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Synthesis, structure and reactivity of fluorovinyl nickel complexes: formation of a phosphonioethenyl complex †

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Treatment of [Ni(COD)$_2$] with trifluoroiodoethene or 1,1-dibromodifluoroethene in the presence of PEt$_3$ effects the formation of the complexes *trans*-[NiI(CF=CF$_2$)(PEt$_3$)$_2$] (**1**) and *trans*-[NiBr(CBr=CF$_2$)(PEt$_3$)$_2$] (**2**), respectively. Reaction of **1** with NaBAr′$_4$ and acetonitrile gives *trans*-[Ni(CF=CF$_2$)(NCMe)(PEt$_3$)$_2$]BAr′$_4$ (**4**) [Ar′ = 3,5-C$_6$H$_3$-(CF$_3$)$_2$]. Treatment of **1** with NaBAr′$_4$ in the presence of CO yields the cationic complex *trans*-[Ni(CF=CF$_2$)(CO)-(PEt$_3$)$_2$]BAr′$_4$ (**5**), which is only stable in a CH$_2$Cl$_2$ solution. The reaction of **1** with NaBAr′$_4$ and ^{t}BuNC affords the compound *trans*-[Ni(CF=CF$_2$)(CN^{t}Bu)(PEt$_3$)$_2$]BAr′$_4$ (**6**). On treatment with NaBAr′$_4$ and PEt$_3$ complex **6** can be converted into the dicationic phosphonioethenyl compound *trans*-[Ni{CF=CF(PEt$_3$)}(CN^{t}Bu)(PEt$_3$)$_2$][BAr′$_4$]$_2$ (**7**). The structures of complexes **2** and **7** have been determined by X-ray crystallography. The phosphonioethenyl ligand in **7** is bound at nickel with a Ni–C distance of 1.893(5) Å. The C=C and the CF–P bond lengths are 1.309(6) Å and 1.794(5) Å, respectively.

Introduction

Organofluorine compounds attract interest for their many technological applications and are increasingly used as building blocks in several areas of chemistry such as medical, organic and polymeric chemistry.[1,2] There is also a strong interest in phosphine ligands containing fluorinated organic fragments.[3] The introduction of polyfluorovinyl groups into organic compounds can be accomplished by metal reagents such as lithium, cadmium, copper or other metal derivatives.[2,4,5] Catalytic cross coupling reactions are also well established.[2,5,6] Besides, the use of fluorinated vinyl groups as building blocks in the coordination sphere of a *transition metal* in stoichiometric or catalytic coupling reactions is still limited.[2,6–8] This is generally due to the special properties of anionic carbofluorine ligands bound to a transition metal centre.[4,9–15] Complexes bearing these ligands exhibit a stronger metal carbon bond compared to the non-fluorinated counterparts and show a completely different reactivity.[9–13,15,16]

In this paper we present studies on the synthesis and reactivity of a variety of nickel compounds bearing of fluorinated vinyl ligand. We show that neutral and cationic complexes are accessible. The highly electrophilic properties of the vinyl ligand in the cationic derivatives leads to the formation of a dicationic complex bearing a phosphonioethenyl ligand.

Results

1 Formation of *trans*-[NiI(CF=CF$_2$)(PEt$_3$)$_2$] (1)

Reaction of [Ni(COD)$_2$] with PEt$_3$ in the presence of trifluoroiodoethene in hexane yields *trans*-[NiI(CF=CF$_2$)(PEt$_3$)$_2$] (**1**) (Scheme 1). The ^{31}P NMR spectra of **1** displays a virtual quartet at δ 16.8 for the two equivalent phosphorus nuclei coupled to fluorine atoms with an apparent coupling of J = 6.9 Hz (Table 1). The ^{19}F NMR spectrum shows three signals at at δ −156.12, −131.29, −89.06, which appear at almost the same chemical shift as those found for *trans*-[NiCl(CF=CF$_2$)L$_2$] (L = PEt$_3$, PPh$_3$).[17,18] The presence of the trifluorovinyl group at nickel is also revealed in the ^{13}C NMR spectrum, which shows two resonances at δ 131.1 and δ 155.9. The latter signal corresponds to the β-carbon and is split into a doublet of doublet of doublet of triplets due to three different couplings to fluorine atoms as well as the coupling to the two phosphorus nuclei (J_{CF} = 303.1, 252.4, 41.1, J_{PC} = 5.8 Hz).

2 Formation of *trans*-[NiBr(CBr=CF$_2$)(PEt$_3$)$_2$] (2)

In a reaction analogous to that with trifluoroiodoethene, treatment of [Ni(COD)$_2$] with 1,1-dibromodifluoroethene in the presence of PEt$_3$ in toluene instantly affords *trans*-[NiBr(CBr=CF$_2$)(PEt$_3$)$_2$] (**2**) (Scheme 1). If the reaction is carried out in hexane instead of toluene as a solvent no oxidative addition product is formed and the compound [NiBr$_2$(PEt$_3$)$_2$] (**3**) is isolated instead.[19] The presence of the difluorovinyl group in **2** is revealed by two doublet of triplets in the ^{19}F NMR spectrum at δ −91.63 (J_{FF} = 74.5, J_{PF} = 6.8 Hz) and δ −67.47 (J_{FF} = 75.7, J_{PF} = 6.9 Hz). An absorption band at 1692 cm^{-1} in the IR spectrum is characteristic for a fluorovinyl ligand at nickel.[17,18]

3 Crystal structure of *trans*-[NiBr(CBr=CF$_2$)(PEt$_3$)$_2$] (2)

The orange complex **2** was crystallised from toluene at −30 °C. Its structure was determined by X-ray diffraction at low temperature (Fig. 1). Selected bond lengths and angles are summarized in Table 2. The angles between the adjacent ligands at nickel vary from 90.90(5)° to 89.324(13)°. The dihedral angle between the nickel coordination plane and the plane of the vinyl group is 87.2° (89.1°). The nickel–carbon distance of 1.868(2) Å is shorter than in *trans*-[Ni(CCl=CCl$_2$)(C$_6$H$_2$Me$_3$)-(PMe$_2$Ph)$_2$] [1.933(3) Å],[20] but comparable to the nickel–carbon bond length obtained for *trans*-[NiCl{(CCl=CCl(C$_6$H$_2$Me$_3$)}-(PMe$_3$)$_2$] [1.855(6) Å] or *trans*-[NiF(C$_6$F$_5$)(PEt$_3$)$_2$] [1.878(7) Å].[21,22] Because of a disorder of the α-bromine and the [C(14), F(1), F(2)] unit the structure provides no reliable data for the C13–C14 double bond length.

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† Dedicated to Professor Dieter Naumann on the occasion of his 60th birthday.

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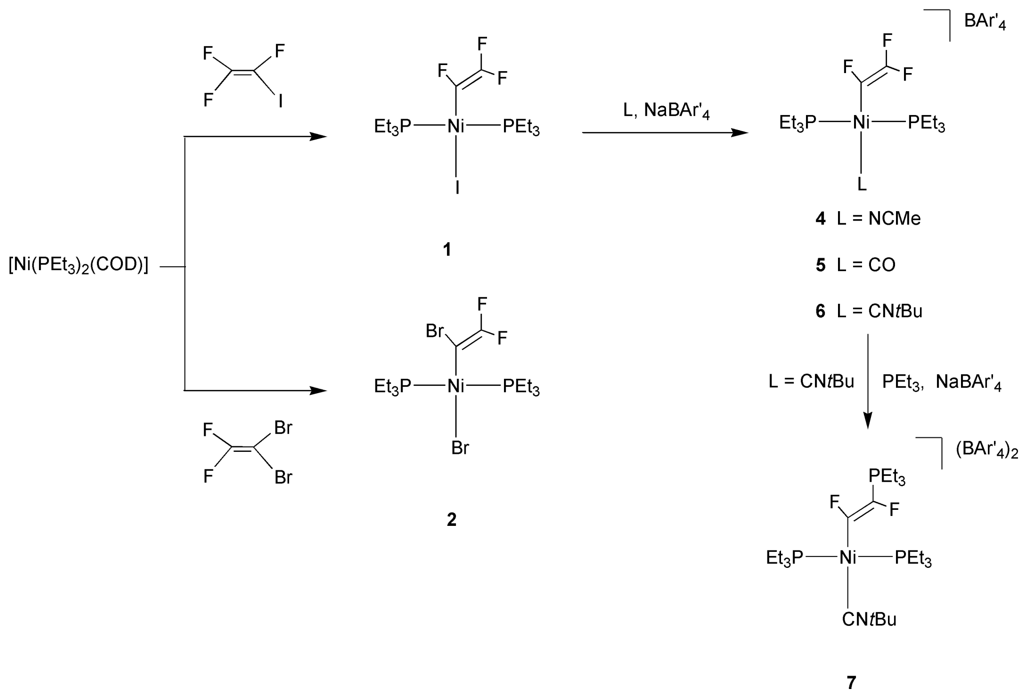


Scheme 1 Synthesis and reactivity of fluorovinyl complexes.

Table 1 NMR data at 298 K; δ(J/Hz)

Complex	^{1}H	^{31}P{^{1}H}	^{19}F	^{13}C{^{1}H}
1 (C_6D_6)	0.95 (m, 18 H, CH_3), 1.70 (m, 12 H, CH_2)	16.8 (vq, apparent J_{PF} 6.9)	−156.12 (ddt, J_{FF} 107.8, 35.3, J_{PF} 6.9, 1F), −131.29 (ddt, J_{FF} 113.3, 110.1, J_{PF} 6.9, 1F), −89.06 (ddt, J_{FF} 113.3, 35.3, J_{PF} 6.9, 1F)	8.6 (s, CH_3), 16.8 (vt, apparent J_{PC} 13.9, CH_2), 131.1 (dm, J_{CF} 305.2, CF), 155.9 (dddt, J_{CF} 303.1, 252.4, 41.1, J_{PC} 5.8, CF_2)[a]
2 (C_6D_6)	0.85 (m, 18 H, CH_3), 1.02 (m, 12 H, CH_2)	14.5 (vt, apparent J_{PF} 6.8)	−91.63 (dt, J_{FF} 74.5, J_{PF} 6.8, 1F), −67.47 (dt, J_{FF} 75.7, J_{PF} 6.9, 1F)	8.2 (s, CH_3), 14.4 (vt, apparent J_{PC} 13.2, CH_2), 73.9 (m, CBr), 149.7 (ddt, J_{CF} 297.2, 262.0, J_{PC} 5.9, CF_2)
4 (CD_2Cl_2)	1.20 (m, 18 H, CH_2CH_3), 1.71 (m, 12 H, CH_2), 2.35 (s, 3H, $NCCH_3$), 7.58 (s, 4H, CH), 7.73 (s, 8H, CH)	18.4 (vq, apparent J_{PF} 6.9)	−165.38 (ddt, J_{FF} 110.2, 37.8, J_{PF} 8.0, 1 F), −129.02 (ddt, J_{FF} 110.2, 106.7, J_{PF} 6.9, 1 F), −86.06 (ddt, J_{FF} 106.7, 37.8, J_{PF} 6.9, 1 F), −61.59 (s, 24 F, CF_3)	
5 (CD_2Cl_2)	1.21 (m, 18 H, CH_3), 2.00 (m, 12 H, CH_2), 7.58 (s, 4H, CH), 7.73 (s, 8H, CH)	29.9 (s, br)	−165.92 (dm, J_{FF} 97.5, 1 F), −123.83 (m, 1 F), −83.19 (dm, J_{FF} 103.2, 1 F), −61.59 (s, 24 F, CF_3)	
6 (CD_2Cl_2)	1.18 (m, 27 H, CH_3), 1.83 (m, 12 H, CH_2), 7.58 (s, 4 H, CH), 7.73 (s, 8 H, CH)	24.7 (vq, apparent J_{PF} 6.5)	−165.87 (ddt, J_{FF} 106.7, 36.7, J_{PF} 7.5, 1 F), −127.10 (vtt, apparent J_{FF} 107.3, J_{PF} 6.9, 1 F), −85.23 (ddt, J_{FF} 109.0, 36.8, J_{PF} 6.9, 1 F), −61.58 (s, 24 F, CF_3)	
7 (CD_2Cl_2)	1.14–1.25 (m, 36 H, CH_3), 1.79 (m, 12 H, CH_2), 1.25 (dq, J_{PF} 12.6, J_{HH} 7.5, 6 H, CH_2), 7.58 (s, 8 H, CH), 7.73 (s, 16 H, CH)	24.3 (vq, apparent J 5.7, NiP), 31.1 (dt, J_{PF} 68.8, J_{PP} 6.3, = CFP)	−173.06 (ddt, J_{FF} 125.0, J_{PF} 68.8, 5.7, 1 F), −96.5 (dt, J_{FF} 124.9, J_{PF} 4, 1 F), −61.51 (s, 48 F, CF_3)	

[a] In CD_2Cl_2.

4 Formation of *trans*-[Ni(CF=CF$_2$)(NCMe)(PEt$_3$)$_2$]BAr′$_4$ (4)

The reaction of **1** with NaBAr′$_4$ [Ar′ = 3,5-$C_6H_3(CF_3)_2$] in the presence of acetonitrile leads to the cationic complex *trans*-[Ni(CF=CF$_2$)(NCMe)(PEt$_3$)$_2$]BAr′$_4$ (**4**) (Scheme 1). Compound **4** was characterised by its NMR and IR data.[13,17,18] The presence of the bound acetonitrile is indicated by a signal in the ^{1}H NMR spectrum at δ 2.35 as well as a weak absorption band at 2286 cm^{-1} in the IR spectrum. The ^{19}F NMR spectrum reveals three signals at δ −165.38, −129.02, −86.06 for the fluorine atoms at the vinyl ligand and a broad singlet at δ −61.59 due to the anion. The reaction of **4** with NaI in d_8-thf was monitored by NMR spectroscopy. After 3 days **4** is completely converted to complex **1**, free acetonitrile and NaBAr′$_4$.

5 Formation of *trans*-[Ni(CF=CF$_2$)(CO)(PEt$_3$)$_2$]BAr′$_4$ (5)

After we had shown that we can replace the iodo ligand by acetonitrile and synthesise cationic compounds, we became interested in extending these studies to prepare other cations. On treatment of a dichloromethane solution of **1** with CO and NaBAr′$_4$ the carbonyl complex *trans*-[Ni(CF=CF$_2$)(CO)-

Table 2 Selected bond lengths (Å) and angles (°) of *trans*-$[\mathrm{NiBr(CBr{=}CF_2)(PEt_3)_2}]$ (**2**) with the estimated standard deviations in parentheses

Ni(1)–C(13)	1.868(2)	C(13)–Br(2)	1.842(2)
Ni(1)–Br(1)	2.3341(2)	C(13)–Br(2A)	1.850(2)
Ni(1)–P(1)	2.2235(4)	C(14)–F(2)	1.296(8)
Ni(1)–P(2)	2.2212(5)	C(14)–F(1)	1.412(7)
C(13)–C(14)	1.341(6)	C(14A)–F(2A)	1.321(12)
C(13)–C(14A)	1.431(10)	C(14A)–F(2A)	1.334(11)
C(13)–Ni(1)–P(2)	90.36(5)	C(14A)–C(13)–Ni(1)	124.5(5)
C(13)–Ni(1)–P(1)	90.90(5)	Br(2)–C(13)–Ni(1)	117.43(11)
P(2)–Ni(1)–P(1)	177.285(18)	Br(2A)–C(13)–Ni(1)	122.02(11)
C(13)–Ni(1)–Br(1)	179.22(6)	F(2)–C(14)–C(13)	131.5(6)
P(2)–Ni(1)–Br(1)	89.324(13)	F(2)–C(14)–F(1)	106.1(4)
P(1)–Ni(1)–Br(1)	89.441(13)	C(13)–C(14)–F(1)	122.3(6)
C(14)–C(13)–Br(2)	113.9(4)	F(2A)–C(14A)–C(13)	127.4(9)
C(14A)–C(13)–Br(2A)	113.5(5)	F(2A)–C(14A)–F(1A)	110.1(8)
C(14)–C(13)–Ni(1)	128.7(4)	C(13)–C(14A)–F(1A)	122.5(9)

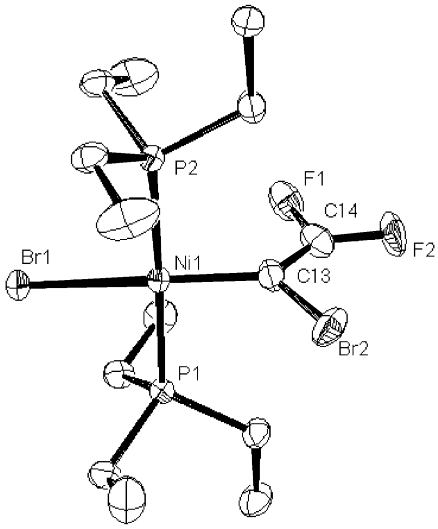


Fig. 1 An ORTEP diagram of **2**. Ellipsoids are drawn at the 50 % probability level. Note that the rotational disorder (53 : 47) of Br(2) and the [C(14), F(1), F(2)] unit leads to average locations across the vinyl ligand.

$\mathrm{(PEt_3)_2]BAr'_4}$ (**5**) was obtained. Compound **5** is only stable in $\mathrm{CH_2Cl_2}$ and could not be isolated in the solid state. However, the NMR and IR data of **5** clearly reveal the formation of a cationic compound bearing a vinyl and a carbonyl ligand. The IR spectrum shows a strong absorbtion band at 2092 $\mathrm{cm^{-1}}$ characteristic for a cationic nickel carbonyl complex.[23,24] An absorbtion band at 1710 $\mathrm{cm^{-1}}$ indicates the presence of the vinyl ligand.[17,18]

6 Formation of *trans*-$[\mathrm{Ni(CF{=}CF_2)(CN^tBu)(PEt_3)_2]BAr'_4}$ (6)

Treatment of a solution of **1** with $\mathrm{CN^tBu}$ and $\mathrm{NaBAr'_4}$ leads to the formation of the cationic isonitrile complex *trans*-$[\mathrm{Ni(CF{=}CF_2)(CN^tBu)(PEt_3)_2]BAr'_4}$ (**6**). The ^{19}F NMR spectroscopic data of **6** are comparable to these found for compounds **4** and **5** and need no further discussion. The presence of the isonitrile ligand at a cationic metal centre is revealed by a strong absorbtion band at 2183 $\mathrm{cm^{-1}}$ in the infrared spectrum.[25]

7 Formation of *trans*-$[\mathrm{Ni\{CF{=}CF(PEt_3)\}(CN^tBu)(PEt_3)_2}]$-$[\mathrm{BAr'_4}]_2$ (7)

Treatment of complex **6** with $\mathrm{PEt_3}$ and $\mathrm{NaBAr'_4}$ affords the dicationic derivative *trans*-$[\mathrm{Ni\{CF{=}CF(PEt_3)\}(CN^tBu)(PEt_3)_2}]$-$[\mathrm{BAr'_4}]_2$ (**7**) bearing a phosphonioethenyl ligand. The ^{31}P NMR spectrum of **7** shows a virtual quartet at δ 24.3 for the two *trans* phosphines with an apparent coupling of $J = 5.7$ Hz to the two fluorine and the phosphorous nuclei at the vinyl ligand. The presence of the $\mathrm{PEt_3}$ group in the phosphonioethenyl ligand is revealed by a doublet of triplets at δ 31.1 with coupling to only one fluorine atom and to the *trans* phosphines at nickel ($J_{\mathrm{PF}} = 68.8$, $J_{\mathrm{PP}} = 6.3$ Hz). The ^{19}F NMR spectrum displays two signals for the phosphonioethenyl group at δ −173.06 and −96.5 with a coupling of $J = 125$ Hz suggestive of a *trans* or a *geminal* orientation of the two fluorine atoms.[17,18] Comparison with the ^{19}F NMR data found for **2** leads to the conclusion that the fluorines are probably in *trans* position. The absorption band for the isonitrile ligand in the infrared spectrum at 2195 $\mathrm{cm^{-1}}$ appears at a higher wave number than the corresponding band in **6**, which reflects the presence of a dicationic compound.

8 Crystal structure of *trans*-$[\mathrm{Ni\{CFCF(PEt_3)\}(CN^tBu)}$-$\mathrm{(PEt_3)_2][BAr'_4]_2}$ (7)

The colourless compound **7** was crystallised from diethyl ether at 0 °C. The structure was determined by X-ray diffraction at low temperature (Fig. 2). Selected bond length and angles are summarised in Table 3. The angles between the adjacent ligands at nickel vary from 91.47(14)° to 87.95(13)°. The nickel coordination plane and the phosphoniovinyl group are almost orthogonal (dihedral angle 84.9°). An *E*-configuration of the nickel phosphonioalkenyl moiety is observed. The nickel–carbon bond length to the phosphonioethenyl ligand of 1.893(5) Å is slightly longer than the comparable distance found in **2** [1.868(2) Å]. The distance of the carbon–carbon double bond [1.309(6) Å] is shorter than those found in other organometallic compounds with a comparable zwitterionic ligand such as $[\mathrm{Ru(CO)_2\{C(Me){=}C(Ph)PEt_3\}(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})}]$ [1.344(3) Å], $[\mathrm{Ru\{CH{=}CR(PPh_3)\}(\eta^5\text{-}C_9H_7)(PPh_3)_2]PF_6}$ (R = 1-cyclohexenyl) [1.371(7) Å], but is in accordance with the bond lengths given in the dicationic complex *cis*-*trans*-$[\mathrm{IrCl\{CH{=}CH(PPh_3)\}_2(CO)(PPh_3)_2]\,[ClO_4]_2}$ [1.24(2), 1.280(19) Å].[26–30] All four carbon–phosphorous bond lengths in the phospho-

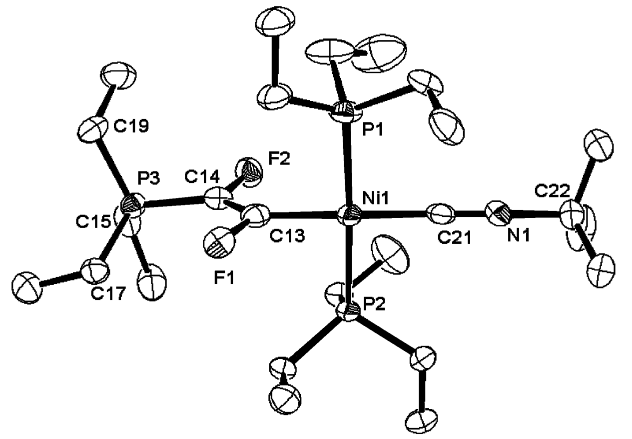
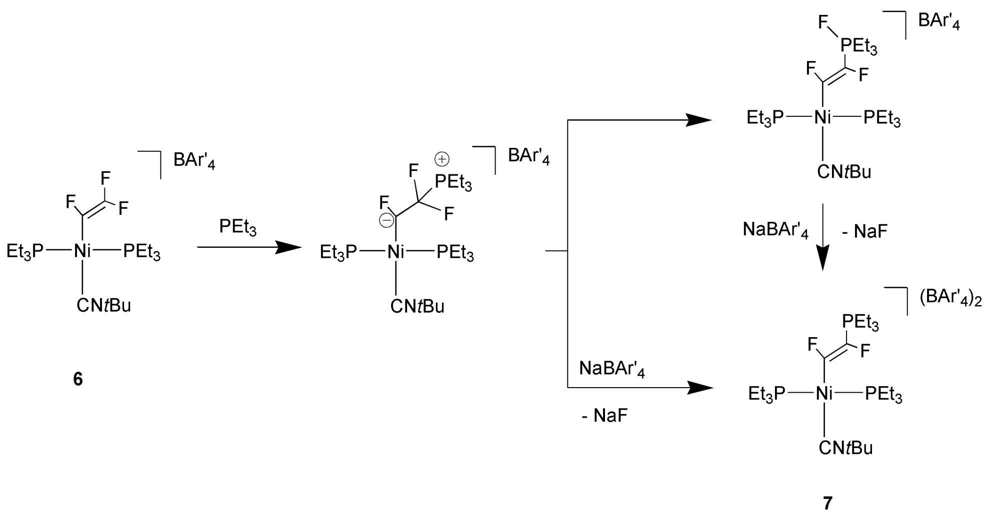


Fig. 2 An ORTEP diagram of the dication in **7**. Ellipsoids are drawn at the 50% probability level.



Scheme 2 Proposed mechanism for the formation of **7**.

Table 3 Selected bond lengths (Å) and angles (°) of *trans*-[Ni{CF=CF(PEt$_3$)}(CN^{t}Bu)(PEt$_3$)$_2$][BAr′$_4$]$_2$ (**7**) with the estimated standard deviations in parentheses

Ni(1)–C(21)	1.839(5)	P(3)–C(14)	1.794(5)
Ni(1)–C(13)	1.893(5)	P(3)–C(15)	1.790(4)
Ni(1)–P(1)	2.2307(13)	P(3)–C(17)	1.801(5)
Ni(1)–P(2)	2.2333(12)	P(3)–C(19)	1.798(4)
F(1)–C(13)	1.394(5)	N(1)–C(22)	1.482(6)
F(2)–C(14)	1.380(5)	N(1)–C(21)	1.156(6)
C(13)–C(14)	1.309(6)		
C(21)–Ni(1)–C(13)	176.8(2)	N(1)–C(21)–Ni(1)	178.2(5)
C(21)–Ni(1)–P(1)	91.47(14)	C(14)–C(13)–F(1)	113.0(4)
C(13)–Ni(1)–P(1)	89.48(13)	C(14)–C(13)–Ni(1)	130.9(4)
C(21)–Ni(1)–P(2)	90.98(14)	F(1)–C(13)–Ni(1)	116.0(3)
C(13)–Ni(1)–P(2)	87.95(13)	C(13)–C(14)–F(2)	116.3(4)
P(1)–Ni(1)–P(2)	176.64(5)	C(13)–C(14)–P(3)	131.6(4)
C(21)–N(1)–C(22)	178.5(5)	F(2)–C(14)–P(3)	112.1(3)

nioethenyl unit are in the same range. The CF–PEt$_3$ bond [1.794(5) Å] is longer than the CH–PMe$_3$ separation found in [ReO{CH=CH(PMe$_3$)}(CH$_2$SiMe$_3$)$_3$] [1.737(10) Å], where a P=C double bond character has been discussed. However, it is comparable to the CR–PPh$_3$ distance found in [Ru{CH=CR(PPh$_3$)}(η^5-C$_9$H$_7$)(PPh$_3$)$_2$]PF$_6$ [1.790(6) Å] or the CF–PEt$_3$ bond length found in the phosphoniumtetrafluoroborate [(F$_5$S)CF=CF(PMe$_3$)]BF$_4$ [1.807(7) Å].[27,31,32] The Ni–C bond to the isonitrile ligand of 1.839(5) Å is in the same range as the Ni–C distances in [NiCl(CNXyl)$_2$(dppe)$_2$]PF$_6$ (Xyl = *o*-xylyl) [1.845(8) and 1.849(8) Å].[25] The carbon–nitrogen bond of 1.156(6) Å length is also not significantly different from these found in [NiCl(CNXyl)$_2$(dppe)$_2$]PF$_6$.[25]

Discussion

The syntheses of the complexes *trans*-[NiI(CX=CF$_2$)(PEt$_3$)$_2$] (**1**: X = F; **2**: X = Br) by reaction of trifluoroiodoethene or 1,1-dibromodifluoroethene with [Ni(COD)(PEt$_3$)$_2$], which can be prepared *in situ* from [Ni(COD)$_2$] and PEt$_3$, are shown in Scheme 1.[33] Similar compounds have been prepared also by oxidative addition or *via* nucleophilic displacement of bromo ligands starting from a Ni(II) precursor.[17,18,34] The formation of complex **3** can be explained by a radical reaction mechanism previously outlined by Fahey *et al.*[35] Such a mechanism is consistent with the observed formation of 1-bromo-2,2-difluoroethene, which could be detected by ^{19}F and ^{1}H NMR spectroscopy.[36]

Compound **1** can be converted into cationic complexes of the general composition *trans*-[Ni(CF=CF$_2$)(L)(PEt$_3$)$_2$]BAr′$_4$ (**4**: L = NCMe; **5**: L = CO; **6**: CN^{t}Bu). A comparable synthesis to prepare a cationic acetonitrile complex bearing a fluorinated pyridyl ligand was described by Perutz *et al.*, who generated the compound *trans*-[Ni(2-C$_5$NF$_4$)(NCMe)(PEt$_3$)$_2$]BAr′$_4$ by reaction of the fluoride *trans*-[NiF(2-C$_5$NF$_4$)(PEt$_3$)$_2$] with NaBAr′$_4$ in acetonirile.[13] Cationic nickel carbonyl complexes are rare and as square planar compounds only stable at low temperature or with a strong electron withdrawing anionic ligand.[23,24]

The reaction of [Ni(CF=CF$_2$)(CN^{t}Bu)(PEt$_3$)$_2$]BAr′$_4$ (**6**) with PEt$_3$ and NaBAr′$_4$ affords the replacement of one fluorine atom yielding the dicationic isonitrile complex *trans*-[Ni{CF=CF(PEt$_3$)}(CN^{t}Bu)(PEt$_3$)$_2$][BAr′$_4$]$_2$ (**7**).

Tertiary phosphines often lead to a variety of defluorinations and coupling reactions in fluorinated olefins.[37] However, the mechanism for the formation of **7** probably involves a nucleophilic attack of free phosphine at the β-position of the vinyl-ligand in **6** (Scheme 2).[38,39] The resulting carbanionic charge at the α-carbon atom might possibly be stabilised by the metal centre.[40] Direct elimination of fluorine at the β-carbon or reaction *via* a vinyl phosphorane affords the phosphonioethenyl ligand (Scheme 2). The resulting dication is stabilised by a second BAr′$_4^-$ anion. Note that the formation of phosphoranes *via* reaction of phosphines with fluorinated olefins has been described before.[38,39] A full mechanistic investigation of this reaction is under study. Phosphonioethenyl complexes are usually generated by nucleophilic addition of phosphine to an η^2-coordinated alkyne.[26–31,41] The synthesis of α-methoxyphosphonioethenyl derivatives was performed by nucleophilic attack of the ylide Me$_3$P=CHR (R = H, Me) to a carbonyl ligand in a manganese or iron carbonyl complex followed by deprotonation and subsequent methylation at the oxygen using MeOSO$_2$F.[42,43] Non-coordinated phosphonioethenid compounds are only stable in the free form, if the anionic charge is resonance stabilised.[44]

The X-ray analysis of compound **7** implies a zwitterionic structure for the phosphonioethenyl ligand with a formal positive charge at the phosphine bound in β-position. A resonance stabilisation of the Ni–CF=CF(PEt$_3$) unit by a carbene-like structure, which has been discussed for comparable compounds, can be excluded, because of a C=C double bond length of 1.309(6) Å.[28,31,42]

Conclusions

This paper reports the syntheses of cationic nickel complexes *trans*-[Ni(CF=CF$_2$)(L)(PEt$_3$)$_2$]BAr′$_4$ (**4**: L = NCMe; **5**: L = CO; **6**: CN^{t}Bu) bearing a trifluorovinyl ligand. The compounds **4** and **6** are stable in the solid state. In contrast, the carbonyl complex **5** could only be characterised in solution and represents a rare example of a square planar, cationic carbonyl nickel complex.[23,24] Reaction of **6** with triethylphosphine and $NaBAr'_4$ provides a new entry to compounds with a metal bound phosphonioethenid ligand. Moreover, **6** and **7** might be excellent starting materials for reactions with nucleophiles to obtain organometallic compounds bearing interesting fluorinated units or phosphorus containing building blocks. Further investigations on the reactivity of these complexes are in progress.

Experimental

Most of the synthetic work was carried out on a Schlenk line or a nitrogen-filled glove box with oxygen levels below 10 ppm. All solvents were purified and dried by conventional methods and distilled under argon before use. Benzene-d_6 and THF-d_8 were dried by stirring over potassium and then distilled under vacuum. CN^{t}Bu was obtained from Aldrich. $NaBAr'_4$ and $[Ni(COD)_2]$ were prepared according to the literature.[45,46] The fluorinated olefins were obtained from Fluorochem Ltd and distilled before use.

The NMR spectra were recorded with a Bruker DRX 500 spectrometer. The ^{1}H NMR chemical shifts were referenced to residual C_6D_5H at δ 7.15, $CHDCl_2$ at δ 5.3, or THF-d_7 at δ 1.8. The $^{13}C\{^1H\}$ spectra were referenced to C_6D_6 at δ 128.0 and CD_2Cl_2 at δ 53.7. The ^{19}F NMR spectra were referenced to external C_6F_6 at δ 162.9. The $^{31}P\{^1H\}$ NMR spectra were referenced externally to H_3PO_4 at δ 0. Infrared spectra were recorded on a Bruker IFS-66 spectrometer. NMR data are listed in Table 1. The molar conductivities Λ_M were measured in CH_2Cl_2 with a Schott CG 853 conductometer and a LF 1100T cell (Schott).

Synthesis of *trans*-$[NiI(CF{=}CF_2)(PEt_3)_2]$ (1)

$[Ni(COD)_2]$ (237 mg, 0.86 mmol) was suspended in hexane (30 mL), and PEt_3 (278 µL, 2.00 mmol) was added, giving a yellow solution. The solution was cooled at 0 °C and trifluoroiodoethene (94 µL, 1.00 mmol) was added. After the reaction mixture had been warmed to room temperature, the solution was filtered through a cannula. The red solution was concentrated under vacuum to 15 mL and dark red crystals were obtained overnight at −35 °C. Yield 400 mg (93%). (Found: C, 33.57; H, 5.86. $C_{14}H_{30}F_3INiP_2$ requires C, 33.48; H, 6.02). IR [KBr, ν/cm^{-1}]: 1705s (C=C).

Synthesis of *trans*-$[NiBr(CBr{=}CF_2)(PEt_3)_2]$ (2)

$[Ni(COD)_2]$ (154 mg, 0.56 mmol) was suspended in toluene (20 mL), and PEt_3 (181 µL, 1.23 mmol) was added, giving a yellow solution. After adding 1,1-dibromodifluoroethene (59 µL, 0.61 mmol) the volatiles were removed under vacuum. The remaining yellow solid was dissolved in hexane (10 mL) and the solution was filtered through a cannula. The yellow solution was concentrated under vacuum to 5 mL and yellow crystals were obtained after 2 d at −35 °C. Yield 164 mg (57%). (Found: C, 32.70; H, 5.87. $C_{14}H_{30}Br_2F_2NiP_2$ requires C, 32.54; H, 5.85). IR [KBr, ν/cm^{-1}]: 1692m (C=C).

Synthesis of *trans*-$[Ni(CF{=}CF_2)(NCMe)(PEt_3)_2]BAr'_4$ (4)

A solution of **1** (200 mg, 0.40 mmol) in acetonitrile (20 mL) was treated with $NaBAr'_4$ (353 mg, 0.40 mmol). After stirring for 1 d at 55 °C, the solvent was removed under vacuum and the yellow residue was extracted with CH_2Cl_2 (5 mL). The extract was then filtered through a cannula, the solvent was pumped off and the yellow solid was washed with hexane (20 mL). Yield 375 mg (74%). (Found: C, 45.05; H, 3.55; N, 0.92. $C_{48}H_{35}BF_{27}NNiP_2$ requires C, 45.03; H, 3.54; N, 1.09). IR [KBr, ν/cm^{-1}]: 2286vw (N≡C),1710m (C=C).

Formation of *trans*-$[Ni(CF{=}CF_2)(CO)(PEt_3)_2]BAr'_4$ (5)

A slow stream of CO was passed for 10 min through a solution of of **1** (50 mg, 0.10 mmol) in CD_2Cl_2 (3 mL). The solution was then treated with $NaBAr'_4$ (88 mg, 0.10 mmol) and for another 2 min with a stream of CO. After the suspension was filtered through a cannula, a yellow solution of **5** was obtained. IR [CD_2Cl_2, ν/cm^{-1}]: 2092s (CO),1710w (C=C).

Synthesis of *trans*-$[Ni(CF{=}CF_2)(CN^tBu)(PEt_3)_2]BAr'_4$ (6)

A solution of **1** (294 mg, 0.58 mmol) in dichloromethane (30 mL) was treated with $NaBAr'_4$ (618 mg, 0.58 mmol). After 1 min CN^{t}Bu (66 µL, 0.98 mmol) was added and the suspension was stirred for 15 min. The suspension was then filtered through a cannula. The solvent was pumped off, the remaining yellow solid was washed with hexane (5 mL) and was then dissolved in diethyl ether (5 mL). After the solution was filtered through a cannula, it was concentrated under vacuum to 3 mL. Yellow crystals of **6** precipitated at −20 °C. Yield 507 mg (66%). (Found: C, 46.46; H, 4.00; N, 0.99). $C_{51}H_{51}BF_{27}NNiP_2$ requires C, 46.32; H, 3.89; N, 1.06). IR [KBr, ν/cm^{-1}]: 2183s (C≡N),1714m (C=C). Molar conductivity: [Λ_M/S cm^2 mol^{-1}] 27.

Synthesis of *trans*-$[Ni\{CF{=}CF(PEt_3)\}(CN^tBu)(PEt_3)_2][BAr'_4]_2$ (7)

A suspension of **6** (205 mg, 0.15 mmol) and $NaBAr'_4$ (206 mg, 0.23 mmol) in dichloromethane (20 mL) was treated with PEt_3 (23 µL, 0.15 mmol). After the suspension was stirred for 2 d, it was filtered through a cannula. The volatiles were removed under vacuum and the yellow solid was washed with hexane (5 mL). The yellow solid was then dissolved in diethyl ether (3 mL) and the solution was filtered through a cannula. After 2 d colourless crystals of **7** precipitated at −20 °C. Yield 204 mg (58%). (Found: C, 46.64; H, 3.64; N, 0.57. $C_{89}H_{78}B_2F_{50}NNiP_3$ requires C, 46.79; H, 3.44; N, 0.61). IR [KBr, ν/cm^{-1}]: 2195s (C≡N). Molar conductivity: [Λ_M/S cm^2 mol^{-1}] 59.

Structure determination for complex 2

Yellow crystals of **2** were obtained from a solution in toluene at at −30 °C. Diffraction data were collected for a block with the dimensions 0.32 × 0.26 × 0.18 mm on a Nonius KappaCCD diffractometer.

Crystal data for 2. $C_{14}H_{30}Br_2F_2NiP_2$, $M = 516.85$, monoclinic, space group $P2_1/c$, $a = 11.9720(2)$, $b = 10.9550(2)$, $c = 16.3510(3)$ Å, $\beta = 99.1400(2)°$, $U = 2117.26(7)$ Å^3, $T = 100(2)$ K, $Z = 4$, μ(Mo-Kα) = 4.850 mm^{-1}, 41632 reflections measured, 6140 unique ($R_{int} = 0.036$). The structure was solved by direct methods (SHELXTL PLUS) and refined with full matrix least square methods on F^2 (SHELX-97).[47,48] The disorder of Br(2) and the [C(14), F(1), F(2)] unit was refined to an occupancy of 53 : 47. Final R_1, wR_2 values on all data 0.0383, 0.0632. R_1, wR_2 values on [$I_o > 2\sigma(I_o)$, 5117 reflections] data 0.0272, 0.0589.

Structure determination for complex 7

Colourless crystals of **7** were obtained from a solution in diethyl ether at at 0 °C. Diffraction data were collected for a block with the dimensions 0.28 × 0.12 × 0.10 mm on a Nonius KappaCCD diffractometer.

Crystal data for 7·0.5Et₂O. $C_{91}H_{83}B_2F_{50}NNiO_{0.5}P_3$, $M = 2321.82$, triclinic, space group, $P\bar{1}$, $a = 13.4000(1)$, $b = 16.9040(1)$, $c = 24.1850(2)$ Å, $\alpha = 75.4550(3)°$, $\beta = 78.5900(4)°$, $\gamma = 74.6890(5)°$, $U = 5063.45(6)$ Å^3, $T = 100(2)$ K, $Z = 2$, μ(Mo-Kα) = 0.376 mm^{-1}, 69322 reflections measured, 17524 unique ($R_{int} = 0.091$). The structure was solved by direct methods (SHELXTL PLUS) and refined with full matrix least square methods on F^2 (SHELX-97).[47,48] Final R_1, wR_2 values on all data 0.1273, 0.1409. R_1, wR_2 values on [$I_o > 2\sigma(I_o)$, 10945 reflections] data 0.0678, 0.1188.

CCDC reference numbers 178083 and 178084.

See http://www.rsc.org/suppdata/dt/b2/b200739h/ for crystallographic data in CIF or other electronic format.

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