually small FF coupling constant (2.4 cps) observed in the ^{19}F NMR spectrum[9] provides further evidence that the bonding of the fluorine atoms is unusual. This decrease in the *cis*-FF-coupling constant may be associated with the lengthening of the F–C=C–F linkage (overall length 4.24 Å) which is comparable to the F–C–C–F length of 4.2 Å in fluoroalkanes.

The Mn–C(F) distance is 1.95 Å and may be slightly smaller than the sum of the covalent radii (*ca.* 2.1 Å)[13]. Unfortunately, structural data for any related alkyl- or vinyl-manganese compounds are not available for comparison. Alternatively, to avoid the problems inherent in the use of atomic radius values, the method of Churchill can be applied, and the distances M–C (hydrocarbon or fluorocarbon group) compared with the M–CO distances for known compounds (Table 2). The difference is intermediate in value between those of the fluoroalkyl compound and that of the ethyl compound. Hence the data do not disagree with a proposed shortening of the

TABLE 2

A COMPARISON OF METAL–CARBON BOND LENGTHS

Compound	*Bond*	*Distance (Å)*	*Difference (Å)*
π-$C_5H_5Rh(CO)(C_2F_5)I$[1]	$Rh{-}CF_2$	2.08	0.11
	$Rh{-}CO$	1.97	
$K_3[Co(CN)_5CF_2CF_2H]$[2]	$Co{-}CF_2$	1.990	0.063
	$Co{-}CN$	1.927	
cis-$CFH{=}CFMn(CO)_5$	Mn–CO (axial)	1.73	0.22
	Mn–CF	1.95	0.16
	Mn–CO (equat.)	1.79	
π-$C_5H_5Mo(CO)_3C_2H_5$[14]	$Mo{-}CH_2$	2.38	0.41
	Mo–CO	1.97	

Mn–CF bond in *cis*-CFH=CFMn(CO)$_5$, but certainly do not provide conclusive evidence*. A final point worth mentioning is the value of 130° observed[10] for the Mn–C=C angle of *cis*-CFH=CFMn(CO)$_5$, this also being consistent with the Mn–CF bond having a bond order greater than one[1].

The lengthening of the C–F distances, the low frequencies of the C–F stretching vibrations, the anomalous features of the ^{19}F NMR spectrum, and the unique molecular dimensions of *cis*-CFH=CFMn(CO)$_5$ provide the best evidence to date of the π-bonding properties of fluorinated organic groups. The most elegant explanation is that requiring a flow of manganese $d\pi$ electrons into the antibonding C–F orbitals, an effect which is probably enhanced in this particular compound through participation of the vinylic $>C=C<$ π-system.

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* *Note added in proof:* A value of 1.39 Å has recently been proposed (F. A. COTTON AND D. C. RICHARDSON, *Inorg. Chem.*, 5 (1966) 1851) for Mn in derivatives of Mn(CO)$_5$. Th Mn–C distance, assuming the radius of C (sp^2 hydrization) to be 0.68 Å, should then be 2.07 Å. It is therefore very clear that the Mn–CF distance is shortened considerably in *cis*-CFH=CFMn(CO)$_5$.