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Journal of Organometallic Chemistry 622 (2001) 172–179

Journal of Organometallic Chemistry

ω-Monofluoroalkylrhodoximes: synthesis and structures of $[Rh\{(CH_2)_nF\}(dmgH)_2(PPh_3)]$ ($n = 1, 3$) and C–F activation reactions

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Received 21 July 2000; received in revised form 5 October 2000; accepted 8 November 2000

Dedicated to Professor Brigitte Sarry on the occasion of her 80th birthday.

Abstract

$[Rh(dmgH)_2(PPh_3)]^-$ ($[Rh]^-$), synthesized by reduction of [Rh]–Cl with $NaBH_4$ in methanolic KOH, reacts with 1,ω-dihaloalkanes $X(CH_2)_nF$ (X = Cl, $n = 1$; X = Br, $n = 3$) forming [Rh]–CH_2F (**2a**) and [Rh]–$(CH_2)_3F$ (**2b**). Reaction of $[Rh]^-$ with $BrCH_2CH_2F$ affords instead of the expected 2-fluoroethyl complex the dinuclear complex [Rh]–CH_2CH_2–[Rh] (**4**) exhibiting an unexpected C–F bond activation. Complexes **2a** and **2b** were fully characterized by NMR spectroscopy (^1H, ^{13}C, ^{31}P, ^{19}F) and by X-ray diffraction. Complex **2a** crystallizes as a dimer with crystallographically imposed C_i symmetry. The monomeric entities are linked via two O–H···O hydrogen bridges. Complex **2b** is monomeric in solid state. In both complexes there is a nearly linear P–Rh–C moiety. Structural and NMR *trans* influence of fluoromethyl and 3-fluoropropyl ligand is discussed.

Keywords: Organorhodoximes; Fluoroalkyl complexes; Dinuclear complexes; C–F Activation; Crystal structures

1. Introduction

Transition metal complexes with fluoroalkyl ligands — except for perfluoroalkyl ligands [1] — belong to a less thoroughly investigated class of organometallic compounds. In general, carbon–fluorine bonds in saturated hydrocarbons are inert and their activation is a topic of considerable recent interest [2].

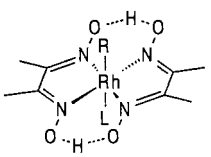

Fig. 1. Organorhodoximes (general formula).

These two aspects led us to investigate the synthesis and characterization of bis(dimethylglyoximato) complexes of rhodium (rhodoximes) with ω-fluoroalkyl ligands of the type [Rh]–$(CH_2)_nF$ ($n = 1, 3$).

Organorhodoximes $[RhR(dmgH)_2(L)]$ (Fig. 1; R = hydrocarbyl, L = axial base: py, PPh_3, PMe_3, H_2O...), first prepared by Weber and Schrauzer [3], have been extensively investigated. They are readily accessible and normally quite stable compounds. When a *P*-donor is used as axial base [4] the electronic structure in the linear complex fragment P–Rh–C can be thoroughly studied by NMR spectroscopy ($I = 1/2$; ^{103}Rh, ^{31}P, ^{13}C) [5]. For $L = PPh_3$ organorhodoximes with all basic types of hydrocarbyl ligands R (sp^3: alkyl; sp^2: vinyl, aryl, allenyl; sp: alkinyl), with functionalized organo ligands such as $-(CH_2)_nYR_x$ and $-CH{=}CHYR_x$ (Y = element of group 15–17) [4] and dinuclear complexes [Rh]–$(CH_2)_n$–[Rh] ($n = 2$–5) [6] were synthesized.

Organocobaloximes $[CoR(dmgH)_2(L)]$ (L = py, PPh_3, $P(OMe)_3$...) with fluoroalkyl ligands have been described [7], especially those with perfluorinated carbon

Abbreviations: [Rh], $[Rh(dmgH)_2(PPh_3)]$; $dmgH_2$, dimethylglyoxime.

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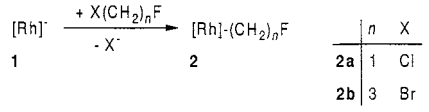
PII: S0022-328X(00)00886-X



Scheme 1.

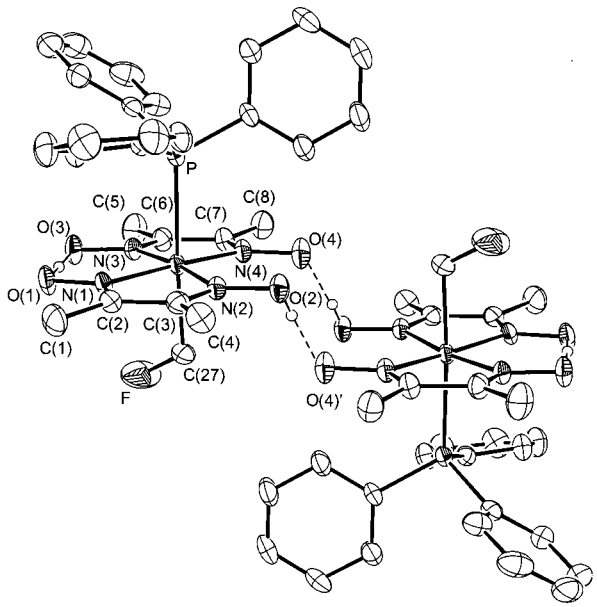


Fig. 2. Structure of [Rh]–CH_2F (**2a**) in the crystal (only major occupied position of F atom is shown). Ellipsoids are drawn at 30% probability level. Apart from the O–H···O bridges, hydrogen atoms have been omitted for clarity. The mononuclear entities are related by an inversion center.

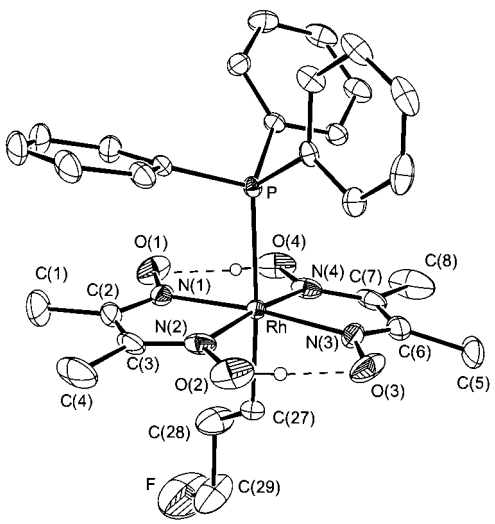


Fig. 3. Structure of [Rh]–$(CH_2)_3F$ (**2b**) in the crystal. Ellipsoids are drawn at 30% probability level. Apart from the O–H···O bridges, hydrogen atoms have been omitted for clarity.

atoms ($R = CF_3$, CF_2CF_3, $CF(CF_3)_2$, CH_2CF_3) [8]. Complexes in which the alkyl ligand carries hydrogen and fluorine at the same carbon atom are rare. Complexes with $R = CF_2CHF_2$, CF_2CHFCl were obtained in reactions of the cobalt(I) precursor with fluorinated olefins [9]. The difluoromethyl complex ($R = CHF_2$) was obtained as side product in the preparation of the trifluoromethyl complex and directly in the reaction of $[Co(dmgH)_2(L)]^-$ with $ClCHF_2$. In the latter case, partial replacement of F by H occurred, yielding the CH_2F complex as side product [10]. Fluoromethyl- and difluoromethylcobalamins, vitamin B_{12} analogues with CH_2F and CHF_2, respectively, replacing CN, were synthesized [11]. The latter one was also structurally characterized [12].

Except for $[Rh(CH_2CF_3)(dmgH)_2(py)]$ [4b,13], oganorhodoximes with fluoroalkyl ligands have not yet been described. Structures of transition metal complexes with monofluoromethyl ligands $L_xM–CH_2F$ or those with terminal CH_2F groups $L_xM–(CH_2)_n–CH_2F$ ($n = 1–6$) are not known at all. We report here syntheses, characterization and structures of fluoromethyl and 3-fluoropropyl rhodoximes [Rh]–CH_2F and [Rh]–$(CH_2)_3F$. Furthermore, we report unprecedented C–F bond activation in the reaction with corresponding 2-fluoroethyl moiety.

2. Results and discussion

2.1. Monofluoroalkyl complexes

2.1.1. Synthesis

$[Rh]^-$ (**1**), prepared by reduction of [Rh]–Cl with $NaBH_4$ in methanolic KOH [14], reacts with $ClCH_2F$ at room temperature within 4 h to give the fluoromethyl complex [Rh]–CH_2F (**2a**, yield: 37%), cf. Scheme 1. $Br(CH_2)_3F$ reacts with $[Rh]^-$ in ratio 1.3:1 within five min to give the 3-fluoropropyl complex [Rh]–$(CH_2)_3F$ (**2b**, yield: 84%). Complex **2b** could also be prepared in the same yield (82%) from the reaction of $Br(CH_2)_3F$ with two equivalents $[Rh]^-$ showing high stability of the C–F bond against nucleophilic substitution (oxidative addition). Under these conditions $Br(CH_2)_3Br$ was found to react with $[Rh]^-$ yielding the trimethylene-bridged dinuclear complex [Rh]–$(CH_2)_3$–[Rh] [6]. The fluoroalkyl complexes **2a** and **2b** form yellow air stable crystals. Their identities were confirmed by microanalysis, NMR spectroscopy (^1H, ^{13}C, ^{31}P, ^{19}F) and X-ray structure analyses. Complex **2a** is monomeric in $CHCl_3$ as was shown by osmometric molecular weight determination (found 615.3 g mol^{-1}, calc. for [Rh]–CH_2F 628.4 g mol^{-1}).

2.1.2. Structures

Molecular structures of **2a** and **2b** are shown in Figs. 2 and 3. Selected bond lengths and angles are listed in Table 1. Complex **2a** crystallizes as a dimer that exhibits crystallographically imposed C_i symmetry. The

monomeric entities are linked via two O–H···O hydrogen bridges. Crystals of complex **2b** contain discrete monomeric molecules. In both complexes the rhodium atoms display a distorted octahedral coordination with the dimethylglyoximato ligands in the equatorial plane and triphenylphosphine and the fluoroalkyl ligand in the axial positions. In complex **2a** the fluoromethyl ligand is disordered due to a location of fluorine and two hydrogens in two positions with an occupancy of 64.2 and 35.8%. This corresponds to a 'rotation' of CH_2F ligand around the Rh–C(27) axis by about 79°.

Whereas in other rhodoximes [4] the two dimethylglyoximato ligands are stabilized by two strong intramolecular hydrogen bonds, complex **2a** exhibits only one and the two intermolecular O–H···O bridges described above. The O···O distances [O(1)···O(3) 2.484(5) Å, O(2)···O(4)′ 2.459(5) Å] show that these are strong hydrogen bonds [15]. As a consequence of the strong intramolecular O(1)–H(1)···O(3) hydrogen bridge the angle N(1)–Rh–N(3) is smaller than the opposite angle N(2)–Rh–N(4) [96.7(1) vs 108.7(1)°]. The P–Rh–C units are nearly linear [C(27)–Rh–P: **2a** 176.2(1)°; **2b** 176.3(1)°]. In organorhodoximes [Rh]–R the Rh–P bond lengths reflect the structural *trans* influence of organo ligand R. Comparison of the Rh–P distances in **2a** and **2b** with those in rhodoximes with simple organo ligands R indicate a relatively high *trans* influence of the fluoroalkyl ligand [16]: C≡CPh (2.409(1) Å) < $CH{=}CH_2$ (2.447(1) Å) < Me (2.454(1) Å) < Et (2.461(2) Å) ≈ $(CH_2)_3F$ **2b** (2.467(1) Å) ≈ CH_2F **2a** (2.471(1) Å) < *i*-Pr (2.489(2) Å) ≈ *t*-Bu (2.492(1) Å). The dmgH ligands are tilted away from the triphenylphosphine ligand. This distortion can be described by the angle α between the normal vectors of the dmgH planes and by the displacement *d* of the Rh atom out of the mean plane passing through the four *N*-donor atoms towards the P atom [17]. There are no remarkable differences between angles α and displacements *d* in **2a** (3.0(2)°, 0.073(1) Å) and **2b** (11.6(2)°, 0.115(1) Å) and those in other alkylrhodoximes [Rh]–R (9.5–13.5°, 0.048–0.130 Å [16]).

Table 1
Selected bond lengths (Å) and bond angles (°) for **2a** and **2b**

	[Rh]–CH_2F (**2a**)	[Rh]–$(CH_2)_3F$ (**2b**)
Bond lengths		
Rh–C(27)	2.059(4)	2.102(4)
C(27)–F	1.307(7)/1.25(1) [a]	
C(27)–C(28)		1.455(7)
C(28)–C(29)		1.532(8)
C(29)–F		1.361(8)
Rh–P	2.471(1)	2.467(1)
Rh–N(1)	1.991(3)	1.976(3)
Rh–N(2)	2.032(3)	1.973(3)
Rh–N(3)	1.997(3)	1.979(3)
Rh–N(4)	2.042(3)	1.965(3)
Bond angles		
C(27)–Rh–P	176.2(1)	176.3(1)
F–C(27)–Rh	118.1(4)/118.7(6) [a]	
F–C(29)–C(28)		107.1(6)
N(1)–Rh–N(2)	77.3(1)	78.6(2)
N(1)–Rh–N(3)	96.7(1)	173.3(1)
N(1)–Rh–N(4)	172.2(1)	100.9(2)
N(2)–Rh–N(3)	173.1(1)	100.6(2)
N(2)–Rh–N(4)	108.7(1)	173.3(1)
N(3)–Rh–N(4)	77.0(1)	79.1(2)

[a] First value refers to F(1) (occupancy 64.2%) and the second one to F(2) (occupancy 35.8%).

Table 2
Selected NMR data (chemical shifts in ppm, coupling constants in Hz) of complexes [Rh]–$(CH_2)_nF$ **2a** ($n = 1$) and **2b** ($n = 3$)

	2a	**2b**
δ(^{13}C): α-/β-/γ-CH_2	93.3	27.4/29.9/85.9
δ(^{19}F)	−226.9	−215.9
^1J(Rh,C)/^1J(Rh,P)	24.7/61.0	20.6/63.5
^nJ(Rh,F)	16.0 ($n = 2$)	
^nJ(P,F)	31.7 ($n = 3$)	4.9 ($n = 5$)
$^1J/^2J/^3J$(F,C)	225.0	167.0/18.6/4.5

Median of C–F bonds in organic –CH_2F compounds (omitting 1,2-difluorides) is 1.399 Å (lower/upper quartile 1.389/1.408 Å) [18]. Compared with that, the C–F bond length in **2b** is decreased by 0.04 Å and that in **2a** by 0.09 Å[1]. Rh–C bond in **2a** is shorter than that in the corresponding methyl complex (2.059(4) vs 2.119(4) Å [16d]. Fluorine substitution may strengthen the rhodium–carbon bond by ionic-covalent resonance and/or by two-orbital–four-electron π-type interaction [19].

2.1.3. NMR spectroscopy

Both compounds **2a** and **2b** were fully characterized by NMR spectroscopy. Selected values are shown in Table 2. The assignment of the ^{13}C and ^{1}H signals was proved by HETCOR experiments and attached proton test (APT) spectra. Due to coupling with ^{19}F, ^{31}P, ^{103}Rh ($I = 1/2$, natural abundance 100%), ^{13}C resonances are first order multipletts, see Fig. 4 as example. Fluorine substitution gives rise to a strong down-field shift of the carbon atom which is F bonded as the comparison with other haloalkyl complexes [Rh]–$(CH_2)_nX$ and with the requisite alkyl complexes (X = H) shows [4e,6]: $\delta(^{13}C)$ ($n = 1$): X = F (**2a**) (93.3 ppm) < X = Cl (47.4 ppm) < X = Br (39.2 ppm) < X = H (15.1 ppm); $\delta(^{13}C)$ ($n = 3$): X = F (**2b**) (85.9 ppm) < X = Cl (45.5 ppm) < X = H (16.2 ppm).

Due to coupling with $I = 1/2$ nuclei (^{19}F, ^{31}P, ^{103}Rh), ^{19}F-NMR signals are complex first order multipletts, see Fig. 5 as example. The ^{19}F chemical shift in the

[1] Value refers to the major occupied position. Due to disorder of fluorine atom, discussion must not be exaggerated.

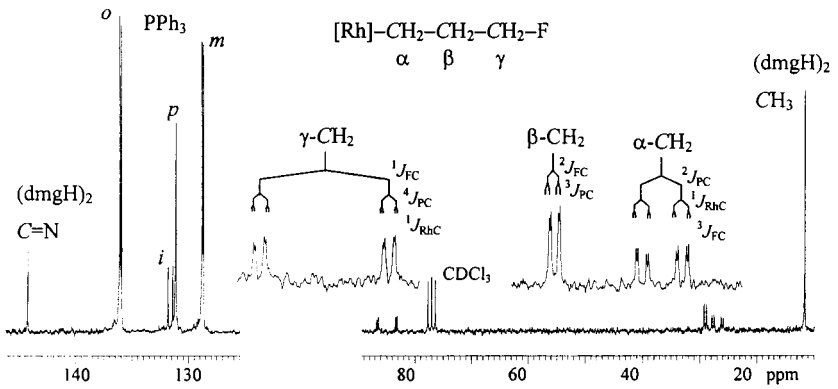


Fig. 4. 125 MHz ^{13}C-NMR spectrum of [Rh]–$(CH_2)_3F$ (**2b**) in $CDCl_3$.

fluoromethyl complex **2a** was found at -226.9 ppm. This corresponds to a down-field shift by 41 ppm in comparison with CH_3F ($\delta(^{19}F) = -267.9$ ppm [20]). On the other hand, in the fluoropropyl complex **2b** and in $MeCH_2CH_2F$ the ^{19}F chemical shifts are virtually the same (-215.9 vs -218.6 ppm [20]). The ^{31}P chemical shifts (**2a**: 9.1 ppm; **2b**: 9.4 ppm) are in the range expected for organorhodoximes with triphenylphosphine as axial base [4]. In complexes [Rh]–R magnitudes of the coupling constants $^1J(^{103}Rh,^{31}P)$ can be regarded as a measure for (NMR) *trans* influence of organo ligands R such that higher values reflect lower *trans* influence [4e,5]. For haloalkyl complexes [Rh]–$(CH_2)_nX$ [4e,6] the order ($n = 1$) X = Br (70.8 Hz) > X = Cl (68.4 Hz) > X = F (**2a**) (61.0 Hz) and ($n = 3$) X = Cl (64.8 Hz) > X = F (**2b**) (63.5 ppm) points to an increasing *trans* influence with increasing electronegativity of the halo substituent. Fig. 6 shows shows for organorhodoximes [Rh]–R the correlation ($r^2 = 0.91$) between *trans* influence parameters ^1J(Rh,P) and d(Rh–P). Complexes **2a** and **2b** with their fluorinated alkyl ligands fit this correlation quite well.

2.2. Reaction of [Rh]$^-$ with 1-bromo-2-fluoroethane

In contrast to the reactions with $ClCH_2F$ and $BrCH_2CH_2CH_2F$ yielding the fluoroalkyl complexes **2a** and **2b**, the reaction of [Rh]$^-$ with $BrCH_2CH_2F$ readily proceeded at room temperature within five min to give the dinuclear dimethylene-bridged complex [Rh]–CH_2CH_2–[Rh] (**4**) in 46% yield (Scheme 2). The identity of complex **4** was confirmed by NMR spectroscopy (^{1}H, ^{13}C, ^{31}P) and comparison with an authentical sample [6]. Two facts are worth mentioning in this context: (i) The reaction of [Rh]$^-$ with XCH_2CH_2X' yielding complex **4** is faster when X/X′ = Br/F (room temperature, 5 min, yield 46%) than when X/X′ = Br/Cl (room temperature, 60 min, yield 44%) or X/X′ = Cl/Cl (room temperature, 120 min, yield 24%) [6]. (ii) The yield of complex **4** (values given in parantheses) is quite high when $BrCH_2CH_2F$ is used. Moreover, the yield increased up to 80%, when the reaction of [Rh]$^-$ with $BrCH_2CH_2F$ was performed at -78°C and when the reaction mixture was allowed to warm up at room temperature within 12 h.

Most likely the reaction proceeds via the 2-fluoroethyl complex **3** as an intermediate (Scheme 2). But until now, attempts failed to detect **3** by NMR spectroscopy also when [Rh]$^-$ was added to an excess (1:5) of $BrCH_2CH_2F$ or when the reaction was performed in *n*-butanol. In the absence of KOH, [Rh]$^-$ (prepared by reduction of [Rh]–Cl with $NaBH_4$ in dimethylformamide) reacts slowly (15 h) with $BrCH_2CH_2F$ forming the dinuclear complex **4** in traces only.

The reaction of $BrCH_2CH_2F$ with [Rh]$^-$ yielding the dinuclear complex **4** clearly shows an activation of the β-C–F bond. In the analogous reactions with

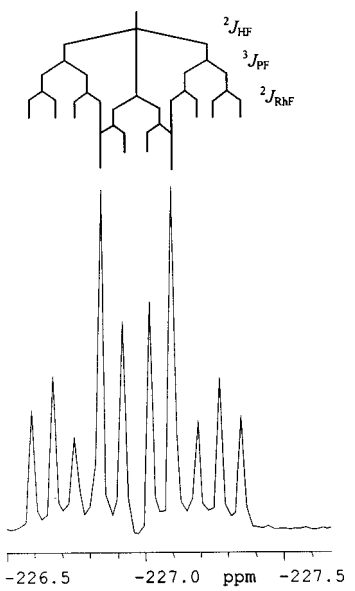


Fig. 5. 188 MHz ^{19}F-NMR spectrum of [Rh]–CH_2F (**2a**) in $CDCl_3$.

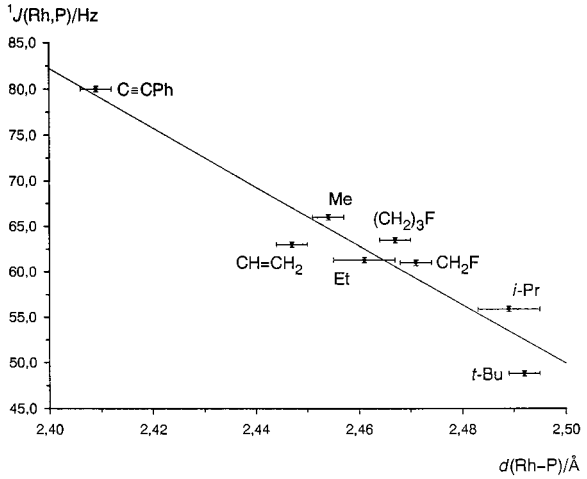
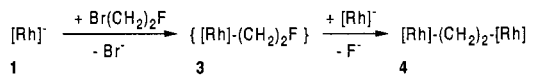
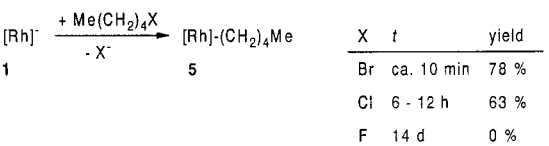


Fig. 6. Comparison between structural and NMR *trans* influence in organorhodoximes [Rh]–R. Error bars for bond lengths d(Rh–P) are $\pm 3\sigma$ and for coupling constants ^1J(Rh,P) ± 0.3 Hz.



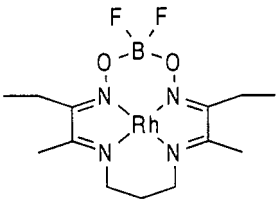
Scheme 2.



Scheme 3.

$X(CH_2)_nF$ (X = Cl, $n = 1$; X = Br, $n = 3$) (see above) an activation of the α-C–F and α-C–F bond, respectively, was not observed. Furthermore, it was shown that simple alkyl halides as $Me(CH_2)_4X$ (X = Br, Cl, F) exhibit in the reaction with $[Rh]^-$ the expected reactivity yielding *n*-pentylrhodoxime **5** (Scheme 3): In accordance with the increasing bond dissociation energies (ΔH_{C-X}: C–Br 285 kJ mol^{-1}, C–Cl 327 kJ mol^{-1}, C–F 485 kJ mol^{-1} [21]) *n*-pentyl bromide and chloride react within 10 min and 6–12 h, respectively, whereas *n*-pentyl fluoride does not react at all.

The formation of a M–C bond with cleavage of a C–F bond is rather unusual for a nucleophilic substitution reaction (that can be regarded in the wider sense as an oxidative addition) at an saturated sp^3-hybridized carbon atom. The reason for this unusual reactivity is not clear. A neighboring group activation of C–F bond by the bis(dimethylglyoximato)rhodium(III) entity in (non-seen) intermediate 2-fluoroethyl complex **3** may play a role. Collman and coworkers [22] reported such effects in several reactions of 1,ω-dihalogenalkanes $X(CH_2)_nX$ ($n = 2, 3$; X = Cl, Br, I) with neutral Rh^I-nucleophil [Rh(PPDOBF$_2$)] (**6**). But more exact kinetic measurements by the same authors could not establish this effect, except for reaction of **6** with 1,2-dibromoethane yielding the dimethylene-bridged complex [(PPDOBF$_2$)Rh–CH$_2$CH$_2$–Rh(PPDOBF$_2$)] that may involve neighboring group activation of bromine by Rh(III) macrocycle in (non-seen) intermediate 2-bromoethyl complex [Rh{(CH$_2$)$_2$Br}(PPDOBF$_2$)] [23].



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To summarize, reactions of $[Rh]^-$ with $X(CH_2)_nF$ ($n = 1–3$; X = Br, Cl) afford for $n = 1$ and $n = 3$ stable ω-fluoroalkyl rhodoximes [Rh]–CH_2F (**2a**) and [Rh]–$(CH_2)_3F$ (**2b**), respectively. In the case of the reaction with $BrCH_2CH_2F$ the probable intermediate 2-fluoroethyl complex **3** reacts further to give the dimethylene-bridged dinuclear complex [Rh]–$(CH_2)_2$–[Rh] (**4**) in an intermolecular substitution reaction. The investigations contribute to the understanding of stability and reactivity of fluoroalkyl metal complexes and of the electronic influence of fluorinated alkyl ligands.

3. Experimental

3.1. General

All reactions with Rh^I were carried out under argon using Schlenk techniques. [Rh]–Cl was prepared according to a published method [24]. The other chemicals were commercial materials used without further purification. Solvents were dried by standard methods and distilled prior use. Microanalyses (C, H, N) were performed by the University of Halle microanalytical laboratory using CHNS-932 (LECO) and vario EL (elementar Analysensysteme) elemental analyser, respectively. ^{1}H-, ^{13}C-, ^{19}F- and ^{31}P-NMR spectra were recorded on Varian Unity 500 and Gemini 200 spectrometers operating at 499.88 and 199.97 MHz for ^{1}H, respectively. Solvent signals (^{1}H, ^{13}C) were used as internal standards. $\delta(^{31}P)$ and $\delta(^{19}F)$ are referred to external H_3PO_4 (85%) and trifluoromethylbenzene (0.05% in C_6D_6), respectively. Two-dimensional heteronuclear correlation NMR spectra (HETCOR) were recorded on the UNITY 500 spectrometer. A CP9000 (Chrompack) was used for gaschromatographic analyses. For the osmometric molecular weight determination a Vapor Pressure Osmometer No. A0280 (Knaur) was used.

3.2. Synthesis of [Rh]–CH_2F (**2a**) and [Rh]–$(CH_2)_3F$ (**2b**)

To a solution of [Rh]–Cl (957 mg, 1.52 mmol) in methanolic KOH (75 ml, 0.15 M), a solution of $NaBH_4$ (76 mg, 2.01 mmol) in methanolic KOH (25 ml, 0.15 M) was added dropwise and stirred for 2 h at 20°C to give a deep violet solution of $[Rh]^-$. Compound **2a**: To this a solution of $ClCH_2F$ (ca. 18 mmol) in methanol (25 ml) was added within 2 min. After the color had turned yellow (4 h) water (100 ml) was added. The reaction mixture was neutralized (pH = 7–8) with solid CO_2 and extracted with CH_2Cl_2 (3 × 10 ml). The extract was dried (Na_2SO_4) and concentrated. The precipitate was dissolved in acetone and reprecipitated with heptane. Yield: 350 mg (37%). Compound **2b**: To the solution of $[Rh]^-$ a solution of $Br(CH_2)_3F$ (280 mg, 1.99 mmol) in methanol (20 ml) was added within 2 min. After the color had turned yellow (5 min) water (100 ml) was added. The reaction mixture was neutralized (pH = 7_8) with solid CO_2. After standing for 12–24 h the yellow precipitate of **2b** was filtered off, washed with diethyl ether and recrystallized from acetone. Yield: 840 mg (83%).

Compound **2a**: m.p. 175–185°C (dec.). Anal. Found: C, 50.2; H, 4.8; N, 8.5. Calc. for $C_{27}H_{31}FN_4O_4PRh$: C, 51.6; H, 5.0; N, 8.9%. ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.81 (2 H, d, $^5J_{P,H}$ 1.9 Hz, 4 CH_3), 4.90 (2 H, ddd, $^2J_{Rh,H}$ 1.1 Hz, $^3J_{P,H}$ 2.4 Hz, $^2J_{F,H}$ 47.5 Hz, α-CH_2), 7.3 (15 H, m, 3 C_6H_5). ^{13}C-NMR ($CDCl_3$, 125 MHz): 11.4 (s, 4 CH$_3$), 128.0 (d, $^3J_{P,C}$ 9.2 Hz, C_m), 129.7 (d, $^1J_{P,C}$ 30.8 Hz, C_i), 129.8 (d, $^4J_{P,C}$ 1.7 Hz, C_p), 133.2 (d, $^2J_{P,C}$ 10.8 Hz, C_o), 149.1 (s, 4 C=N). ^{19}F-NMR ($CDCl_3$, 188 MHz): −226.9 ($^2J_{Rh,F}$ 16.0 Hz; $^3J_{P,F}$ 31.7 Hz; $^2J_{F,H}$ 47.5 Hz). ^{31}P-NMR ($CDCl_3$, 80 MHz): 9.1 ($^1J_{Rh,P}$ 61.0 Hz, $^3J_{P,F}$ 31.7 Hz), further values see Table 2.

Compound **2b**: m.p. 170–180°C (dec.). Anal. Found: C, 52.8; H, 5.6; N, 8.1. Calc. for $C_{29}H_{35}FN_4O_4PRh$: C, 53.1; H, 5.4; N, 8.5%. ^{1}H-NMR ($CDCl_3$, 500 MHz): 1.10 (2 H, m, α-CH_2), 1.35 (2 H, m, β-CH_2), 1.82 (12 H, d, $^5J_{P,H}$ 2.1 Hz, 4 CH_3), 4.15 (2 H, dt, $^3J_{H,H}$ 6.3 Hz, $^2J_{F,H}$ 47.7 Hz, γ-CH_2), 7.2 (15 H, m, 3 C_6H_5). ^{13}C-NMR ($CDCl_3$, 125 MHz): 11.5 (s, 4 CH$_3$), 129.3 (d, $^3J_{P,C}$ 9.1 Hz, C_m), 131.0 (d, $^4J_{P,C}$ 2.0 Hz, C_p), 131.4 (d, $^1J_{P,C}$ 30.2 Hz, C_i), 134.5 (d, $^2J_{P,C}$ 11.1 Hz, C_o), 149.7 (s, 4 C=N). ^{19}F-NMR ($CDCl_3$, 188 MHz): −215.9 ($^5J_{P,F}$ 4.9 Hz; $^2J_{F,H}$ 47.7 Hz). ^{31}P-NMR ($CDCl_3$, 80 MHz): 9.4 ($^1J_{Rh,P}$ 63.5 Hz, $^5J_{P,F}$ 4.9 Hz), further values see Table 2.

3.3. Reactions of $[Rh]^-$ with $Me(CH_2)_4X$ (X = Br, Cl, F)

To a solution of $[Rh]^-$ in methanolic KOH, prepared as described above, a solution of $Me(CH_2)_4X$ (2.0 mmol) in methanol (20 ml) was added within 5 min. After the color had turned yellow (10 min, X = Br; 6–12 h, X = Cl) water (100 ml) was added. The reaction mixture was neutralized (pH = 7–8) with solid CO_2 and extracted with CH_2Cl_2 (3 × 10 ml). The extract was dried (Na_2SO_4) and concentrated. The precipitate of [Rh]–$(CH_2)_4$Me (**5**) was dissolved in acetone and reprecipitated with heptane. Yields: X = Br, 795 mg (78%); X = Cl, 640 mg (63%). In the case of X = F after two weeks no reaction product could be isolated.

Compound **5**: m.p. 160–170°C. Anal. Found: C, 56.1; H, 6.1; N, 8.1. Calc. for $C_{31}H_{40}N_4O_4PRh$ C, 55.9; H, 6.1; N, 8.4%. ^{1}H-NMR ($CDCl_3$, 500 MHz): 0.73 (3 H, t, ε-CH_3), 0.90–1.27 (8 H, m, α-δ-CH_2), 1.84 (12 H, d, $^5J_{P,H}$ 2.1 Hz, 4 CH_3), 7.4 (15 H, m, 3 C_6H_5). ^{13}C-NMR ($CDCl_3$, 125 MHz): 11.5 (s, 4 CH$_3$), 13.9 (s, ε-CH_3), 22.3 (d, $^5J_{P,C}$ 1.5 Hz, δ-CH$_2$), 23.9 (d, $^4J_{P,C}$ 10.8 Hz, γ-CH$_2$), 27.8 (d, $^3J_{P,C}$ 3.0 Hz, β-CH$_2$), 35.5 (d, $^2J_{P,C}$ 75.2 Hz, $^1J_{Rh,C}$ 19.8 Hz, α-CH$_2$), 128.0 (d, $^3J_{P,C}$ 9.2 Hz, C_m), 129.6 (s, C_p), 130.5 (d, $^1J_{P,C}$ 28.5 Hz, C_i), 133.4 (d, $^2J_{P,C}$ 10.8 Hz, C_o), 148.2 (s, 4 C=N). ^{31}P-NMR ($CDCl_3$, 80 MHz): 8.8 ($^2J_{Rh,P}$ 61.0 Hz).

3.4. Reactions of $[Rh]^-$ with $BrCH_2CH_2F$

A solution of $BrCH_2CH_2F$ (380 mg, 3.0 mmol) in methanol (20 ml) was added within 2 min at room temperature to a solution of $[Rh]^-$ in methanolic KOH (prepared from 1.52 mmol [Rh]–Cl as described above). After the color had turned yellow (5 min) and stirring for further 30 min, water (100 ml) was added. The precipitate of **4** is filtered off, washed with acetone (2 × 10 ml) and dried in vacuo. Yield: 425 mg (46%). The identity of **4** was confirmed by NMR spectroscopy (^{1}H, ^{13}C, ^{31}P) [6].

Variation of reaction conditions: When the reaction was performed at −78°C (2 h) and then reaction mixture was allowed to warm at room temperature within 12 h, **4** was obtained with a yield of 80% (740 mg). Using *n*-butanol instead of methanol the reaction takes 6 h and **4** was obtained with 21% yield (195 mg). Using dimethylformamide instead of methanol in the absence of KOH after 15 h **4** was obtained only in traces (ca. 3–4 mg).

3.5. Crystallographic studies

Suitable single crystals of **2a** and **2b** were obtained by recrystallization from acetone. The X-ray measurements were performed on a STOE-Stadi4 four circle diffractometer (**2a**) and on a STOE IPDS image plate system (**2b**), respectively. The F atom in **2a** is disordered over two positions with an occupancy of 64.2 and 35.8%, respectively. Crystal data collections and processing parameters are listed in Table 3. Compound **2b** is numerically corrected for absorption. The structures were solved with direct methods (SHELXS-86 [25]) and subsequent Fourier difference syntheses revealed the

positions of all non-hydrogen atoms which were refined with anisotropic displacement parameters by full-matrix least-squares routines against F^2 (SHELXL-93 [26]). Hydrogen atoms of **2a** were added to the model in their calculated positions, except for the oxygen bound H atoms, which were found in the difference Fourier map. In **2b** all H atoms were found in the difference Fourier map, except those on C28 and C29, which were placed in calculated positions. All H atoms were refined isotropically.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Center, CCDC Nos. 151804 (**2a**) and 151805 (**2b**), respectively. Copies of this data may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Table 3
Crystal data collection and processing parameters for complexes **2a** and **2b**

	2a	**2b**
Molecular formula	$C_{27}H_{31}FN_4O_4PRh$	$C_{29}H_{35}FN_4O_4PRh$
M_r	628.44	656.49
Color	Yellow	Yellow
Size (mm^3)	$0.3\times0.1\times0.1$	$0.30\times0.20\times0.08$
Temperature (K)	298(2)	220(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/a$
a (Å)	11.1228(12)	14.798(4)
b (Å)	10.9712(17)	13.308(5)
c (Å)	22.679(2)	15.056(6)
β (°)	100.129(11)	94.10(3)
V (Å^3)	2724.4(6)	2957.4(18)
Z	4	4
λ_0 (Å)[a]	0.71073	0.71073
D_{calc} (g cm^{-3})	1.532	1.474
μ (mm^{-1})	0.733	0.678
θ range (°)	1.82–24.96	2.04–25.00
Reflections collected	5056	24334
Independent reflections	4768	5192
Final R indices $[I>2\sigma(I)]$	$R_1=0.0366$, $wR_2=0.0860$	$R_1=0.0379$, $wR_2=0.1028$
R indices [all data]	$R_1=0.0544$, $wR_2=0.1039$	$R_1=0.0547$, $wR_2=0.1114$
Largest residual peaks (e Å^{-3})	0.612, −0.362	1.500, −0.813

[a] Mo–K_α radiation.

Acknowledgements

We gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie as well as the loan of chemicals from the companies Merck (Darmstadt) and Degussa (Hanau).

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