Journal of Organometallic Chemistry, 90 (1975) 299—307

THE SYNTHESIS AND THE MAGNETIC PROPERTIES OF PERFLUOROALKYL ORGANOMETALLIC CHROMIUM(III) COMPLEXES CONTAINING *N*-SUBSTITUTED SALICYLALDIMINES AND OTHER LIGANDS

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(Received December 5th, 1974)

Summary

Perfluoroalkyl derivatives of Cr^{III} containing tetradentate or bidentate ligands derived from *N*-substituted salicylaldimines have been prepared by the reaction between the ligands and dihaloperfluoroalkylchromium acetonitrile complexes. The compounds show considerable solid-state and solution stability. Their magnetic moments are all greater than the spin-only value for a d^3 system, and a molecular orbital bonding scheme is suggested to explain this observation.

Introduction

A variety of alkyl and aryl σ-bonded organometallic compounds of Cr^{III} containing 'simple' coordinated ligands in addition to the organic group or groups have been reported, e.g. $[Cr(H_2O)_5R]^{2+}$ where R = $CH_2C_6H_5$ [1-3], CH_3 [4], 2-, 3- or 4-$C_5H_5NCH_2$ [5], CF_3 [6]; $RCrCl_2L_3$ where L = tetrahydrofuran or pyridine, R = CH_3 [7,8], $CH_2C_6H_5$ [3], *p*-tolyl [9], C_6H_5 [10].

Such compounds vary considerably in stability to thermal decomposition and this property appears to be influenced both by the nature of the organic group bonded to Cr as well as by the other ligands in the coordination sphere of the metal. Thus $[Cr(H_2O)_5CH_3]^{2+}$ has a half-life at 0° of several hours [4] while $[Cr(H_2O)_5CF_3]^{2+}$ has been reported to be stable for several weeks in aqueous solution [6]; $CH_3CrCl_2 \cdot THF_3$ decomposes readily at room temperature while $CH_3CrCl_2py_3$ is stable at 160° [8].

In view of the stabilisation of Co^{III}—C σ-bonds by the presence of a variety of chelating ligands such as tetradentate Schiff bases or macrocyclic ligands [11] it was of interest to see whether similar types of derivatives of Cr^{III} could be prepared which could show improved stability in the Cr—C bond above that of the types of compounds previously reported.

A number of perfluoroalkyl chromium(III) derivatives of this type have been prepared by the reaction of an appropriate ligand with preformed organometallic derivatives of the type $R_FCrCl_2(CH_3CN)_3$. The ligands used involve *N,N'*-substituted bis(salicylaldimines) together with some related bidentate ligands as well as salicylaldehyde and acetylacetone. The compounds are very stable to decomposition at room temperature in the solid state or in solution.

Attempts to prepare the analogous $CH_2C_6H_5$ and *p*-tolyl organometallic derivatives by related routes have so far been unsuccessful.

Results and discussion

Cr^{II} compounds are known to react with a number of organic halides to yield a mixture of a chromium(III) organometallic compound and a chromium(III) halide [1,2,5,12]. The majority of such reactions have involved an $H_2O—Cr^{II}$ species as the main reagent although Kochi and Powers [12] have shown that other coordinating groups attached to Cr^{II} can allow a wider range of organic halides to react. The mechanism for such reactions is considered to involve an initial halogen abstraction and formation of a free radical, followed by reaction of the free radical with a further Cr^{II} species [2].

$$Cr^{II} + RX \rightarrow Cr^{III}X + R^{\cdot}$$

$$Cr^{II} + R^{\cdot} \rightarrow Cr^{III}R$$

$H_2O—Cr^{III}$ species such as $[Cr(H_2O)_5R]^{2+}$ would be expected to be resistant to substitution by other ligands such as the tetradentate Schiff-base compounds which were of interest in this study and attention was directed to the formation of Cr^{III} compounds of the form $RCrCl_2L_3$ (L = pyridine or some suitable ligand) anticipating that Tl^I salts of appropriate ligands might then be usefully employed in subsequent reaction steps [13] or that free ligands indeed may react directly in the presence of a Lewis base such as triethylamine.

Sneeden and Throndsen [3] have reported the preparation of $C_6H_5CH_2CrCl_2py_3$ by reaction of $C_6H_5CH_2Cl$ and $CrCl_2py_2$ in pyridine, but while this compound reacted readily with Tl_2Salen, in pyridine the major product recovered was ClCrSalen·py and no evidence for the desired organometallic compound $C_6H_5CH_2$CrSalen · py was found. GLC examination of the volatile components of the reaction mixture showed that toluene had been formed.

The analogous fluoroalkyl chromium derivatives $R_FCrCl_2py_3$ could not be formed since reaction did not occur between perfluoroalkyl iodides and $CrCl_2py_2$. The corresponding CH_3CN derivatives however were readily synthesised by the addition of R_FI ($R_F = C_3F_7, C_2F_5, CF_3$) to a suspension of $CrCl_2(CH_3CN)_2$ in CH_3CN.

The light blue solid rapidly dissolved to give dark green-brown solutions. Thin layer chromatographic examination of the solution showed that two species were present. One, deep orange in colour, was a perfluoroalkyl derivative, most probably $R_FCrCl_2(CH_3CN)_3$, while the other green material contained a halide complex or a mixture of complexes $CrCl_{3-x}I_x(CH_3CN)_n$.

Addition of water to such a solution results in a deep red-orange solution being formed, the colour remaining for many days even when the solution contains 1 *M* HCl. The ions $[Cr(H_2O)_5R_F]^{2+}$ are believed to be present in such solutions by analogy with the reaction [3] of $C_6H_5CH_2CrCl_2py_3$ with water which yields $[Cr(H_2O)_5C_6H_5CH_2]^{2+}$.

No attempt was made to isolate the $R_FCrCl_2(CH_3CN)_3$ complexes but they were allowed to react further by subsequent addition of an appropriate amount of ligand to the acetonitrile solution together with the base triethylamine. The perfluoroalkyl derivatives R_FCrL were formed together with either the corresponding halide complexes ClCrL when tetradentate ligands were employed or CrL_3 compounds were detected when bidentate ligands were used. Recrystallization of the organometallic compounds from solvents containing pyridines gave the pyridinates $R_FCrL \cdot py$ as red crystalline products. The compounds are listed in Table 1.

A feature of this method of synthesis has been the facile preparation of complexes containing bidentate ligands such as salicylaldehyde, acetylacetone and *N*-substituted salicylaldimines. The analogous types of Co^{III} compounds have not so far been prepared.

Other alkyl halides such as MeI, n-PrI, n-BuBr and benzyl chloride did not react with $CrCl_2(CH_3CN)_2$.

TABLE 1

CHROMIUM(III) PERFLUOROALKYL DERIVATIVES[a]

	Found (Calcd.) (%)			
	C	H	N	F
$CF_3CrSalen \cdot py$	56.8	4.33	9.04	12.3
	(56.7)	(4.11)	(9.01)	(12.2)
$C_2F_5CrSalen \cdot py$	54.1	3.79	8.49	18.2
	(53.5)	(3.71)	(8.14)	(18.4)
$C_3F_7CrSalen \cdot py$	50.8	3.41	7.52	23.4
	(50.9)	(3.38)	(7.42)	(23.5)
$C_2F_5CrSalphen \cdot py$	57.3	3.53	7.21	16.7
	(57.5)	(3.39)	(7.44)	(16.8)
$C_3F_7CrSalphen \cdot py$	55.0	3.48	6.68	21.4
	(54.7)	(3.12)	(6.84)	(21.6)
$C_2F_5CrAcen \cdot py$	47.1	4.91	8.50	19.8
	(48.3)	(4.91)	(8.89)	(20.1)
$C_3F_7CrAcen \cdot py$	46.1	4.32	7.92	25.3
	(46.0)	(4.44)	(8.04)	(25.5)
$C_2F_5Cr(Sal\text{-}N\text{-}p\text{-}tol)_2 \cdot py$	62.6	4.35	5.97	14.5
	(62.7)	(4.36)	(6.27)	(14.2)
$C_3F_7Cr(Sal\text{-}N\text{-}p\ tol)_2 \cdot py$	59.8	3.95	5.68	18.7
	(60.0)	(4.06)	(5.83)	(18.5)
$C_3F_7Cr(Sal\text{-}N\text{-}n\text{-}C_4H_9)_2 \cdot py$	55.2	4.88	6.45	19.9
	(54.9)	(5.09)	(6.40)	(20.3)
$C_3F_7Cr(Sal)_2 \cdot py$	48.4	2.92	2.55	23.9
	(48.7)	(2.79)	(2.58)	(24.5)
$C_3F_7Cr(Acac)_2 \cdot py$	43.4	3.75	2.79	27.2
	(43.4)	(3.84)	(2.81)	(26.7)
$C_3F_7Cr(Bzac)_2 \cdot py$	54.0	3.73	2.03	21.3
	(54.2)	(3.74)	(1.97)	(21.4)

[a] Salen = *N,N'*-ethylenebis(salicylaldiminato)(2−); Salphen = *N,N'*-*o*-phenylenebis(salicylaldiminato)(2−); Acen = *N,N'*-ethylenebis(acetylacetonato)(2−); Sal-N-*p*-tol = *N*-*p*-tolylsalicylaldiminato(1−); Sal-N-n-C_4H_9 = *N*-n-butylsalicylaldiminato (1−); Sal = Salicylaldehydato (1−); Acac = Acetylacetonato (1−); Bzac = Benzoylacetonato (1−); $SalenH_2$, etc. represent the neutral ligands.

TABLE 2

ELECTRONIC SPECTRA (cm^{-1}) AND MAGNETIC MOMENTS (B.M.)

Compound	Solvent	$^4A_2 \rightarrow {}^4T_2$					μ_{eff}(300 K)
$C_2F_5CrSalen \cdot py$	C_2H_5OH	18868		23697			3.90
$C_2F_5CrSalen \cdot py$	py	18520		22880	29240	32470	3.90
$C_2F_5CrSalphen \cdot py$	C_2H_5OH	19608 (sh)	21186				3.96
$C_2F_5CrAcen \cdot py$	CH_3OH	18350 (sh)	21780		26320		3.86
		20250 (sh)	22420				
$C_3F_7Cr(Sal\text{-}N\text{-}n\text{-}C_4H_9) \cdot py$	C_2H_5OH	18020		24570		30770 (sh)	4.02 (290 K)
$C_3F_7Cr(Acac)_2 \cdot py$ [15]	C_2H_5OH	19231		23529	25000 (sh)	32467 (sh)	3.86 (90 K)
					28571		
$[CrSalen(H_2O)_2]Cl$ [15]	H_2O	20620 (sh)	21740 (sh)		26250		3.86
$ClCrSalen \cdot py$							3.85
$C_6H_5CH_2CrCl_2 \cdot py_3$ [3]	py			23260 sh	26390		3.93
$CH_3CrCl_2 \cdot THF_3$ [17]	THF	14400		23000		35000	3.84
$SalenH_2$	CH_3OH			24000		31000	

A further reaction between the complex *p*-tolyl$CrCl_2(THF)_3$ [9] and Tl_2-Salen or SalenH_2 in tetrahydrofuran (THF)—pyridine mixture also yielded Cl-CrSalen · py as the only Cr compound to be identified, just as was found for reactions involving a preformed benzyl complex.

It has not yet been established unambiguously whether the failure to form benzylCrSalen or *p*-tolylCrSalen is due to some instability in the Cr—C bond or to a competing reaction accompanying the coordination of the ligand which preferentially removes the organic group rather than a halide ion.

Properties of perfluoroalkylchromium derivatives

The outstanding feature of the compounds is their general stability under normal laboratory conditions compared to most previously reported chromium(III) organometallic compounds. The compounds appear to be stable indefinitely in the presence of air or moisture and do not decompose readily in solution in organic solvents on exposure to light or on continued heating in pyridine or chlorobenzene. This parallels the photochemical and general stability found for the related perfluoroalkylcobalt(III) derivatives [14].

The complex C_2F_5CrSalen · py lost pyridine on heating in vacuo at 130° and the product did not reabsorb water from the atmosphere.

Studies on the chemical reactions of these molecules will be presented in a subsequent paper.

Electronic spectra

The R_FCrL · py complexes form beautiful orange-red crystals and retain this colour in pyridine or alcoholic solutions; the acetylacetonato derivative giving a slightly more pink colouration. The solution electronic spectral bands are given in Table 2; in one case a diffuse reflectance measurement gave identical band positions implying that the molecular structure remains unaltered in solution. Although there are differences in detail, the spectra essentially consist of a weak band at ca. 18000 cm^{-1} with $\epsilon \approx 20$, assigned to the first spin-allowed transition $^4A_2 \rightarrow {}^4T_2$ (using O_h symmetry labels, the true symmetry being much less than this), together with much more intense bands beginning at ca. 23000 cm^{-1} ($\epsilon \approx 2000$). The latter are assigned most likely to metal—ligand charge transfer and/or intraligand transitions, although Mabbs et al. [15] have considered a strong band at 26250 cm^{-1} in the related $CrSalen(H_2O)_2^+$ ion to possess a significant *d—d* component.

In the spectra of some of the present complexes the band (or shoulder) at ca. 21000 cm^{-1} is most likely due to the split component of the $^4T_2$ parent caused by the low symmetry ligand-field. Within the limited series C_2F_5CrL · py the chelate dependence of 10 *Dq* appears to be Salphen > Salen ≈ Acen; whilst for $C_3F_7CrL_2$ · py the order is Acac > Sal-*N*-n-C_4H_9. The average 10 *Dq* value for the R_FCrL · py species is about the same as that in the tris-chelate Cr(Sal—NR)$_3$ [16], slightly less than that in the non-carbon bonded system $[CrSalenL_2]^+$, and significantly higher than that [17] in the green non-chelate organo complex $CH_3CrCl_2(THF)_3$.

Magnetic properties

The magnetic moments are given in Table 2. In all cases the values are greater than or equal to the spin-only d^3 value of 3.87 B.M.; in one case being greater than 4.0 B.M. Moments of this magnitude have also been observed in $[\mathrm{CrSalenL_2}]^+$ derivatives (L = H_2O, py, etc.) [15] and in a number of organochromium(III) species [3,8]. Theory predicts that mononuclear pseudo-octahedral chromium(III) should possess moments slightly reduced from the spin-only value due to spin—orbit coupling with the higher ${}^4T_{2g}$ state, the quantitative expression for the ${}^4A_{2g}$ ground state being $\chi_{\mathrm{eff}} = 5N\beta^2/4kT\,(2-8\lambda/10Dq)^2$ where λ is positive; there is also a small T.I.P. contribution $\chi_{\mathrm{T.I.P.}} = 8N\beta^2/10Dq$. A Curie dependence with temperature is normally followed, i.e. μ_{eff} independent of temperature. The susceptibility for $C_3F_7Cr(\mathrm{Sal\text{-}N\text{-}n\text{-}C_4H_9})_2 \cdot \mathrm{py}$ was determined over the range 300-90 K and Curie behaviour was observed but with some curvature at high temperatures. Having established that the μ_{eff} values could be consistently reproduced and were not just within experimental error a number of calculations were made to try to explain their magnitude. A g value greater than 2 would be required to explain such values. The temperature dependence of μ_{eff} observed for $C_3F_7Cr(\mathrm{Sal\text{-}N\text{-}n\text{-}C_4H_9})_2 \cdot \mathrm{py}$ suggests that weak antiferromagnetic exchange interactions might be present, although chemical intuition would favour a monomeric structure. It is possible, nevertheless, to fit the data to a weakly-coupled linear chain model [18] with the parameter $g = 2.08$, $J = -1$ cm^{-1}, T.I.P. = 100×10^{-6} cm^3 mol^{-1}.

If a monomeric structure is assumed then, within a crystal-field model, it is not possible to sensibly reproduce the μ_{eff} values. Second-order spin-orbit coupling within octahedral symmetry would require that the ${}^4T_2$ component would have to lie at an unrealistically low position above the ground state. For less than octahedral symmetry it was found, contrary to previous proposals [15], that no suitable excited state could be mixed into the ground state. If a zero-field splitting of the ${}^4A_2$ ground state is assumed calculations show that μ_{eff} is lowered below $\mu_{\text{spin-only}}$ irrespective of which Kramers doublet ($\pm\frac{1}{2}$ or $\pm\frac{3}{2}$) lies lowest in energy.

Some success is achieved if a molecular-orbital approach, similar to that used previously to explain the g values in copper(II) complexes [17] is adopted. The e_g orbitals are σ-bonding in nature whilst the t_{2g} are π-bonding. The wave functions for the ground and excited states now consist of linear combinations of the appropriate metal d orbital and ligand orbitals [19]. It is possible to deduce g values of the form

$$g_{\parallel} = 2 - \frac{8\alpha^2\beta^2}{10Dq_{\parallel}}\left(\frac{1-2\alpha^1 S}{\alpha} - \frac{\alpha^1\beta^1 \mathrm{T}(n)}{2\alpha\beta}\right)$$

where α, α^1, β, β^1 are mixing coefficients (α would equal 1 for the crystal-field case or α^1 for equal sharing of an electron between metal and ligand orbitals), S is the overlap integral and T(n) is a constant depending on the ligand orbital hybridization. A similar expression pertains for $g_{\perp}$.

The g value can now approach 2 and become greater than 2 for α^1/α or β^1/β ratios > 1. Strong in-plane σ- and π-bonding and out-of-plane σ-bonding are required for this to be the case; out-of-plane π-bonding does not affect the g values. The present situation of a chelate ligand in-plane and strong Cr—R_F bond out-of-plane is qualitatively in agreement with such a prediction.

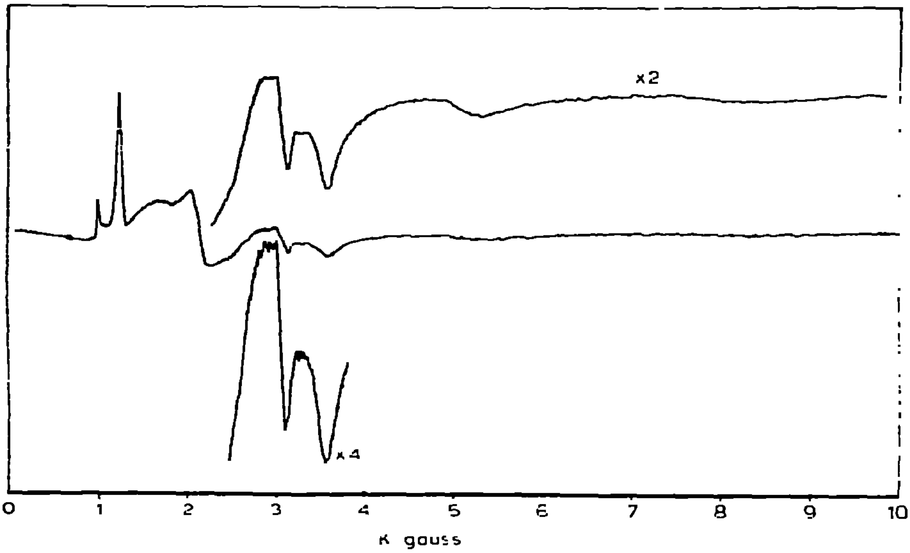

Fig. 1. X-band ESR spectrum of C_2F_5CrSalen · py in frozen pyridine/ethanol (100 K).

X-band ESR spectra of the perfluoroalkyl organochromium chelates have been recorded in frozen pyridine/ethanol solutions. The line shapes are quite complex and are generally similar in all cases; the spectrum of C_2F_5CrSalen · py being shown in Fig. 1. It is typical of a tetragonally distorted octahedral chromium(III) system [20,21], and has a very similar spectrum to that shown [20] by *trans*-$[\text{Cren}_2(\text{OH})_2]^+$.

Experimental

Preparation of R_FCrchel · py compounds

Chromium metal (1 g, 100 mesh) was treated under a nitrogen atmosphere with concentrated HCl (7 ml) until all the metal had dissolved. The solution was evaporated to dryness on a water bath and the residue stirred with successive volumes of deaerated acetone (50 ml) decanting the supernatant liquid between each addition. The procedure removed traces of Cr^{III} salts and the remaining $CrCl_2 \cdot 2H_2O$ was dried in a stream of nitrogen. The compound was redissolved in deaerated ethanol (15 ml) and hot acetonitrile added (150 ml). An immediate precipitate of $CrCl_2(CH_3CN)_2$ formed. The mixture was allowed to cool and excess fluoroalkyl iodide added. The suspended solid slowly dissolved over several hours to form a brown-green solution. Then was added a solution of an equivalent amount of the appropriate ligand dissolved in acetonitrile together with excess triethylamine. After stirring the mixture for 20 min the solvent was removed and the residue extracted with pyridine. Water was added to the filtered pyridine extract together with some additional ethanol and the solution set aside to crystallize. The product was recrystallized from the minimum amount of ethanol containing 10% pyridine to yield orange or red crystals of the appropriate complex as a pyridinate.

Preliminary detection of organometallic compounds

The technique of thin layer chromatography was used extensively to test for the formation of organometallic chromium compounds. A solution believed to contain such a compound together with chromium halide complexes was applied to a silica-coated plate and then the dried 'spot' eluted with ether. Microscope slides, coated with a 2 mm layer of silica (Merck HF_{254}), were used for this purpose. All the Cr^{III} organometallic compounds involved in this work, whether new compounds or previously known, were found to elute as orange to brown spots whereas other Cr^{III} complexes containing chromium—halide bonds were not eluted by ether. In the cases of the reactions involving the bidentate ligands *N-p*-tolylsalicylaldimine, *N*-n-butylsalicylaldimine, acetylacetone, benzoylacetone and salicylaldehyde where CrL_3 derivatives of these ligands were formed, these compounds were eluted by ether but were readily distinguished from the accompanying organometallic species by comparison of their chromatographic behaviour (R_F values) with authentic samples. In each case the CrL_3 compound was more readily eluted than the perfluoroalkyl organometallic compound accompanying it.

The reaction of dichlorotris(pyridine)benzylchromium(III) with Schiff-base ligands

$C_6H_5CH_2CrCl_2 \cdot py_3$ was prepared by the reaction of $CrCl_2 \cdot py_2$ with benzyl chloride and separated from accompanying $CrCl_3 \cdot py_3$ by the procedure of Sneeden and Throndsen [3].

The solid complex was dissolved in pyridine and stirred with an equivalent amount of Tl_2Salen for several hours. The relatively insoluble, yellow Tl_2Salen slowly reacted and white TlCl formed. The mixture was filtered and a portion submitted to TLC examination. No evidence for a readily eluted component which could indicate an organometallic derivative was found. Deaerated water was then added to the bulk of the solution and ClCrSalen · py was precipitated. The compound was identified by comparison of its infrared spectrum with that of an authentic sample (Found: C, 58.3; H, 4.43. $C_{21}H_{19}ClN_3O_2Cr$ calcd.: C, 58.2; H, 4.40%.)

The reaction of dichlorotris(tetrahydrofuran)p-tolylchromium(III)

$CH_3C_6H_4CrCl_2 \cdot THF_3$ was prepared as a solution in tetrahydrofuran by the reaction of $CH_3C_6H_4MgBr$ with $CrCl_3 \cdot THF_3$ [9]. Magnesium salts were eventually precipitated by the addition of dioxan, the solution filtered and $Tl_2SalenH_2$ and triethylamine added. The mixtures were stirred for several hours at room temperature during which TlCl (or some NEt_3HCl) precipitated. The solution was filtered and a portion examined by TLC. No evidence for a possible organometallic compound was found. The remaining solution was evaporated under vacuum and the residue extracted with pyridine to give pyCrSalenCl.

Instrumentation

Magnetic susceptibility measurements were made using the Gouy method. ESR measurements were kindly performed by Mr. D.J. Cookson and Dr. J. Boas (Department of Physics, Monash University) using a Varian E12. Electronic spectra were determined with a Unicam SP 800 instrument.

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