A facile synthesis of metalla-octafluorocyclopentane complexes of ruthenium and nickel

Waltraud Gasafi-Martin, Gabriele Oberendfellner, and Konrad von Werner

Abstract: Reduction of the dihalogeno complexes $RuCl_2(PPh_3)_4$ and $NiBr_2L_2$ (L = tertiary phosphine) with sodium hydride in MeCN in the presence of tetrafluoroethylene gives complexes containing five-membered MC_4F_8 rings. 1,2-Dihydrotetrafluoroethane is a by-product of these syntheses, especially when hydrogen is added. The M—C bonds of the metalla-perfluorocyclopentane complexes are remarkably stable against hydrogenolysis.

Key words: metalla-octafluorocyclopentanes of ruthenium(II) and nickel(II).

Résumé : La réduction des complexes dihalogénés $RuCl_2(PPh_3)_4$ et $NiBr_2L_2$ (L = phosphine tertiaire) avec de l'hydrure de sodium dans MeCN, en présence de tétrafluoroéthène, conduit à des complexes contenant des cycles MC_4F_8 à cinq chaînons. Le 1,1,2,2-tétrafluoroéthane est un sous-produit de ces synthèses, particulièrement lorsqu'on ajoute de l'hydrogène. Les liaisons M—C des complexes du métalla-perfluorocyclopentane sont particulièrement stables vis-à-vis de l'hydrogénolyse.

Mots clés : métalla-octafluorocyclopentanes du ruthénium(II) et du nickel(II).

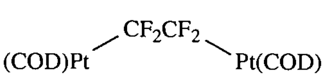
[Traduit par la rédaction]

Metal(O) complexes of group VIII metals are known to react with tetrafluoroethylene (TFE) to give a variety of different products by means of oxidative additions to the metal center. Typical reactions and products are listed below:

(*i*) Formation of a side-on bonded complex: $(Ph_3P)_2\,Pt(\eta_2\text{-}C_2F_4)$ (1).

(*ii*) Insertion of TFE into a metal-metal bond: $(OC)_4\,Co\text{-}CF_2CF_2\text{-}Co\,(CO)_4$ (2).

(*iii*) Bridging of two metal centers by two molecules of TFE:



(3).

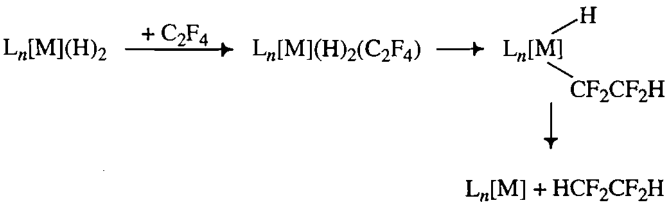
(*iv*) Coupling of two TFE units at the metal center, resulting in the formation of MC_4F_8 rings: $Fe(C_4F_8)(CO_4)$ (4), $Ru(C_4F_8)(CO)_2(PPh_3)_2$ (5), and $Ni(C_4F_8)(1.5\text{-}COD)$ (6).

We have shown that sodium hydride in acetonitrile is a very efficient reagent for the reduction of dihalide complexes of group VIII metals, affording metal(O)–carbonylphosphine complexes of nickel, palladium, and ruthenium in high yield when the reaction is performed under CO (7). We now have extended the reduction with NaH to the preparation of metallaoctafluorocyclopentane derivatives of nickel(II) and ruthenium(II) (see Table 1). Starting materials were $RuCl_2(PPh_3)_4$ and $NiBr_2L_2$ (L = tertiary phosphine or diphosphine) and tetrafluoroethylene. In contrast, similar reactions of $PdCl_2(PPh_3)_2$ or $FeBr_2(PPh_3)_2$, with two equivalents of PPh_3 added to the iron compound, did not result in the formation of MC_4F_8 complexes in the presence of TFE. The method also failed to work with the nickel complexes L_2NiBr_2 (L_2: N,N′-chelating ligand). However, NiC_4F_8 (bipy) could be obtained from $NiC_4F_8(PPh_3)_2$ by means of ligand exchange in MeCN in good yield.

We believe that the formation of the metallaoctafluorocyclopentane complexes occurs through the following reaction sequence: (*a*) displacement of halide ions by hydride to give dihydridocomplexes, (*b*) reductive elimination of hydrogen resulting in the formation of metal(O) complexes, (*c*) sequential coupling of two molecules of TFE at the metal(O)center.

It is interesting to note that all of the crude reaction mixtures obtained from the NaH reactions contained some 1,2-dihydrotetrafluoroethane, the hydrogenation product of TFE. A further point of interest concerns the fact that $(Ph_3P)_2NiC_4F_8$ is formed even in the presence of carbon dioxide, acetaldehyde, or hydrogen. When the reaction was run under simultaneous application of TFE and hydrogen (10 bar each; 1 bar = 100 kPa), the yield of the complex rose to 30%.

The observation that 1,2-dihydrotetrafluoroethane is always found can be explained by assuming the following reaction sequence:



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This paper is dedicated to Professor Howard C. Clark in recognition of his contributions to Canadian chemistry.

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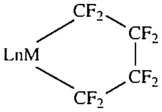
Table 1. Metalla-octafluorocyclopentane complexes of ruthenium(II) and nickel(II).

		Reaction conditions		Yield (%)	Colour	^{19}F NMR[a]		
		T(°C)	t(h)			α-CF_2	β-CF_2	Solvent
1	$Ru(C_4F_8)(PPh_3)_4$ $L_2Ni(C_4F_8)$	30	12	33	Pale yellow	−47.6 36.7 Hz, ^3J(PF)*trans* 17.2 Hz, ^3J(PF)*cis*	−60.5 (m)	CD_3CN
2	L = PPh_3	40	12	20	Pale yellow	−28.1 (broadened)[b]	−61.4	$CDCl_3$
3	$L_2 = Ph_2P(CH)_2)_2PPh_2$	50	10	30	Yellow	−26.1 t, 28.1 Hz, ^3J(PF)	−60.4	CD_3CN
4	$L_2 = Ph_2P(CH_2)_3PPh_2$	50	7	35	Yellow	−24.5 t, 29.5 Hz, ^3J(PF)	−60.4	$CDCl_3$
5	L_2 = 2.2′-Bipyridine	20	1	75	Yellow	−31.3	−61.6	Acetone-d_6

[a] At 282.4 MHz and 30°C, δ ^{19}F (ppm), upfield from CF_3CO_2H (external reference); δ CF_3CO_2H = −77.5 ppm vs. $CFCl_3$.

[b] Unresolved coupling, ^3J (PF).

Table 2. Elemental analyses.

		Calculated				Found			
Compound	Formula	C	H	F	M	C	H	F	M
1	$C_{76}H_{60}F_8P_4Ru$	67.60	4.48	11.36	7.49	67.4	4.4	11.3	7.6
2	$C_{40}H_{30}F_8P_2Ni$	61.33	3.86	19.40	7.49	61.2	3.8	19.5	7.5
3	$C_{30}H_{24}F_8P_2Ni$	54.83	3.68	23.13	8.93	55.0	3.7	23.2	8.9
4	$C_{14}H_8F_8N_2Ni$	40.53	1.94	36.63	14.15	40.7	1.9	36.5	14.0

The unsaturated species L_n[M] is required for metallacycle formation. A high excess of tetrafluoroethylene will favour the formation of the metallacycle, whereas an addition of hydrogen should be expected to favour the formation 1,2-dihydrotetrafluoroethane.

The metal–carbon bonds of the complexes **1–4** are very stable against hydrogenolysis. Complex **1** did not react with hydrogen (20 bar) in toluene solution even in the presence of a very active hydrogenation catalyst (2% palladium on Al_2O_3) up to 60°C. Hydrogenation of **2** with the same catalyst in MeCN gave a surprising result: hydrogenation of the triphenylphosphine ligands set in at ca. 100°C; however, the NiC_4F_8 group was still intact.

Experimental part

All reactions and work-up procedures were carried out under dry nitrogen or argon, using carefully dried solvents. MeCN was distilled from P_4O_{10} through a column, and the main run was stored over molecular sieve (3 Å).

Typical procedure for the synthesis of 1–4

A stainless steel autoclave (150 mL), equipped with manometer, gas inlet, a thermocouple for temperature control, and a PTFE-coated stirring bar, was charged with a solution of $(Ph_3P)_4RuCl_2$ (or of a nickel complex L_2NiBr_2) in anhydrous MeCN (3.0 mmol of the complex in 50 mL solvent). Sodium hydride (6.6 mmol), as a 20% suspension of NaH in DAB9 mineral oil (obtained from Merck), was added with a syringe. The autoclave was closed, cooled to 0°C, and pressurized with TFE (10 bar), and the reaction was carried out with stirring under the conditions given in Table 1. After cooling to room temperature and releasing the pressure, the contents of the autoclave were transferred to a flask and the solvent was removed in vacuo. The residue was stirred with toluene (50 mL) at 40°C and filtered through a frit that contained 2 g of Celite. In the case of **3** and **4**, a mixture of toluene (40 mL) and CH_2Cl_2 (10 mL) was used. The filtrate was concentrated under vacuum and crystallization was induced by adding ether and (or) *n*-hexane and cooling. The product was collected on a frit, washed with cold *n*-hexane, and dried in vacuo. Recrystallization from CH_2Cl_2 and *n*-hexane and drying at 50°C at 10^{-3} mbar finally gave the pure products.

We did not attempt to fully optimize the yields.

Synthesis of 2,2′-bipyridine-nickelaoctafluorocyclopentane, 5

2,2′-Bipyridine (85.9 mg, 0.55 mmol) was added to a stirred solution of complex **2** (392 mg, 0.5 mmol) in 5 mL of MeCN. The solution soon became cloudy. After 1 h, *n*-hexane (2 mL) was added and the crystalline product was filtered off, washed with 5 mL of cold *n*-hexane, and dried at 10^{-3} mbar (yield: 253 mg). The element analyses of the complexes **1–5** are shown in Table 2.

Spectra

The IR spectra of all products in Nujol were measured with a Perkin Elmer 882 spectrophotometer. The bands observed for the compounds **2**, **3**, and **5** in the region of 1300–750 cm^{-1} are in good agreement with the data reported in ref. 6 (maximum deviation: 15 cm^{-1}), although the methods of preparation were different. The spectra of **3** and **4** are very similar. The ruthenium complex **1** showed the following bands in the above region: 1306 w, 1261 m, 1210 w, 997 w, 916 w, 852 w, 799 s.

^{19}F NMR spectra were measured with a Bruker AC 300 instrument at 30°C. The couplings reported in Table 1 are based on the following assumptions:

1: $(AMX_2)_2$ spin system, where A is ^{31}P *cis* to α-CF_2, M is ^{31}P *trans* to α-CF_2 and X is ^{19}F of α-CF_2.

2, **3**, and **4**: $(AX_2)_2$ spin system, where A is ^{31}P and X is ^{19}F of α-CF_2.

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