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LIGAND SUBSTITUTION BY FLUOROALKYL GROUPS IN THE REACTION OF PERFLUOROALKYL IODIDES WITH A Co^I COMPLEX

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Summary

The perfluoroalkyl iodide C_3F_7I reacts with $[Co^ISalphen]^{-1}$ at −78°C to yield a mixture of $ICo^{III}Salphen$ and $Co^{II}Salphen$ accounting for ca. 95% of the original Co^I complex, together with the organometallic compound $C_3F_7Co^{III}$-Salphen (2%). Other Co^{III} and Co^{II} complexes were identified in very low yields containing C_3F_7 groups substituted in the ligand, one organometallic derivative being shown to have a C_3F_7 group substituted in the 4-position of the phenylene ring.

Introduction

Perfluoroalkyl iodides react with Co^I species containing quadridentate Schiff-base ligands to yield perfluoroalkylcobalt(III) organometallic compounds [1]. The related iodo complex $ICo^{III}(SB)$ may also form in the reactions to an extent determined by the particular Schiff-base ligand but generally represented less than 10% conversion of the starting compound. In the case where the initial complex contained the ligand 1,2-*N*,*N'*-phenylenebis(salicylaldimine), i.e. $[Co^I$-Salphen$]^{-1}$ (Fig. 1) the iodo complex was obtained in high yield and no organometallic compound was recovered initially.

Subsequently the desired compounds R_FCoSalphen have been prepared by the direct reaction of CH_3CoSalphen with R_FI. A more detailed examination of the original reaction between $[Co^ISalphen]^{-1}$ and C_3F_7I has disclosed that the organometallic compound is formed in very low yields at −78°C together with a number of other related complexes also in low yields in which C_3F_7 groups appear as substituents in the Schiff-base structure. For convenience such compounds will be represented by symbols such as CoSalphen·C_3F_7.

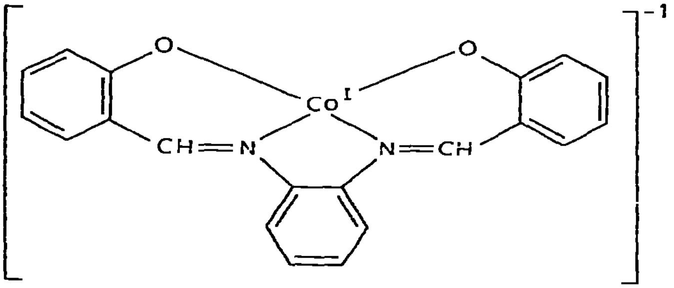


Fig. 1. The complex $[Co^{I}Salphen]^{-1}$.

Results

Synthesis of R_FCoSalphen derivatives

Radical exchange occurred when a cobalt alkyl such as RCoSalphen·H_2O (R = CH_3, C_2H_5) was heated in methanol with a perfluoroalkyl iodide R_FI (R_F = C_3F_7, C_2F_5) at 80°C in a sealed tube.

The products were R_FCoSalphen·H_2O and RI, together with some Co^{II}-Salphen. The crude reaction product did not contain any detectable amounts of CoI compounds. The complexes were obtained as red crystalline solids stable to the air and stable to light for an indefinite period. The infrared and NMR spectra showed very similar features to those previously reported for other perfluoroalkylcobalt Schiff-base compounds [1].

The reaction of $[Co^{I}Salphen]^{-1}$ with R_FI

Co^{II}Salphen is readily reduced in tetrahydrofuran solution to yield the green anion $[Co^{I}Salphen]^{-1}$. At −78°C this ion reacts rapidly with C_3F_7I to form both ICo^{III}Salphen and Co^{II}Salphen in the proportions 3/2 which accounted for ca. 95% of the original Co^{II}Salphen. Thin layer chromatography enabled a number of other products of the reaction to be identified. The organometallic compound C_3F_7CoSalphen H_2O was isolated in ca. 2% yield, together with a second organometallic compound in ca. 0.2% yield having a further C_3F_7 group present in the molecule, as evidenced by analysis and mass spectroscopic examination. It is represented for convenience as C_3F_7CoSalphenC_3F_7·H_2O. At least two other organometallic compounds having additional C_3F_7 groups were detected by TLC examination, but in much smaller amounts.

A further group of at least 12 separate Co^{II} compounds was also detected. Analysis of the mixture of Co^{II} species indicated that C_3F_7 groups were present in the complexes in such proportions as to average between 2 and 3 groups per Co. However, none of the products were present in sufficiently large amounts to enable separate study and identification.

The additional reaction products detected were NaI and the fluorocarbon C_3F_7H.

When the reaction was carried out at room temperature a similar overall distribution of products was obtained but the yields of the two main Co^{III} organometallic derivatives were increased, viz. C_3F_7CoSalphen·H_2O, ca. 30%, and

C_3F_7CoSalphen $C_2F_7 \cdot H_2O$, 3%. Reactions involving [Co^{I}Salphen]$^{-1}$ and C_2F_5I or CF_3I gave similar types of compounds to those obtained with C_3F_7I.

In a related experiment Ni^{II}Salphen was reduced by Na/Hg in tetrahydrofuran and the product reacted with C_3F_7I. The major product was Ni^{II}Salphen (> 90%), but a fraction was isolated which TLC analysis showed to contain two compounds. Analysis of the mixture indicated a ratio of one C_3F_7 group per Ni-Salphen moiety.

The constitution of the complex $C_3F_7CoSalphenC_3F_7 \cdot H_2O$

It was established that the compound contained a C_3F_7 group substituted in the ligand in addition to the group directly bonded to Co, by considering the mass and ^{19}F NMR spectra of the complex.

The most intense peak in the mass spectrum occurs at *m/e* = 541 corresponding to an ion containing Co, a Salphen residue minus one hydrogen atom and a C_3F_7 group. A further peak at *m/e* = 710 corresponds to the molecular ion (C_3F_7CoSalphenC_3F_7)$^{\cdot}$ but is of much lower intensity than the former (ca. 10%).

The mass spectra of other perfluoroalkylcobalt organometallics containing related types of ligands show a similar pattern, in that the most intense peaks in their spectra represent the ions [CoSB]$^{\cdot}$ which have lost the metal-bonded R_F group, with the molecular ions being detected but having much lower peak intensities (ca. 10%). The nickel complex having the formula Ni^{II}SalphenC_3F_7 also shows a similar spectrum to the Co species with the most intense peak being at *m/e* = 540 corresponding to (NiSalphenC_3F_7)$^{\cdot}$.

A notable feature of the mass spectrum of C_3F_7CoSalphenC_3F_7 is the existence of low intensity peaks at *m/e* values corresponding to ions of the form [SalphenCo(C_3F_7)$_n$] (*n* = 3-5 and possibly higher). The complex used in measuring the spectrum was a pure sample, as far as elemental analysis and TLC examination could show, so that the occurrence of the peaks is not considered to be due to impurities in the sample but to recombination reactions in the mass spectrometer. This pattern of behaviour is similar to that reported [2] for the mass spectrum of CH_3Co^{III} phthalocyanine, in which species having up to four additional CH_3 groups beyond the bare methyl derivative were detected. A similar phenomenon occurs in the spectrum of the Ni complex, in which species having up to two (C_3F_7) groups attached to NiSalphen were detected.

The ^{19}F NMR spectrum of C_3F_7CoSalphen$C_3F_7 \cdot H_2O$ shows two sets of resonances which can be allotted to the α, β and γ fluorines in two separate C_3F_7 groups (Table 1). The chemical shifts of one set of resonances are very close to those obtained for the CF_3 and the α and β-CF_2 fluorines of C_3F_7CoSalphen$\cdot H_2O$ and may thence be assigned to the C_3F_7 group directly bonded to Co. The second set is comparable to that observed for fluorines in the mixture of complexes NiSalphenC_3F_7 and is thus allotted to a C_3F_7 group substituted in the ligand since the nickel complexes cannot be considered as Ni^{III} organometallic compounds.

The ^{13}C spectrum of C_3F_7CoSalphen$\cdot H_2O$ shows a peak at 206 ppm (rel. to TMS) which is close to the value found for C atoms in CH=N arrangements having aromatic rings attached to C and N [3]. This absorption is also observed unchanged in C_3F_7CoSalphen$C_3F_7 \cdot H_2O$ so that substitution at the azomethine carbon is not involved. Further assignments of the ^{13}C spectrum in the "aromatic"

TABLE 1

^{19}F NMR SPECTRA OF R_FCoSalphen COMPOUNDS

Spectra measured in $(CD_3)_2SO$, δ values given in ppm upfield from $CFCl_3$ (δ = 0): (br = broad, t = triplet)

Compound	Fluoroalkyl group					
	α-CF_2		β-CF_2		γ-CF_3	
	a	*b*	*a*	*b*	*a*	*b*
$C_3F_7CoSalen \cdot H_2O$	91.0(br)		121.0		78.4t	
$C_3F_7CoSalphen \cdot H_2O$	94.7(br)		121.9		78.5t	
$C_3F_7CoSalphenC_3F_7 \cdot H_2O$	94.7(br)	109.0t	122.0	124.9	78.7t	82.6t
$NiSalphenC_3F_7$		110.8t		126.2		81.0t

[a] Co—C_3F_7 group resonances. [b] C_3F_7 substituted in ligand.

region were not attempted in the absence of detailed studies of related systems, but changes in chemical shifts and relative intensities were observed when comparing the two complexes.

The ^{1}H NMR spectra of a number of Co compounds including C_3F_7Co-$SalphenC_3F_7 \cdot H_2O$ are shown in Fig. 2. RCoSalphen (R = alkyl) complexes in

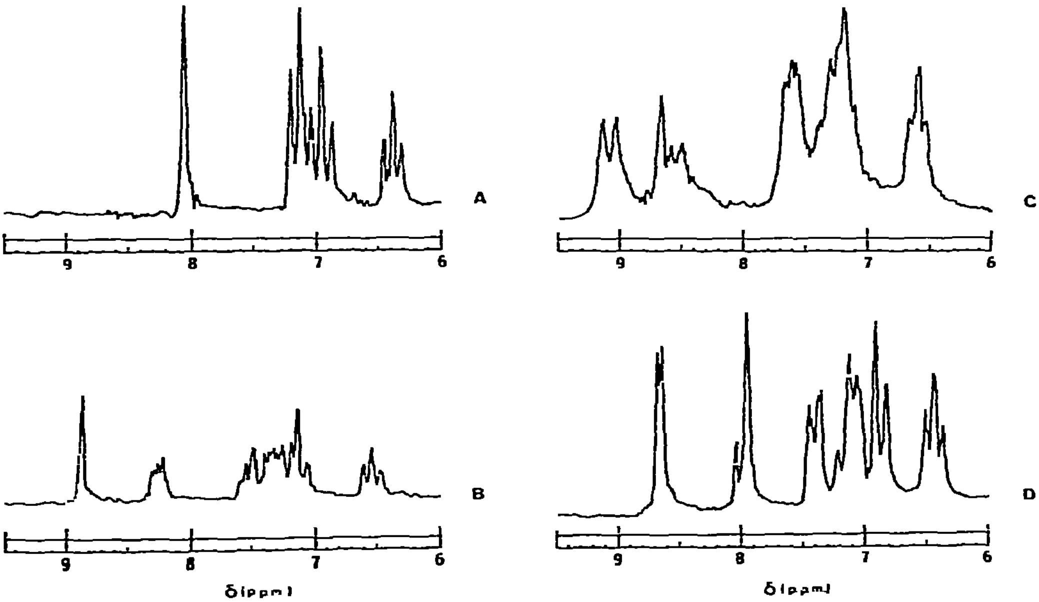


Fig. 2. The ^{1}H NMR spectra of some organometallic cobalt(III) complexes.

A: Aquo-*N,N'*-ethylenebis(salicylaldiminato)cobalt(III) heptafluoropropyl ($C_3F_7CoSalen \cdot H_2O$).

B: Aquo-1,2-*N,N'*-phenylenebis(salicylaldiminato)cobalt(III) heptafluoropropyl ($C_3F_7CoSalphen \cdot H_2O$).

C: Aquo-1,2-*N,N'*-4-heptafluoropropylphenylenebis(salicylaldiminato)cobalt(III) heptafluoropropyl ($C_3F_7CoSalphenC_3F_7 \cdot H_2O$).

D. Aquo-1,2-*N,N'*-4-methylphenylenebis(salicylaldiminato)cobalt(III) methyl ($CH_3CoSalphenCH_3 \cdot H_2O$).

general show similar complex patterns related to their aromatic protons [4]. A typical example is provided by $CH_3CoSalphen$, which shows a group of peaks in the region δ 8.00-8.33, the integrated intensity of which corresponds to 2 protons. A further complex multiplet is observed in the region δ 6.83-7.67, equivalent to 8 protons, and a final group of three resonance peaks centred at about δ 6.6, equivalent to 2 protons, accounts for the 12 aromatic protons of such complexes. The azomethine proton is indicated by a peak occurring at δ 8.81. $C_3F_7CoSalphen \cdot H_2O$ shows a similar spectrum with groups of peaks in the regions δ 8.0-8.3 (2 protons), 7.0-7.5 (8 protons) and 6.4-6.7 (2 protons). The azomethine protons absorb at δ 8.8.

The complex $C_3F_7CoSalen \cdot H_2O$ does not show a group of resonances in the region δ 8.08-8.30, and instead the azomethine protons absorb at δ 8.4. This suggests that the four resonance peaks occurring in this region for the complex $C_3F_7CoSalphen \cdot H_2O$ and equivalent in intensity to 2 protons are due to two protons in the phenylene ring. The ligand substituted complex $C_3F_7CoSalphenC_3F_7 \cdot H_2O$ shows a three peak pattern centred at δ 6.6 very similar to that of the unsubstituted compound, but the four peak pattern in the δ 6.80-8.30 region has been replaced by two peaks, an intense singlet and a doublet. The pattern of the multiplet in the region δ 6.80-7.56 has been altered to a seemingly less complex structure and is reduced in overall intensity. The CH=N proton peak has been split and appears as a doublet centred at δ 9.1 indicating a change in symmetry of the molecule brought about after introduction of the C_3F_7 group to the ligand.

The complex 1,2-*N*,*N'*-4-methylphenylenebis(salicylaldiminato)cobalt(III) methyl has an ^1H resonance pattern for aromatic protons very similar to that shown by $C_3F_7CoSalphenC_3F_7 \cdot H_2O$ but with a general shift of resonance positions downfield. In particular there are two peaks, one notably more intense than the other, in the region δ 7.6-8.0 corresponding to phenylene ring protons. The azomethine peak is also split and has shifted downfield to δ 8.6.

The combined sample of the $Ni^{II}SalphenC_3F_7$ isomers also shows similar changes in ^1H NMR spectra when compared with $Ni^{II}Salphen$ alone.

The form of the spectrum suggests that the two Ni species indicated by TLC examination have very similar ^1H resonances.

The complex $C_3F_7CoSalphenC_3F_7 \cdot H_2O$ thus has a C_3F_7 substituent in the 4-position of the phenylene ring (Fig. 3).

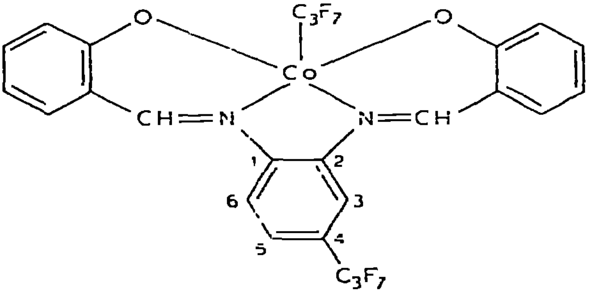
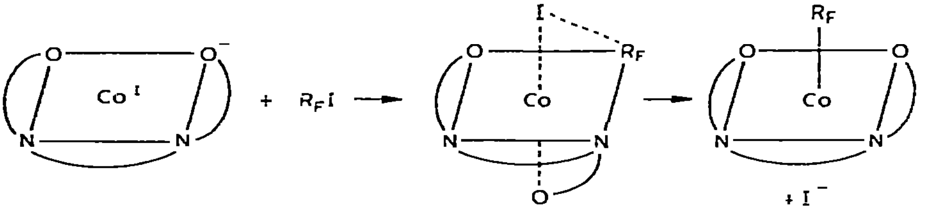


Fig. 3. The complex $C_3F_7CoSalphenC_3F_7 \cdot H_2O$.

The reaction mechanism

The very high yields of ICoSalphen and CoSalphen obtained, compared with the low yield of R_FCoSalphen, is quite opposite to the result of the reaction of R_FI with various other Co^I species containing tetradentate Schiff-base ligands. The added observation of R_F substitution in the ligand is a further side reaction not detected previously.

The previous hypothesis [1] to explain the reactions of R_FI and Co^I species suggested that they proceeded by an S_N2 process in which R_FI adds to the Co^I complex to form a six-coordinate intermediate in which the normally planar ligand has been distorted out of the plane. Iodide was considered to be expelled preferentially from the transition state intermediate thus forming the fluoroalkyl organometallic (eqn. 1).



(1)

The conjugated nature of the Salphen ligand was considered to make it resistant to distortion from the plane so that the dominating reaction path would then involve the nucleophilic attack of Co^I on the $I^{\delta+}$ of the $R_F^{\delta-}$—$I^{\delta+}$ bond. Electron transfer could then occur to yield the iodo complex and, presumably, fluorocarbanions. The latter presumably are able to abstract hydrogen from the solvent to form R_FH (eqn. 2).

$$\begin{aligned}[\mathrm{Co^I Salphen}]^{-1} + R_FI \rightarrow\ & \mathrm{SalphenCo^{I^-}}\cdots I^{\delta+}\cdots R_F^{\delta-} \\ & \downarrow \\ & \mathrm{SalphenCo{-}I} + R_F^- \end{aligned} \qquad (2)$$

The present study indicates the likelihood of a second reaction path in view of the formation of Co^{II}Salphen, viz. direct electron transfer (eqn. 3).

$$[\mathrm{Co^I Salphen}]^{-1} + R_FI \rightarrow \mathrm{Co^{II}Salphen} + (R_FI)^{-1} \qquad (3)$$

This initial reaction would then be expected to lead to the formation of I^- and $R_F\cdot$ radicals, the latter being available for reaction with Co^{II}Salphen to form C_3F_7CoSalphen (eqns. 4 and 5).

$$(R_FI)^{-1} \rightarrow I^{-1} + R_F\cdot \qquad (4)$$

$$\mathrm{Co^{II}Salphen} + R_F\cdot \rightarrow R_F\mathrm{Co^{III}Salphen} \qquad (5)$$

Schrauzer and Deutsch [5] considered this mechanism as an alternative to the concept of an S_N2 process for the reactions of Co^I nucleophiles with organic halides but concluded that their evidence was in favour of the S_N2 process. Halpern however obtained evidence to support a free radical mechanism for the reactions of Co^{II}Salphen and other Co^{II} complexes with benzyl halides suggesting that they proceed by an initial electron transfer [6] or halogen abstraction [7] to give either Co—I or Co^{III} and I$^-$ together with release of a free radical and reaction of this with a further molecule of Co^{II} complex.

Co^{II}Salphen does not react directly with R$_F$I under any conditions examined so that the formation of ICoSalphen cannot be ascribed to such a process.

The formation of compounds having R$_F$ groups substituted in the ligand is also explicable in terms of free radical attack, and it is interesting to note the predominant formation of the compound having a C_3F_7 group in the 4-position in the phenylene ring. Coe and Milner [8] have also reported substitutions by perfluoroalkyl radicals on aromatic substrates and have commented on the different distribution of isomers compared with reactions involving alkyl radicals. The radicals could attack either Co^{III} or Co^{II} species and there is evidence that the "Co^{II}" fraction containing C_3F_7 groups also contains a small amount of iodide, suggesting the accompanying formation of a benzene soluble ICoSalphen$(C_3F_7)_x$ species. C_3F_7H could also be produced by displacement of hydrogen in the ligand substitution reactions.

It is uncertain whether the greatly enhanced yield of C_3F_7CoSalphen and C_3F_7CoSalphen$C_3F_7 \cdot H_2O$ obtained when the reaction is performed at room temperature may be ascribed to an increased flexibility of the ligand at higher temperatures, allowing the 6-coordinate S_N2 process to become more important, or whether an overall increase in rate of formation of Co^{II} and free R$_F\cdot$ radicals allows a higher yield of the two R$_F$ substituted products.

Experimental

^{1}H and ^{19}F NMR spectra were measured in a Varian 56.4/60A spectrometer with DMSO-d_6 as solvent, and ^{13}C spectra with a Bruker WH-90. ^{19}F shifts were determined in $(CD_3)_2SO$ upfield relative to $CFCl_3$, ^{1}H and ^{13}C shifts relative to TMS. Mass spectra were recorded on a Hitachi—Perkin—Elmer RMU6E.

Reaction of CH_3CoSalphen$\cdot H_2O$ and R_FI

CH_3CoSalphen H_2O was prepared by the reaction of [Co^{I}Salphen]$^{-1}$ with CH_3I in tetrahydrofuran followed by precipitation of the complex with water and recrystallization from acetone. The complex (0.5 g) was dissolved in methanol in a Carius tube fitted with a Rotaflo tap and an excess of the appropriate R$_F$I added (R$_F$ = C_3F_7, C_2F_5) by condensation from a vacuum system. The mixture was heated for 24 h at 80°C, then the tube was opened and the contents separated by chromatography on "thin layer" plates. The fluoroalkyl organometallics were obtained in ca. 20% yield after recrystallization from methanol as stable, red crystalline products. Some Co^{II}Salphen was also detected as well as unchanged alkyl complex in the separation procedure.

C_3F_7CoSalphen$\cdot H_2O$. Found: F, 23.6. $C_{23}H_{16}CoF_7N_2O_3$ calcd.: F, 23.7%.

C_2F_5CoSalphen$\cdot H_2O$. Found: F, 18.3. $C_{22}H_{16}CoF_5N_2O_3$ calcd.: F, 18.6%.

Reactions with [Co^{I}Salphen]$^{-1}$

Co^{II}Salphen (3.73 g, 0.01 mol) was reduced with 1% Na/Hg (100 ml) in anhydrous tetrahydrofuran (100 ml) by stirring the mixture for 3 h. The excess amalgam was decanted, the mixture cooled to −78°C, C_3F_7I (2.95 g, 0.01 mol) added, and the mixture allowed to warm to room temperature. The solvent was then removed under reduced pressure and the dark brown solid residue extracted by successive portions of boiling benzene (3 × 150 ml). The residue then remaining was further extracted with boiling 2-methoxyethanol to remove Co^{II}Salphen leaving ICoSalphen as a black-brown amorphous solid.

The benzene extract was evaporated to yield a red-brown solid which was redissolved in methanol, and the solution passed down a column of alumina enabling the separation of a red material (A) and a brown-green (B). The red material was dissolved in acetone and the solution applied to thin layer chromatography plates (TLC) coated with 2 mm layers of silica gel. Development of the plates by diethyl ether produced two main red-orange bands. These were extracted with methanol and the constituent compounds recovered by addition of water as C_3F_7CoSalphen$C_3F_7 \cdot H_2O$ (found: C, 43.3; H, 2.40; F, 36.2; N, 4.1. $C_{26}H_{16}CoF_{14}N_2O_3$ calcd.: C, 42.8; H, 2.20; F, 36.5; N, 3.8%), and C_3F_7CoSalphen·H_2O respectively (found: C, 50.4; H, 3.10; F, 23.8; N, 4.82. $C_{23}H_{16}CoF_7N_2O_3$ calcd.: C, 49.3; H, 2.90; F, 23.7; N, 5.0%). The plates also showed that two other red-orange materials were present in very small amounts.

The green-brown material B was similarly examined using TLC, and at least 12 separate bands could be developed on a plate. The initial mixture of substances was found to be strongly paramagnetic, indicating the presence of Co^{II} species. Analysis of the crude mixture B showed a fluorine content in the region of three C_3F_7 groups per Co together with some I. (Found: C, 35.9; H, 1.7; F, 39.6; I, 3.9; N, 2.8. CoSalphen$(C_3F_7)_3$ calcd.: C, 39.6; H, 1.7; F, 45.2; N, 3.2%.)

When removing the solvent and other volatiles, fractionation in a vacuum system enabled the separation of C_3F_7H and its identification by comparison of its infrared spectrum with an authentic sample.

Yields. The initial crude product of ICo^{III}Salphen and Co^{II}Salphen had an iodine content of 15.4%, corresponding to 61% ICoSalphen and 39% CoSalphen. The product accounted for ca. 95% of the original CoSalphen used in the reaction. C_3F_7CoSalphen·H_2O was recovered in 2% yield and C_3F_7CoSalphen$C_3F_7 \cdot H_2O$ in 0.2% yield.

If the reaction was carried out entirely at room temperature the yield of C_3F_7CoSalphen·H_2O increased to ca. 30% of the available CoSalphen while the amount of C_3F_7CoSalphen$C_3F_7 \cdot H_2O$ increased to 3%. The remaining C_3F_7 substituted products were still only present at chromatographically detectable levels. ICoSalphen and Co^{II}Salphen were still present in largest amounts in the overall reaction.

Reactions were carried out with C_2F_5I and CF_3I at −78°C and analogous behaviour to that with C_3F_7I was found. The C_2F_5 and CF_3 ring substituted compounds however were not obtained in yields large enough to permit adequate purification and the analytical data were poor; however, mass spectral examination of the fractions showed the presence of such molecules.

Reaction of C_3F_7I with reduced Ni^{II}Salphen

Ni^{II}Salphen was reduced with 1% Na/Hg in tetrahydrofuran by an analogous procedure to that used for Co^{II}Salphen, and the deep green solution treated with C_3F_7I. The mixture was then warmed to room temperature. Evaporation of the solvent and extraction of the residue of reformed Ni^{II}Salphen with benzene removed a red-orange material. Thin layer chromatography of the material using ether development indicated the presence of two compounds. The analysis of the mixture gave an empirical formula equivalent to NiSalphenC_3F_7. (Found: C, 51.2; H, 2.9; F, 25.3; N, 5.5. $C_{23}H_{14}F_7N_2NiO_2$ calcd.: C, 51.0; H, 2.6; F, 24.5; N, 5.2%.)

References

1 A. van den Bergen, K.S. Murray and B.O. West, J. Organometal. Chem., 33 (1971) 89
2 P. Day, H.A.O. Hill and M G. Price, J. Chem. Soc., (1968) 90.
3 G.C. Levy and G.L. Nelson, Carbon-13 nuclear magnetic resonance for organic chemists, Wiley—Interscience, New York, 1972, p. 131.
4 N. Rehak, K.S. Murray and B.O. West, unpublished work.
5 G.N. Schrauzer and E. Deutsch, J. Amer. Chem. Soc., 91 (1969) 3341.
6 L.G. Marzilli, P.A. Marzilli and J. Halpern, J. Amer. Chem. Soc., 92 (1970) 5752
7 L.G. Marzilli, P.A. Marzilli and J. Halpern, J. Amer. Chem. Soc., 93 (1971) 1374.
8 P.L. Coe and N.E. Milner, J. Fluorine Chem., 2 (1972/73) 167.