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PRELIMINARY NOTE

Reactions of perfluoroalkyl iodides with CC-multiple bonds induced by transition metal centers

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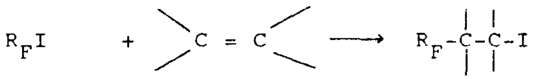
SUMMARY

Additions of perfluoroalkyl iodides R_FI to 1-alkenes can be catalyzed by transition metals, especially by noble metals such as ruthenium or platinum. Complexes of group VI-VIII metals in low oxidation states are even more effective and may also be employed for the addition of R_FI to alkynes. Heterogeneous metal catalysts facilitate the transfer of the perfluoroalkyl group from R_FI to aromatic ring systems.

Iodo-perfluoroalkanes **1** belong to the most important intermediates in organofluorine chemistry [1]. The addition of **1** to alkenes according to



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is known to be a radical process which can be initiated by means of heat, UV- or γ-radiation, electrocatalysis or by organic azo or peroxo compounds.

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[*] With experimental assistance by P. Hierl, J. Pöschl, H. Blank and A. Probst.

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We found that this type of reactions can generally be carried out using two kinds of transition metal catalysts:

Heterogeneous catalysis by transition metals

The metal can either be applied in finely divided form or fixed on an inert support. Noble metal catalysts such as ruthenium or platinum possess the highest life times. Their activity can be enhanced by the addition of small amounts of water and, at least in some cases, by further addition of fluoro surfactants such as $C_8F_{17}SO_3^-NR_4^+$. These additives probably act by preventing the blocking of active centers.

When polar, aprotic solvents (dmf, dmso) are used the reactions start at lower temperatures, however, considerable amounts of metal are transfered from the catalyst into the solution and 1-hydroperfluoralkanes are formed as undesired by-products. It is very likely that the formation of R_FH is due to the decomposition of unstable organometallic intermediates. A reaction of $C_6F_{13}I$ with manganese powder in dimethyl formamide at 60°C gave a 90 % yield of $C_6F_{13}H$, whereas the same reaction in the presence of ethene resulted in the formation of $C_6F_{13}CH_2CH_2I$ as the main product beside only 10 % of R_FH.

Under more drastic conditions, the perfluoroalkyl group can also be introduced into aromatic rings in the presence of transition metals. C_6F_{13}-C_6H_5 was obtained from $C_6F_{13}I$ and benzene under ruthenium catalysis in 88 % yield (165°C, 20 h, K_2CO_3 to neutralize HI), while the reaction under mere thermal conditions at 250°C gave only a yield of 65 % [2] .

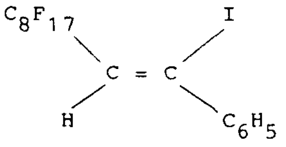
Homogeneous catalysis by metal complexes

It was recently reported that carbonyl complexes of group VIII metals are rather effective catalysts for the addition of compounds 1 to alkenes and alkynes [3] . We found similar catalytic activities also with carbonyls of group VI and VII metals. This type of catalysis is

neither restricted to binary carbonyls nor to the oxidation number zero of the metal. It proved favorable to introduce at least one ligand which improves the complexes solubility and may also exert a bond weakening influence toward other ligands. Organo-phosphates or -phosphites are particularly useful in this regard. Complexes displaying good activity are for instance:
$M(CO)_5L$ (M = Cr, Mo, W; L = PPh_3, $P(OEt)_3$), $Mn(\pi\text{-}Cp)(CO_3)$, $Ru(CO)_2(PPh_3)_3$, $Rh(H)(CO)(PPh_3)_3$ and $Ni(CO)_2(PPh_3)_2$.

Experiments using the nickel(O) complex $Ni(CO)_2(PPh_3)_2$ and mono-substituted alkenes $CH_2{=}CHX$ showed that for a specific compound **1** the rate decreased in the series $X = \text{alkyl} > H \approx Si(OR)_3 > CH_2OH \gg Cl > R_F$, as would be expected for such a reaction under participation of electrophilic R_F-radicals. If the substituent X is an electron attracting group, large amounts of $R_F(CH_2CHX)_2I$ are formed beside the normal 1:1 adduct, however, the yield of the latter can be improved by use of compound **1** in excess. CF_3I reacts slower than its higher homologues. In all cases, the R_F group enters predominantly the site of least steric hindrance, *i.e.* the CH_2-end of the double bond. Similar results were also obtained with vinylidene difluoride.

Additions of **1** to alkynes can also be accomplished with metal complexes. $C_8F_{17}I$ reacted with phenyl acetylene in the presence of $Ni(CO)_2(PPh_3)_2$ (2 mol-% of catalyst, 70°C, 6 h) to give the isomer **2** as the main product.



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The reactions in which transition metals were used were not influenced by radical scavengers, whereas in the case of metal complexes only a small retardation was observed.

These findings point to a cage mechanism. We assume that during the key step the compounds **1** are reduced at the metal centers $[M]$ to give radical anions which supply the R_F-radicals required to start the chain reaction with the unsaturated substrates:

$$R_FI + [M] \longrightarrow R_FI^{\overset{\cdot}{\ominus}}\,[M^+] \longrightarrow R_F\odot + [MI]$$

As for the metal complexes, a primary oxidative addition step of **1** followed by a thermal, homolytic fission of the $M\text{-}R_F$ bond has to be considered as a rational alternative.
The ability of the iron complex $Fe(C_6F_{13})(I)(CO)_4$ to catalyze reactions of **1** with alkenes seems to confirm this possibility, however, further studies are clearly necessary to elucidate the mechanism.

The active metal centers can be regenerated by the followi reaction terminating the radical chain process.

$$R_F\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}\odot + [MI] \longrightarrow R_F\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-I + [M]$$

Such a reaction seems difficult for electronegative metals (e.g. Mn, Zn) or for the majority of the employed complexes. In fact, metal iodide species have been detected at the end of the reactions in all these cases.

Table 1 gives a comparison between heterogeneous and homogeneous catalysts for the simple reaction of $C_8F_{17}I$ with ethene. It shows clearly that the metal complexes exhibit a better activity than the free metals. Since this is a general trend, the complex catalysts can be recommended whenever the compounds **1** have to be reacted under mild conditions, for instance if either the substrate or the product is thermally labile. On the other hand, the complexes become largely deactivated in the course of reaction because of the formation of iodides and their use will thus be restricted mainly to the laboratory scale for economical reasons.

Table 1. Addition of 1 = $C_8F_{17}I$ to ethene [a]

Catalyst	Temperature [°C]	Time [h]	Conversion[b] [%]	Yield[c] [%]
Ru/active carbon	120	12	98.6	93
Pt/active carbon	100	12	99.8	94
Ag/Al_2O_3	125	11	99.7	94.5
$Ni(CO)_2(PPh_3)_2$	70	6	100	96
$W(CO)_5[P(OEt)_3]$	90	5	95.7	89
$Mo(CO)_5(PPh_3)$	80	5	97.9	92

[a] Conditions: 250 ml rocking autoclave, lined with PTFE. 0.1 mol 1, 0.002 mol catalyst, 0.01 mol H_2O in the case of the metallic catalysts. $p(C_2H_4) = 20$ bar.

[b] Determined by GLC. Content of $R_F(CH_2CH_2)_2I < 1$ % in each case.

[c] $R_FCH_2CH_2I$ isolated by distillation ($bp._{10}$ 93-95°C).

A vast amount of addional experimental information concerning the synthetic application of catalytic reactions described in the present paper is given in the references [4] (additions of 1 to alkenes and alkynes using metal complexes), [5] (additions to alkenes with metallic catalysts) and [6] (perfluoralkylation of aromatic compounds).

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