Available online at www.sciencedirect.com
ScienceDirect
Journal of Fluorine Chemistry 128 (2007) 943–951
www.elsevier.com/locate/fluor

Pentamethylcyclopentadienyl rhodium(III) trifluorovinyl phosphine complexes and attempted intramolecular dehydrofluorinative coupling of pentamethylcyclopentadienyl and trifluorovinyl phosphine ligands

Nicholas A. Barnes [a], Alan K. Brisdon [a,*], Mark Nieuwenhuyzen [b], Robin G. Pritchard [a], Graham C. Saunders [b,*]

[a] School of Chemistry, University of Manchester, Manchester M13 9PL, United Kingdom
[b] School of Chemistry and Chemical Engineering, Queen's University Belfast, David Keir Building, Belfast BT9 5AG, United Kingdom

Received 30 January 2007; received in revised form 3 April 2007; accepted 3 April 2007
Available online 7 April 2007

Abstract

The trifluorovinyl phosphine complexes $[\mathrm{Cp^*RhCl_2\{PR_{3-x}(CF{=}CF_2)_x\}}]$ (**1** $x = 1$, **a** R = Ph, **b** Pr^i, **c** Et; **2** $x = 2$, R = Ph) have been prepared by treatment of $[\mathrm{Cp^*RhCl(\mu\text{-}Cl)}]_2$ with the relevant phosphine. The salt $[\mathrm{Cp^*RhCl(CNBu^t)\{PPh_2(CF{=}CF_2)\}}]\mathrm{BF_4}$, **3**, was prepared by addition of $\mathrm{Bu^tNC}$ to **1a** in the presence of $\mathrm{NaBF_4}$. The salt $[\mathrm{Cp^*RhCl\{\kappa P,\kappa S\text{-}(CF_2{=}CF)PPh(C_6H_4SMe\text{-}2)\}}]\mathrm{BF_4}$ was prepared as a mixture of *cis* (**5a**) and *trans* (**5b**) isomers by treatment of $[\mathrm{Cp^*RhCl(\mu\text{-}Cl)}]_2$ with the phosphine-thioether $\mathrm{(CF_2{=}CF)PPh(C_6H_4SMe\text{-}2)}$, **4**, in the presence of $\mathrm{NaBF_4}$. The structures of **1a–c** and **5a** have been determined by single-crystal X-ray diffraction. Intramolecular dehydrofluorinative carbon–carbon coupling between pentamethylcyclopentadienyl and trifluorovinylphosphine ligands of **1a**, **3** and **5** has been attempted. No reaction was observed on treatment of the neutral complex $[\mathrm{Cp^*RhCl_2\{PPh_2(CF{=}CF_2)\}}]$, **1a**, with proton sponge, however, **5a** underwent dehydrofluorinative coupling to yield $[\{\eta^5,\kappa P,\kappa S\text{-}\mathrm{(C_5Me_4CH_2CF{=}CF)PPh(C_6H_4SMe\text{-}2)\}RhCl}]\mathrm{BF_4}$, **6**. Other reactions, in particular addition of HF across the vinyl bonds of **5**, occurred leading to a mixture of products. The cation of **3** underwent similar reactions.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Trifluorovinylphosphines; Rhodium; Pentamethylcyclopentadienyl; C–F bond cleavage; Dehydrofluorinative carbon–carbon coupling

1. Introduction

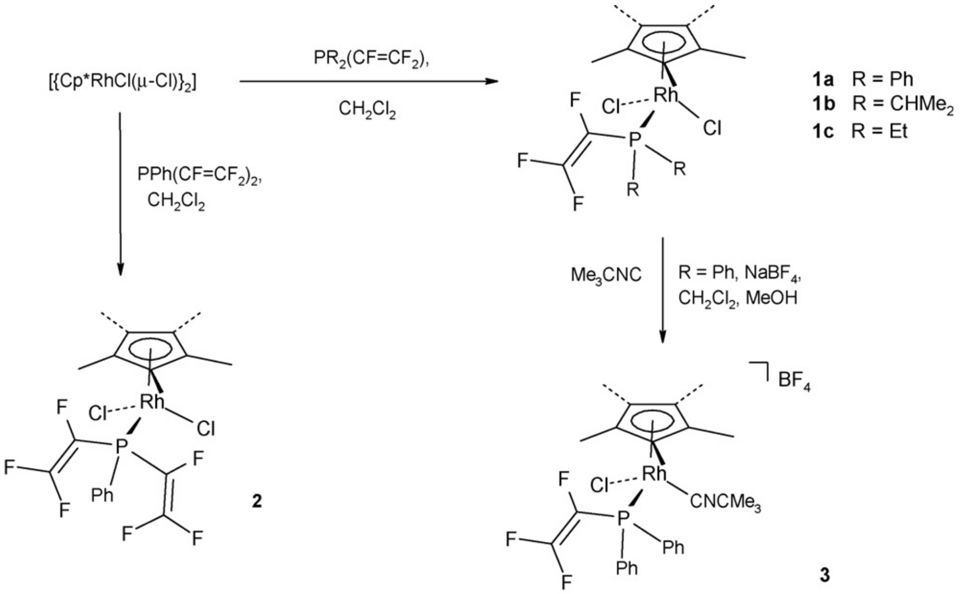
In contrast to fluorinated aryl and alkyl phosphines [1–10], fluoroalkenylphosphines have received relatively little attention [11–13]. Following the development of a convenient synthetic route to $[\mathrm{CF_2{=}CF}]^-\mathrm{Li}^+$ from the readily available HFC-134a ($\mathrm{CF_3CH_2F}$), and subsequent syntheses of trifluorovinylphosphines $\mathrm{R_{3-x}P(CF{=}CF_2)_x}$ [14–16], a number of complexes of trifluorovinylphosphines with molybdenum [15], platinum [15,17] and gold [15] have been reported over the past decade.

The trifluorovinyl substituent is known to be susceptible to nucleophilic attack [16,18], with substitution of the fluorine atom *trans* to the phosphorus atom, which allows the opportunity for functionalizing the phosphine. One attractive possibility is the intramolecular coupling of metal-bound cyclopentadienyl and trifluorovinylphosphine ligands. Rhodium complexes of chelating bi- and tri-functional cyclopentadienyl–phosphine ligands have been synthesized by intramolecular dehydrofluorinative carbon–carbon coupling [19–24]. These ligands contain a three-carbon atom linkage between the cyclopentadienyl ring and the phosphorus atom. To date the complexes synthesized by this method have been restricted to those in which two of the carbon atoms in the linkage are part of a fluoroaromatic group: tetrafluorophenyl [19–21,24], fluorophenyl [22] or trifluoropyridyl [23]. The coupling occurs on addition of proton sponge to the salts $[\mathrm{Cp^*RhCl(PL)}]^+$ (PL = chelating fluoroarylphosphine) or $[\mathrm{Cp^*RhCl_L(P)}]^+$, or by heating a benzene solution of $[\mathrm{Cp^*RhCl(\mu\text{-}Cl)}]_2$ and PL. The reaction is postulated to proceed

---

* Corresponding authors.
E-mail address: g.saunders@qub.ac.uk (G.C. Saunders).

0022-1139/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jfluchem.2007.04.003



Scheme 1.

by generation of a nucleophilic *exo* methylene carbon atom by loss of a proton from the pentamethylcyclopentadienyl ring of the cation and subsequent attack at the *ortho* position of a fluoroarene [19,25]. If this mechanism is correct then the trifluorovinyl group would be suitable as a substituent leading to a three-carbon atom linkage in which two of the carbon atoms are part of an alkene.

Here we report rhodium piano stool complexes comprising trifluorovinylphosphines and an investigation into the intramolecular coupling of η^5-pentamethylcyclopentadienyl to phosphine and phosphine–thioether ligands bearing trifluorovinyl substituents.

2. Results and discussion

2.1. Synthesis and characterization

Cleavage of the chloride bridges of the rhodium(III) dimer $[Cp^*RhCl(\mu\text{-}Cl)]_2$ with two equivalents of the trifluorovinyl phosphines $PR_2(CF{=}CF_2)$ (R = Ph [15], Pr^i [16], Et [16]), afforded deep orange to red complexes of formula $[Cp^*RhCl_2\{PR_2(CF{=}CF_2)\}]$ (R = Ph **1a**, Pr^i **1b**, Et **1c**) in *ca.* 50% yield (Scheme 1). Complexation of the phosphines is confirmed by the $^{31}P\{^1H\}$ NMR spectra (Table 1), which exhibit doublet resonances with coupling constants of *ca.*

Table 1
$^{31}P\{^1H\}$ and $^{19}F\{^1H\}$ NMR spectroscopic data for compounds **1–7**

	δ_P	$^1J_{RhP}$ (Hz)	$\Delta\delta_P$	$^2J_{PFg}$ (Hz)	$^3J_{PFt}$ (Hz)	$^3J_{PFc}$ (Hz)	δ_{Ft}	δ_{Fc}	δ_{Fg}	$^2J_{FtFc}$ (Hz)	$^3J_{FgFt}$ (Hz)	$^3J_{FgFc}$ (Hz)
1a	21.2	149	47.4	73	8	10	−82.1	−98.9	−174.2	39	29	116
1b	35.7	147	43.4	29	11	8	−87.7	−104.0	−176.8	56	32	113
1c	24.8	147	57.1	40	10	10	−85.4	−104.9	−182.0	54	31	114
2	13.7	152	65.5	75	–	–	−79.9	−97.3	−176.1	32	29	117
3[a]	27.8	142	54.0	84	0	8	−79.5	−98.1	−174.5	36	31	117
4	−34.2	–	–	19	9	58	−84.9	−106.8	−177.8	44	30	124
5a[b]	39.0	144	73.2	76	–	–	−79.3	−97.1	−174.8	40	31	119
5b[b]	44.3	141	78.5	107	–	–	−76.7	−94.0	−174.5	[c]	[c]	118
6[d]	44.0	132	–	<5	<5	–	−89.2	–	−154.7[e]	–	<5	–
7	56.1	125	–	38	0	–	−66.0[f,g]	–	−204.5[g,h]	–	14	–
	52.9	147	–	25	0	–	−69.2[f,g]	–	−204.1[g,h]	–	14	–

Recorded in $CDCl_3$. F*t*, F*c* and F*g* represent the fluorine atoms *trans*, *cis* and *geminal* to phosphorus, respectively.

[a] ^{19}F NMR (282.26 MHz, $CDCl_3$): $\delta_F(BF_4) = -153.07$ (0.8F, s, $^{10}BF_4^-$), -153.12 (3.2F, s, $^{11}BF_4^-$).

[b] ^{19}F NMR (282.26 MHz, $CDCl_3$): $\delta_F(BF_4) = -153.64$ (0.8F, s, $^{10}BF_4^-$), -153.70 (3.2F, s, $^{11}BF_4^-$).

[c] The coupling constants could not be obtained due to the low intensity of the resonances.

[d] ^{19}F NMR (282.26 MHz, $CDCl_3$): $\delta_F(BF_4) = -153.10$ (0.8F, s, $^{10}BF_4^-$), -153.20 (3.2F, s, $^{11}BF_4^-$).

[e] *cf.* *trans*-$Ph_2PCF{=}CFBu^n$ δ_F: −159.1 ($^2J_{PF} = 5$ Hz) [16].

[f] CF_3. *cf.* $[(PhCH_2)Ph_2P(CHFCF_3)]^+$: δ −68.8 ($^3J_{FF} = 16$ Hz, $^3J_{HF} = 6$ Hz, $^3J_{PF} = 4$ Hz) [27].

[g] Coupling to hydrogen evident in the ^{19}F NMR spectrum.

[h] CHF. The integration for each resonances is 1/3 of that for the respective CF_3 resonance. *cf.* $[(PhCH_2)Ph_2P(CHFCF_3)]^+$: δ −214.4 (CHF, $^2J_{HF} = 41$ Hz, $^2J_{PF} = 57$ Hz, $^3J_{FF} = 16$ Hz) [27].