

## Reactions of Fluorinated Olefins with Metal Carbonyl Anions

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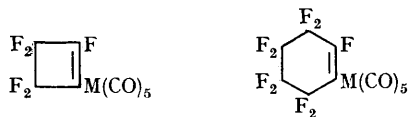
A CHARACTERISTIC reaction of highly fluorinated aromatic and olefinic hydrocarbons is the replacement of one or more of their fluorine atoms by nucleophiles, for example methyl-lithium or

sodium methoxide.<sup>1</sup> We now report that several metal carbonyl anions undergo similar reactions with a variety of fluoro-olefins.

In tetrahydrofuran the sodium salts of the

<sup>1</sup> D. R. Sayers, R. Stephens, and J. C. Tatlow, *J.*, 1964, 3035; *Endeavour*, 1963, 22, 89 and references cited therein.

anions  $\text{Mn}(\text{CO})_5^-$  and  $\text{Re}(\text{CO})_5^-$  readily replace fluorine atoms, in perfluoro-cyclobutene or -hexene to form (60—90% yield) organometallic compounds of structures (I) and (II) [established by elemental analysis, molecular weight measurement, and i.r. and  $^{19}\text{F}$  n.m.r. spectroscopy].



M=Mn or Re

(I)

(II)

The anion  $[\text{Mn}(\text{CO})_4\text{PPh}_3]^-$  reacts with perfluoro-cyclohexene to form predominantly *trans*- $\text{C}_6\text{F}_9\text{Mn}(\text{CO})_4\text{PPh}_3$  (in the metal carbonyl stretching region of the infrared spectrum the complex shows only one strong absorption at  $1995\text{ cm}^{-1}$ ). However, reaction of the pentacarbonylmanganese complex (II) with triphenylphosphine yields a

mixture of *cis*- and *trans*- $\text{C}_6\text{F}_9\text{Mn}(\text{CO})_4\text{PPh}_3$ , the *cis*-isomer showing strong carbonyl absorptions at  $2090$ ,  $2015$ ,  $2008$ , and  $1965\text{ cm}^{-1}$ .

It has been reported<sup>2</sup> that whereas hexafluorobenzene and  $\pi\text{-C}_6\text{H}_5\text{Fe}(\text{CO})_2^-$  react to form  $\pi\text{-C}_6\text{H}_5\text{Fe}(\text{CO})_2\text{C}_6\text{F}_5$ , several other carbonyl anions, including  $\text{Mn}(\text{CO})_5^-$ , do not react with hexafluorobenzene. In contrast to the result with the pentacarbonylmanganese anion, we find that the new compound  $\text{C}_6\text{F}_5\text{Re}(\text{CO})_5$  can be obtained (15% yield) by treating hexafluorobenzene with the sodium salt of pentacarbonylrhenium(-1).

We have also prepared the first trifluorovinyl transition-metal complexes  $\text{CF}_2:\text{CF}\cdot\text{Re}(\text{CO})_5$  and  $\text{CF}_2:\text{CF}\cdot\text{Fe}(\text{CO})_2\pi\text{-C}_5\text{H}_5$ , by treating the carbonyl anions in tetrahydrofuran with chlorotrifluoroethylene. Interestingly, the reaction between  $\text{Mn}(\text{CO})_5^-$  and chlorotrifluoroethylene in the same ether affords the previously described<sup>3</sup> compound  $\text{HCFCl}\cdot\text{CF}_2\cdot\text{Mn}(\text{CO})_5$ , rather than  $\text{CF}_2:\text{CF}\cdot\text{Mn}(\text{CO})_5$ . However, it has been possible to prepare several trifluorovinyl transition-metal complexes by treating the appropriate metal halide complexes with perfluorovinylmagnesium bromide.<sup>4</sup>

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<sup>2</sup> R. B. King and M. B. Bisnette, *J. Organometallic Chem.*, 1964, **2**, 38.

<sup>3</sup> J. B. Wilford, P. M. Treichel, and F. G. A. Stone, *J. Organometallic Chem.*, 1964, **2**, 119.

<sup>4</sup> D. T. Rosevear and F. G. A. Stone, unpublished observations.