

Perfluorovinyl–metal derivatives: a new one-pot synthesis

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The one-pot reaction of the CFC replacement 1,1,1,2-tetrafluoroethane (CF₃CFH₂, HFC-134a) with 2 equiv. of butyllithium in diethyl ether at –78 °C followed by the addition of main-group or transition-metal halides results in good yields of the corresponding metal–perfluorovinyl compounds of high purity.

Although fluorine is capable of replacing hydrogen in many organic systems usually without major structural changes the number of examples of organometallic complexes containing perfluorinated ligands is very much more limited than for the comparable perprotio analogues.¹ Of the examples that do exist in the literature many of the smaller fluorine-containing organic fragments are derived from bromofluorocarbons (BFCs) or chlorofluorocarbons (CFCs). However starting materials like these are currently being phased out under international and national agreements, such as the Montreal Protocol, due to their deleterious effect on the ozone layer. A case in point is the synthesis of perfluorovinyl (CF₂=CF–) derivatives which have previously used bromotrifluoroethene as the starting material. This pyrophoric compound is no longer commercially produced which will ultimately result in it being unavailable for pure research applications and thus this route will become obsolete. Very recent work² has focused on the use of one of the hydrofluorocarbon replacements for CFCs, 1,1,1,2-tetrafluoroethane (CF₃CFH₂, HFC-134a) as an alternative perfluorovinyl source for organic synthesis.

In view of the recent resurgence in interest in the chemistry of organofluorine compounds and in particular their coordination to metal centres to induce C–F bond activation³ we report the ‘one-pot’ synthesis of metal perfluorovinyl compounds using HFC-134a as a perfluorovinyl source. The addition of 2 equiv. of *n*-butyllithium to a diethyl ether solution of HFC-134a at –78 °C results in the double deprotonation and elimination of 1 equiv. of lithium fluoride from HFC-134a to generate the CF₂=CF–Li⁺ reagent **1** in good yields. Compound **1** generated in this way is stable in solution for up to 24 h at this temperature but decomposes rapidly as the temperature is increased above –45 °C. The formation of metal perfluorovinyl complexes is readily achieved by adding concentrated cold diethyl ether or thf solutions of metal halides to the lithium reagent. This immediately results in reaction and the formation of an off-white precipitate of the lithium halide. Multinuclear NMR studies were found to be a convenient method to monitor the progress of these reactions and to determine the degree of perfluorovinyl substitution, prior to work-up procedures. Samples withdrawn from the organic phase of the reaction of CF₂=CF–Li⁺ and HgCl₂ in a 2 : 1 ratio were transferred to NMR tubes and allowed to warm to room temperature. ¹⁹F NMR spectra show replacement of the complex multiplet signals due to HFC-134a at δ –64.9 and –226.5 by three sets of doublets of doublets typical of the AMX pattern previously observed for perfluorovinyl metal complexes⁴ each with associated mercury satellite structure. The extent of substitution of the product may also be conveniently determined by NMR, in this case from the ¹⁹⁹Hg NMR spectra which exhibit a triplet of triplets of triplets so confirming unequivocally the product as [Hg(CF=CF₂)₂]**2**. This compound was isolated as a clear liquid after allowing the reaction mixture to slowly warm to room temperature before

being worked up using existing routes.⁵ Extraction of the organic phases followed by drying and evaporation of the organic solvents results in the generation of the perfluorovinyl metal compound in good yield (typically > 90%, based on the metal complex).

An analogous reaction using a 1 : 1 ratio of mercury(ii) chloride to perfluorovinyl lithium reagent generates the mono-substituted complex. NMR studies suggest that a very small amount of bis(perfluorovinyl)mercury is also present (typically < 5%) in the crude product. The relatively high volatility of fluorine-containing compounds coupled with their thermally robust nature means that further purification of the products, if necessary, may often be achieved by distillation or sublimation. For example sublimation of the crude product from the 1 : 1 reaction at 100 °C (20 mmHg) results in an air-stable, white solid which is analytically pure ClHg(CF=CF₂) **3**.

Having confirmed that this route may be used successfully to synthesise known perfluorovinyl complexes in high yield the extent of its utility as a general method of introducing the –CF=CF₂ moiety into a wide range of substrates was investigated by reaction with a variety of early- and late-transition metal coordination complexes and organometallic compounds. All reactions were carried out in a similar manner to that described above. Confirmation of the identity of the materials synthesised as perfluorovinyl metal complexes was obtained by elemental analysis and spectroscopic measurements.[†] In all cases ¹⁹F NMR spectra clearly demonstrated three sets of doublets of doublets with the anticipated satellite structure due to coupling with spin-active metal nuclei being evident where appropriate. A summary of these reactions is presented in Fig. 1.

The stability of these complexes is variable, with the majority of these complexes being thermally stable, although decomposition does occur in the presence of water or on extended contact with glassware, however the pentacarbonyl manganese perfluorovinyl complex decomposes rapidly under aqueous conditions.

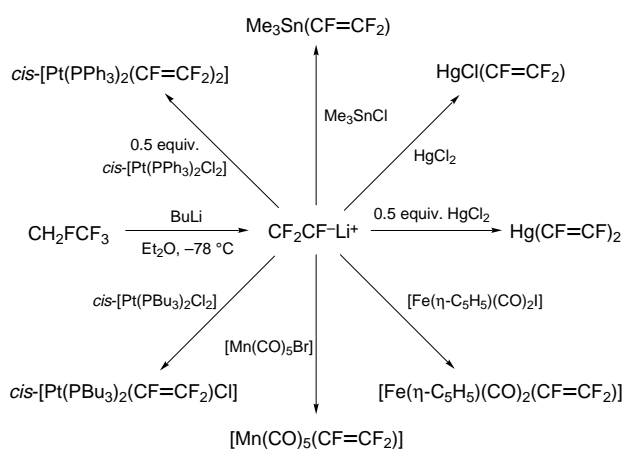


Fig. 1 Reactions of perfluorovinyl lithium, derived from CF₃CH₂F, with a variety of metal halides

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Footnote

† *Selected spectroscopic data:* **2**, $\text{Hg}(\text{CF}=\text{CF}_2)_2$. IR ν/cm^{-1} (neat) 1750, 1275, 1150, 1050. NMR: ^{19}F (188.3 MHz, solvent Et_2O , standard CFCl_3) δ -90.1 [1 F, dd, $J(\text{FF})$ 37, 75 Hz, $\text{CF}=\text{CFF}$], -124.5 [1 F, dd, $J(\text{FF})$ 75, 109 Hz, $\text{CF}=\text{CFF}$], -185.4 [1 F, dd, $J(\text{FF})$ 37, 109 Hz, $\text{CF}=\text{CF}_2$]; ^{13}C (75.49 MHz, neat, standard SiMe_4) δ 165.0 (1 C, m, $\text{CF}=\text{CF}_2$), 161.7 (1 C, m, $\text{CF}=\text{CF}_2$); ^{199}Hg (35.8 MHz, neat, standard HgMe_2) δ 957 [ttt, $J(\text{HgF})$ 816, 224, 32 Hz].

3, $\text{ClHg}(\text{CF}=\text{CF}_2)$. Anal. Found: F, 17.6; Hg, 63.5. Calc. for $\text{C}_2\text{ClF}_3\text{Hg}$: F, 17.97; Hg, 63.27%; IR ν/cm^{-1} (Nujol) 1750, 1277, 1160, 1011. NMR: ^{19}F (188.3 MHz, solvent Et_2O , standard CFCl_3) δ -92.3 [1 F, dd, $J(\text{FF})$ 42, 69, $J(\text{HgF})$ 374 Hz, $\text{CF}=\text{CFF}$], -124.0 [1 F, dd, $J(\text{FF})$ 69, 111, $J(\text{HgF})$ 13 Hz, $\text{CF}=\text{CFF}$], -180.5 [1 F, dd, $J(\text{FF})$ 42, 111, $J(\text{HgF})$ 1169 Hz, $\text{CF}=\text{CF}_2$]; ^{199}Hg (35.8 MHz, solvent Et_2O , standard HgMe_2) δ 876 (ddd).

$\text{Me}_3\text{Sn}(\text{CF}=\text{CF}_2)$. IR ν/cm^{-1} (Nujol) 1646, 1219, 1146, 1036. NMR: ^{19}F (solvent Et_2O) δ -88.6 [1 F, dd, $J(\text{FF})$ 33, 79 Hz, $\text{CF}=\text{CFF}$], -123.5 [1 F, dd, $J(\text{FF})$ 79, 113 Hz, $\text{CF}=\text{CFF}$], -194.6 [1 F, dd, $J(\text{FF})$ 33, 113 Hz, $\text{CF}=\text{CF}_2$].

cis- $[\text{Pt}(\text{PEt}_3)_2(\text{CF}=\text{CF}_2)_2]$. NMR: ^{19}F (solvent Et_2O) δ -98.3 (1 F, m, $\text{CF}=\text{CFF}$), -129.7 [1 F, dd, $J(\text{FF})$ 100.7, 101.0, $J(\text{PF})$ 1.5, $J(\text{PtF})$ 41.5 Hz,

$\text{CF}=\text{CFF}$], -160.8 [1 F, dd, $J(\text{FF})$ 101.0, 32.1, $J(\text{PF})$ 32, $J(\text{PtF})$ 389.1 Hz, $\text{CF}=\text{CF}_2$]; ^{31}P (81.05 MHz, CDCl_3 solution, standard aq. H_3PO_4) δ 5.5 [m, $J(\text{PtP})$ 2111 Hz].

cis- $[\text{Pt}(\text{P}^i\text{Bu}_3)_2(\text{CF}=\text{CF}_2)\text{Cl}]$. NMR: ^{19}F (solvent Et_2O) δ -94.5 [1 F, m, $J(\text{FF})$ 38, 81 Hz, $\text{CF}=\text{CFF}$], -126.0 [1 F, m, $J(\text{FF})$ 81, 109 Hz, $\text{CF}=\text{CFF}$], -183.3 [1 F, m, $J(\text{FF})$ 38, 109 Hz, $\text{CF}=\text{CF}_2$].

$[\text{Mn}(\text{CO})_5(\text{CF}=\text{CF}_2)]$. NMR: ^{19}F δ -98.2 [1 F, dd, $J(\text{FF})$ 25, 55 Hz, $\text{CF}=\text{CFF}$], -109.0 [1 F, dd, $J(\text{FF})$ 55, 124 Hz, $\text{CF}=\text{CFF}$], -149.0 [1 F, dd, $J(\text{FF})$ 25, 124 Hz, $\text{CF}=\text{CF}_2$].

$[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2(\text{CF}=\text{CF}_2)]$. NMR: ^{19}F (solvent Et_2O) δ -85.0 [1 F, dd, $J(\text{FF})$ 42, 101 Hz, $\text{CF}=\text{CFF}$], -131.5 [1 F, dd, $J(\text{FF})$ 101, 115 Hz, $\text{CF}=\text{CFF}$], -183.0 [1 F, dd, $J(\text{FF})$ 42, 115 Hz, $\text{CF}=\text{CF}_2$].

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