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Journal of Organometallic Chemistry 616 (2000) 96–105

Journal of Organometallic Chemistry

CFC replacement HCFC-133a (CF_3CH_2Cl) as a convenient precursor for the synthesis of chlorodifluorovinyl-metal derivatives of main group and transition metal elements: the first X-ray structural characterisation of chlorodifluorovinyl-containing organometallic complexes

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Received 3 June 2000; accepted 3 August 2000

Abstract

The one-pot reaction of the CFC replacement 1-chloro-2,2,2-trifluoroethane (CF_3CH_2Cl, HCFC-133a) with two equivalents of butyllithium in diethylether at −78°C followed by the addition of main group or transition metal halides results in good yields of the metal-chlorodifluorovinyl-containing compounds $R_3Sn(CCl{=}CF_2)$ {R = Me, Et, Bu}, $Sn(CCl{=}CF_2)_4$, $Sb(CCl{=}CF_2)_3$, $Hg(CCl{=}CF_2)_nCl_{(2-n)}$ ($n = 1,2$), *trans*-$[Ni(CCl{=}CF_2)_2(PBu_3)_2]$, *trans*-$[Pd(CCl{=}CF_2)_2(PBu_3)_2]$ and $[Au(CCl{=}CF_2)(PPh_3)]$. The molecular structures of $Hg(CCl{=}CF_2)Cl$, *trans*-$[Pd(CCl{=}CF_2)_2(Bu_3P)_2]$ and $[Au(CCl{=}CF_2)(PPh_3)]$ have been obtained from single crystal data; these are the first such structural data to be reported for any chlorodifluorovinyl-containing organometallic complexes. The molecular structure of $[Au(CF{=}CF_2)(PPh_3)]$, which was prepared using a similar method based on CF_3CH_2F (HFC-134a), is also reported and compared with that of the chlorodifluorovinyl analogue. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: HCFC-133a; Chlorodifluorovinyl; Perfluorovinyl; Synthesis; X-ray diffraction

1. Introduction

Although fluorine is capable of replacing hydrogen in many organic systems, usually without major structural changes, the number of examples of organometallic complexes containing perfluorinated ligands is very much more limited than for the comparable perprotio analogues [1]. There is an even smaller number of systems which contain organic ligands in which the hydrogens are replaced by a mixture of fluorine and chlorine substituents. A case in point is that of the chlorodifluorovinyl ligand for which just seven metal complexes have been reported and all but one of these are based on the Group 10 elements, nickel, palladium and platinum. In 1967 the complex *cis*-$[Pt(CCl{=}CF_2)_2(PEt_3)_2]$ was reported from the reaction of the bromochlorofluorocarbon $CF_2{=}CClBr$ with butyllithium followed by addition of *cis*-$[PtCl_2(PEt_3)_2]$. Shortly afterwards the synthesis of *trans*-$[M_2Br_2(CCl{=}CF_2)_2(PEt_3)_2]$ from $[M_2Br_4(PEt_3)_2]$ {M = Pt,Pd} in a similar fashion was reported, and the subsequent reaction of the platinum complex with pyridine afforded $[PtBr(CCl{=}CF_2)py(PEt_3)]$ [2]. By comparison the complexes *trans*-$[NiCl(CCl{=}CF_2)(PPh_3)_2]$ [3], and *trans*-$[NiCl(CCl{=}CF_2)(AsMe_2Ph)_2]$ [4] were obtained from the reaction of $[Ni(\eta^2\text{-}C_2H_4)(PPh_3)_2]$ and $[Ni(AsMe_2Ph)_4]$, respectively, with $CF_2{=}CCl_2$. These reactions are believed to proceed via initial π-coordination of the chlorofluoroalkene which subsequently undergoes a vinyllic rearrangement to generate the sigma-bound chlorodifluorovinyl-containing nickel complexes of the type $[NiCl(CCl{=}CF_2)L_2]$.

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PII: S0022-328X(00)00565-9

In 1968 the lithium reagent $LiCCl{=}CF_2$ was prepared by proton abstraction from $CHCl{=}CF_2$ [5] and its application in synthetic organic chemistry was investigated; during the course of that work $Et_3Si(CCl{=}CF_2)$ was prepared. Much more recently it has been shown that the CFC-replacement 1,1,1,2-tetrafluoroethane (CF_3CH_2F, HFC-134a) can act as a suitable precursor to the perfluorovinyllithium reagent [6] and we have used this route to synthesise a number of perfluorovinyl main-group and transition-metal containing organometallic compounds [7,8]. More recently we, and others [9], have extended our studies to the use of HCFC-133a (CF_3CH_2Cl) as a source of the chlorodifluorovinyl ligand and in this paper we report our results on the use of this industrially available material as a convenient precursor to chlorodifluorovinyl-containing organometallic complexes.

2. Results and discussion

The addition of two equivalents of *n*-butyllithium to a diethyl ether solution of HCFC-133a at −78°C has been reported to generate the lithium reagent $CF_2{=}CCl^-Li^+$ (**1**) in good yields [9]. By analogy with the reaction of CF_3CH_2F [6], this is believed to occur via a two-step deprotonation process and concomitant elimination of one equivalent of lithium fluoride. The lithium reagent **1** generated in this way is stable in solution at low temperature for many hours but decomposes rapidly when the temperature is increased above −45°C. Following a number of reactions it has become obvious that the lifetime of the lithium reagent is considerably longer in dilute solutions than it is in more concentrated solutions, when, even at low temperature, some decomposition is noted and the solution darkens in colour.

Metal-bound chlorodifluorovinyl-containing complexes were obtained by the slow addition of cold diethyl ether, or THF, solutions of the appropriate metal halides to the lithium reagent **1**. Thus, when a cold, dilute THF solution of mercury(II) chloride was added to a solution of **1** in a 1:2 ratio an immediate reaction was observed with the formation of an off-white precipitate. Subsequent slow warming of the solution to room temperature was followed by the addition of an excess of hexane which resulted in the precipitation of white material that was removed by filtration. Elemental analysis of the solid material identified it as a mixture of lithium halides. After drying the organic phase the solvents were removed under vacuum to yield a liquid product, which was purified, by distillation under reduced pressure, to yield a colourless liquid. The ^{19}F-NMR spectrum of a $CDCl_3$ solution of the product exhibited a pair of doublets at ca. −75.5 and −85.5 ppm, which show mutual coupling of magnitude 36.5 Hz. The appearance of two doublets is consistent with that expected for two non-equivalent fluorine nuclei of the anticipated chlorodifluorovinyl moiety and the observed chemical shifts are comparable with those reported for the complex *cis*-$[Pt(PEt_3)_2(CCl{=}CF_2)_2]$ (−80.0 and −92.2 ppm) by Rest et al. [2]. Both of the doublets exhibit mercury satellite peaks (^{199}Hg, $I = 1/2$, 16.8%) from which the magnitude of J(HgF) is determined to be 246.9 and 131.6 Hz for the resonances at −75.5 and −85.5 ppm respectively. Based on the mercury–fluorine coupling constants the signal at −75.5 ppm, which displays the larger Hg–F coupling, is assigned to the fluorine nucleus *trans* to the mercury centre, whilst the peak at −85.5 ppm is assigned to the *cis*-fluorine. This assignment is consistent with the ordering of the two β-fluorine nuclei in the analogous bis(perfluorovinyl)mercury complex [10].

The extent of substitution can be determined from the ^{199}Hg mercury NMR spectrum, which, in this case, shows an overlapping triplet of triplets, centred at 933.5 ppm. The observation of a triplet-based, rather than doublet-based, pattern confirms that bis-substitution has occurred. Final confirmation of the identity of the product as $Hg(CCl{=}CF_2)_2$ (**2**) is provided by satisfactory elemental analysis figures.

When a similar reaction was carried out using a 1:1 ratio of mercury(II) chloride to the chlorodifluorovinyllithium reagent the resulting crude product was an oily solid, the ^{19}F-NMR spectrum of which displayed four doublets (at −75.5, −78.4, −83.9 and −85.6 ppm), each of which show coupling to one mercury nucleus. Two of the doublets (−75.5 and −85.6 ppm) can be assigned, on the basis of chemical shift position and coupling constants, to the bis-substituted product **2**. Washing of the crude product with a little hexane resulted in an insoluble white solid and a hexane-soluble component. According to NMR spectroscopy the solution contains the bis-substituted compound **2**. Meanwhile, the fluorine NMR spectrum of the hexane-insoluble product, dissolved in $CDCl_3$, consists of two doublets at ca. −78.4 and −83.9 ppm which due to the similarity in chemical shift position and coupling constants [$J(FF) = 40.8$ Hz] with those found for $Hg(CCl{=}CF_2)_2$ suggest that this product is likely to be the desired *mono*-substituted complex **3**. Once again Hg–F coupling is observed to both fluorine nuclei [$|J(HgF)| = 414.4$ and 102.5 Hz] and on this basis the signals at −78.1 and −83.9 ppm are assigned to the *trans*- and *cis*-fluorine nuclei (F1 and F2, see Fig. 1) respectively.

The ^{199}Hg-NMR spectrum of a saturated $CDCl_3$ solution of this product displays a doublet of doublets centred at ca. 702 ppm; this is also consistent with the *mono*-substituted complex, and confirmation of the identity of this product as $Hg(CCl{=}CF_2)Cl$ (**3**) was obtained from elemental analysis results.

We note that there is a significant increase in the magnitude of the *trans*-Hg–F1 coupling constant in the mono-substituted complex [J(HgF) = 414 Hz] compared with that recorded for the bis-substituted analogue [J(HgF) = 217 Hz]. A similar behaviour is observed for the analogous perfluorovinyl compounds where the magnitude of the *trans*-mercury–fluorine coupling constant increases from 224 Hz in $Hg(CF{=}CF_2)_2$ [10] to 401 Hz in $Hg(CF{=}CF_2)Cl$ [11]. This behaviour appears to be consistent with the replacement of the chloride ligand of the mono-substituted product for a, presumably, more electron-withdrawing fluorovinyl ligand, which would result in a decrease in the electron density in the mercury–carbon bond which should be reflected in the reduced coupling constants of any bond-mediated coupling via this linkage.

On leaving chloroform solutions of compound **3** to stand so that the solvent slowly evaporated, small crystals were obtained. Solution of the X-ray diffraction data afforded the molecular structure of **3** which is shown in Fig. 1, and selected bond angles and distances which are given in Table 1. The data provide the first structure for any organometallic chlorodifluorovinyl-containing complex.

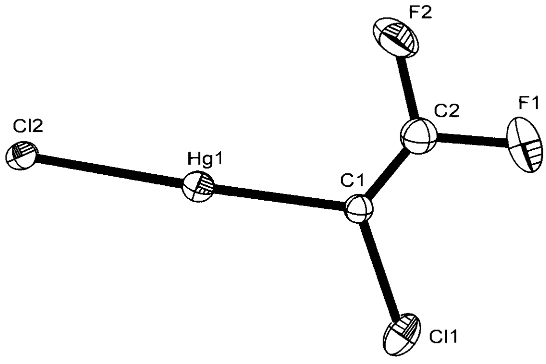


Fig. 1. The molecular structure of $Hg(CCl{=}CF_2)Cl$ (**3**), thermal ellipsoids are shown at the 30% probability level.

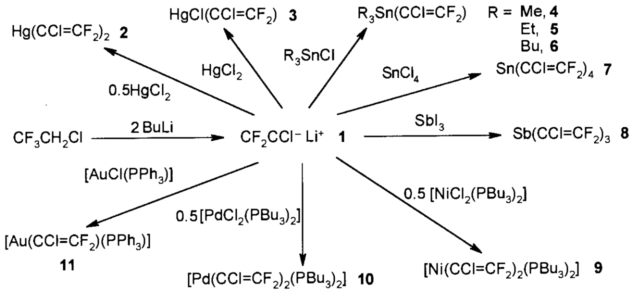
Table 1
Bond lengths (Å) and angles (°) for $Hg(CCl{=}CF_2)Cl$ (**3**)

Cl(2)–Hg(1)	2.325(7)
Cl(1)–C(1)	1.75(3)
Hg(1)–C(1)	2.09(3)
F(1)–C(2)	1.32(4)
F(2)–C(2)	1.37(4)
C(1)–C(2)	1.23(5)
C(1)–Hg(1)–Cl(2)	176.1(8)
C(2)–C(1)–Cl(1)	122(3)
C(2)–C(1)–Hg(1)	121(2)
Cl(1)–C(1)–Hg(1)	116.7(15)
C(1)–C(2)–F(1)	128(3)
C(1)–C(2)–F(2)	124(3)
F(1)–C(2)–F(2)	109(3)

The solid-state structure of **3** is composed of parallel stacks of $HgCl(CCl{=}CF_2)$ molecules separated by ca. 4.24 Å. Within each molecule a near-linear geometry is adopted at the mercury atom, Cl2–Hg–C1 = 176.1(8)°, with Hg–Cl and Hg–C distances of 2.325(7) and 2.09(3) Å respectively, neither of which is exceptional. The bond distances and angles determined within the ligand are more interesting, however because of the dominance of the X-ray scattering from the single heavy mercury atom, which is surrounded by much lighter atoms, there is a relatively large degree of uncertainty in the position of these atoms in the complex **3**. The C=C distance of 1.23(5) Å is considerably shorter than that found in bis(perfluorovinyl)mercury [1.362(6) Å] [10], however, it is not much shorter than that reported for related complexes such as *cis*-1,2-difluorovinylpentacarbonyl manganese [1.281 Å] [12], and for *trans*-bis(trimethylphosphine)*p*-tolyl(trichlorovinyl)-nickel(II) [1.258 Å] [13]. However, it is worth noting that this apparently short distance may be due to a combination of poor definition of the C1 atom and librational effects, which cannot be corrected for in this case. The two C–F distances in compound **3** [1.32(4) and 1.37(4) Å] are within experimental limits the same, a similar situation exists for the C–Cl distances observed for some trichlorovinyl-containing organometallic complexes, such as the 3,4,7,8-tetramethyl-1-10-phenanthralene adduct of $Hg(CCl{=}CCl_2)_2$ [14], but this is not the case in the solid-state structure of $Hg(CF{=}CF_2)_2$ where a small but significant difference between the two β-C–F bond distances [$\Delta d = 0.038(6)$ Å] is observed [10]. However, for compound **3** any such differences may be masked by the poorer resolution observed for the derived distances. Finally, we note that the F1–C2–F2 angle observed for the formally sp^2-hybridised CF_2-carbon [15] is 109(3)°.

Both compounds **2** and **3** appear to be reasonably stable to air and moisture, but we have noticed that the ^{19}F-NMR spectrum of solutions containing pure $Hg(CCl{=}CF_2)Cl$ which have been left aside for some time show peaks due to both $Hg(CCl{=}CF_2)_2$ and $Hg(CCl{=}CF_2)Cl$. This suggests that redistribution of the chloride and chlorodifluorovinyl ligands occurs. In order to support this interpretation one equivalent of $HgCl_2$ was added directly to a solution of complex **2** and the composition of this mixture was followed by NMR spectroscopy. Within 24 h the ^{19}F-NMR spectrum displayed equally intense sets of peaks due to both compounds **2** and **3**, demonstrating that redistribution to generate the symmetrised products does indeed occur readily for these compounds, as it does for many other mercury(II) complexes [16].

Previously we have shown that using CF_3CH_2F (HFC-134a) it is possible to generate a range of perfluorovinyl-containing complexes with relative ease. In



Scheme 1. Reactions of chlorodifluorovinyllithium with a variety of metal halides.

order to determine the extent with which HCFC-133a may be used as a general way of introducing the $-CCl{=}CF_2$ moiety into organometallic complexes, reactions with a variety of main-group and transition-metal starting materials were investigated, as shown in Scheme 1.

The reactions of **1** with R_3SnCl (R = Me, Et, Bu), $SnCl_4$ and SbI_3 were undertaken as representatives of main-group organometallic precursors. In all cases after addition of the halide, but prior to work-up, a sample was withdrawn from the reaction mixture and ^{19}F-NMR spectra were recorded. These spectra showed that the signal at ca. −73 ppm due to CF_3CH_2Cl had been replaced with two doublets within the chemical shift range −65 to −90 ppm. The positions of these signals and the magnitude of the coupling between them are similar to that observed for compounds **2** and **3**, and are indicative that chlorodifluorovinyl complexes have been prepared. After work-up, mobile liquid products were isolated in yields of 70%, or better, which analysed as $R_3Sn(CCl{=}CF_2)$ [R = Me (**4**), Et (**5**), Bu (**6**)], $Sn(CCl{=}CF_2)_4$ (**7**) and $Sb(CCl{=}CF_2)_3$, (**8**). For compound **7** the elemental analysis figures suggest that a small amount of solvent is associated with the final compound, and this is confirmed by the observation of low-intensity signals in the proton NMR spectrum; this corresponds to hexane. Even after redistillation of this material a small amount of solvent appears to remain associated with this compound. Although it was not possible to obtain crystallographic data for any of these liquid materials, unequivocal identification of all the compounds was obtained by a combination of spectroscopic methods and elemental analyses.

In all cases the products obtained appear to be neither air nor moisture sensitive. Indeed, after shaking with water the starting compound can be recovered. The tin-containing materials also appear to be able to act as effective transfer reagents of the chlorodifluorovinyl group. For example, when $HgCl_2$ was treated with one equivalent of $Bu_3Sn(CCl{=}CF_2)$ in ethanol the subsequent NMR data confirmed that a reaction had taken place. The signals due to $Bu_3Sn(CCl{=}CF_2)$ were no longer present, instead two doublets were observed at −78.6 and −84.0 ppm. Both signals show coupling to a mercury nucleus [$|J(\mathrm{HgF})| = 418$ and 105 Hz respectively] and on this basis the signals may be assigned to the *mono*-substituted, rather than bis-substituted, chlorodifluorovinyl mercury complex **3**. We are currently undertaking a wider investigation of the chemistry of these compounds.

The potential utility of **1** for the synthesis of transition-metal chlorodifluorovinyl complexes was also investigated. Prototypical reactions with the late-transition-metal halides $[NiCl_2(PBu_3)_2]$, $[PdCl_2(PBu_3)_2]$ and $[AuCl(PPh_3)]$ were undertaken at low temperature. In each case NMR spectra recorded after work-up indicated that reaction had occurred. For example the product of reaction between $[NiCl_2(PBu_3)_2]$ and **1** in a 1:2 stoichiometric ratio after work-up is a low melting-point, golden-brown coloured solid, which is confirmed as $[Ni(PBu_3)_2(CCl{=}CF_2)_2]$ (**9**) by elemental analysis. The ^{31}P-NMR spectrum of a sample dissolved in $CDCl_3$ exhibits a triplet at 10.3 ppm [$J(\mathrm{PF}) = 6.5$ Hz] which is shifted slightly from that observed for the starting metal complex. The ^{19}F-NMR spectrum shows a doublet [$J(\mathrm{FF}) = 75$ Hz] of triplets [$J(\mathrm{PF}) = 6.5$ Hz] at −72.8 ppm and a doublet [$J(\mathrm{FF}) = 75$ Hz)] at −96.6 ppm. The observation of triplet-based signals in the fluorine NMR spectrum due to phosphorus–fluorine coupling suggests that the two phosphines are equivalent. The fact that P–F coupling is observed on only one of the two signals in the fluorine NMR spectrum is used to assign the resonance at −72.8 ppm to the fluorine nucleus *trans* to the metal-coordinated phosphine (F1).

A similar reaction was performed between **1** and *trans*-$[PdCl_2(PBu_3)_2]$ in a 2:1 ratio which, after work-up, yielded a solid yellow product. The ^{31}P-NMR spectrum of this compound exhibited a multiplet at ca. 9.4 ppm, which is, again, only slightly shifted from that of the starting complex at $\delta = 11.1$ ppm. This multiplet appears to be a quintet, with a measured coupling constant of 5 Hz, which presumably arises from coupling to both the F1 and F2 fluorine nuclei of two chlorodifluorovinyl groups with coupling constants of similar magnitude. The ^{19}F-NMR spectrum shows two resonances at −77.5 and −95.8 ppm. Both of these signals show mutual F–F coupling of 72 Hz and a smaller triplet coupling of 5 Hz corresponding to $J(\mathrm{PF})$. These observations are consistent with a bis-substituted product which is confirmed as $[Pd(CCl{=}CF_2)_2(PBu_3)_2]$ (**10**) by elemental analysis.

Slow evaporation of the solvents from a mixed solvent (dichloromethane and hexane) solution of **10** resulted in crystals suitable for X-ray diffraction studies. Solution of the data resulted in the molecular geometry shown in Fig. 2 and selected bond distances and angles are presented in Table 2. A *trans*-arrangement of the pairs of ligands in an essentially square-planar geometry at the palladium centre is observed with C1–Pd–P1 = 90.8(3)°. This is consistent with the interpretation of the solution-phase NMR data. The Pd–P and Pd–C bond lengths were determined as 2.294(3) and 2.036(10) Å respectively. These distances are not very different from those found in related systems; the Pd–P distance is a little shorter than the average of a series of *trans*-phosphine palladium(II) complexes from the Cambridge Structural database at 2.331 Å, and the Pd–C distance is also just below the average palladium(II)–C distance of 2.058 Å [17]. Within the chlorodifluorovinyl ligand disorder is observed around the metal-bound carbon atom (C1) with two alternative orientations for the CF_2 and Cl parts of this ligand. This resulted in two equally populated sites for the C2 and Cl atoms and subsequently two alternative sites for each of the fluorine atoms. Similar disorder problems have been reported previously within the vinyl section of the related systems *trans*-$[\mathrm{PtCl(PEt_2Ph)_2(CH{=}CH_2)}]$ [18] and *trans*-$[\mathrm{Ni(CCl{=}CCl_2)_2(PMe_2Ph)_2}]$ [19]. Within experimental limits the bond lengths obtained from the chlorodifluorovinyl groups in the two sites are the same, 1.26(2) [*d*(C=C)], 1.846(17) [*d*(C–Cl)] and 1.29(2) [*d*(C2–F1)] and 1.35(3) Å [*d*(C2–F2)]. Although the two C–F distances are different this is only just significant at the 2σ level. The C=C and C–Cl distances are both slightly longer than those observed for compound **3** and the F1–C–F2 angle is again significantly smaller than 120° [109.9(18)°].

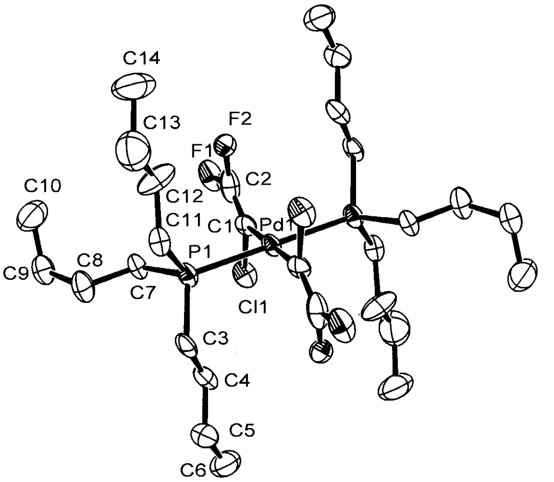


Fig. 2. The molecular structure of *trans*-$[\mathrm{Pd(CCl{=}CF_2)_2(PBu_3)_2}]$ (**10**), thermal ellipsoids are shown at the 30% probability level and hydrogen atoms have been omitted for clarity. Disorder was observed for the chlorodifluorovinyl ligand resulting in two equally populated sites for atoms C2, F1, F2 and Cl1, for clarity only one site for each moiety is shown.

Table 2
Selected bond lengths (Å) and angles (°) for *trans*-$[\mathrm{Pd(CCl{=}CF_2)_2(PBu_3)_2}]$ (**10**) [a]

Pd(1)–C(1)	2.036(10)
Pd(1)–P(1)	2.294(3)
Cl(1)–C(1)	1.846(17)
C(2)–C(1)	1.26(2)
C(2)–F(1)	1.29(2)
C(2)–F(2)	1.35(3)
C(1)–Pd(1)–C(1) # 1	180.000
C(1)–Pd(1)–P(1)	90.8(3)
C(1) # 1–Pd(1)–P(1)	89.2(3)
C(1)–C(2)–F(1)	134(2)
C(1)–C(2)–F(2)	115(2)
F(2)–C(2)–F(1)	109.9(18)
C(2)–C(1)–Cl(1)	109.2(13)
C(2)–C(1)–Pd(1)	134.3(12)
Cl(1)–C(1)–Pd(1)	116.4(6)

[a] Symmetry transformations used to generate equivalent atoms: # 1 $-x+2$, $-y$, $-z+2$.

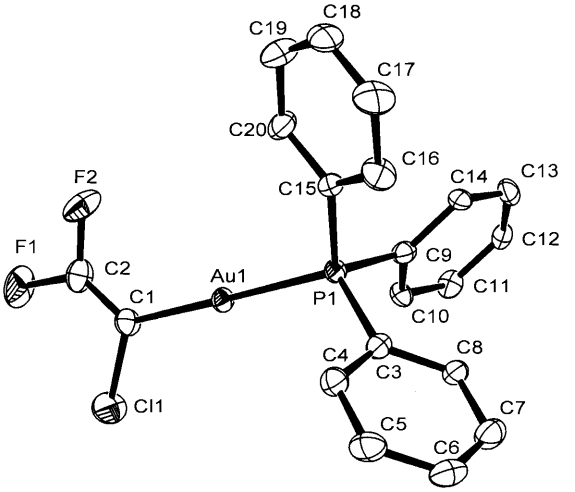


Fig. 3. The molecular structure of $[\mathrm{Au(CCl{=}CF_2)PPh_3}]$ (**11**), thermal ellipsoids are shown at the 30% probability level and hydrogen atoms have been omitted for clarity.

The reaction between **1** and $[\mathrm{AuCl(PPh_3)}]$ was also undertaken. After work-up a light brown coloured solid was obtained which is light sensitive, but otherwise stable. Elemental analysis suggests a formulation of this complex as $[\mathrm{Au(CCl{=}CF_2)(PPh_3)}]$ (**11**), and this is supported by NMR data. The ^{31}P-NMR spectrum consists of a doublet at 42.5 ppm ($J = 18$ Hz) and the ^{19}F-NMR spectrum exhibits a doublets of doublets at -79.1 ppm and a doublet at -89.9 ppm. Both signals show mutual fluorine–fluorine ($J = 53$ Hz) whilst only one of them (the signal at -79.1 ppm) shows additional coupling ($J = 18$ Hz) to the phosphorus nucleus. Crystals of the product suitable for X-ray diffraction studies were obtained by slow evaporation of the solvent from a chloroform–hexane solution in the dark. Solution of the data resulted in a gold complex exhibiting a two-coordinate, near-linear [P–Au–C = 178.7(3)°] structure as shown in Fig. 3. The Au–P distance, Table 3, is 2.266(2) Å and the Au–C distance is 2.026(10) Å. Once again these distances are slightly shorter than the average of those found in related complexes; 2.277 Å for the average gold(I)–triphenylphosphine distance and 2.097 Å for the average Au–C distance [17]. Within the chlorodifluorovinyl ligand the C=C bond length is 1.281(15) Å, the C–Cl and C–F distances are 1.731(10), 1.341(12) and 1.319(14) Å respectively and the F1–C–F2 angle is 106.9(10)°. The two C–F distances are just within 2σ of each other, although it is interesting to note that in this case it is the C–F bond *trans* to the metal which is the longer; this is the reverse of the situation found for the mercury complexes $Hg(CCl{=}CF_2)Cl$ and $Hg(CF{=}CF_2)_2$ [10] but is consistent with the distances obtained for **10**.

Table 3
Selected bond distances (Å) and angles (°) for $[Au(CCl{=}CF_2)PPh_3]$ (**11**)

Au(1)–C(1)	2.026(10)
Au(1)–P(1)	2.266(2)
Cl(1)–C(1)	1.731(10)
F(1)–C(2)	1.341(12)
F(2)–C(2)	1.319(14)
C(1)–C(2)	1.281(15)
C(1)–Au(1)–P(1)	178.7(3)
C(2)–C(1)–Cl(1)	114.5(8)
Cl(1)–C(1)–Au(1)	120.6(6)
C(1)–C(2)–F(2)	125.2(10)
C(1)–C(2)–F(1)	127.9(12)
F(2)–C(2)–F(1)	106.9(10)

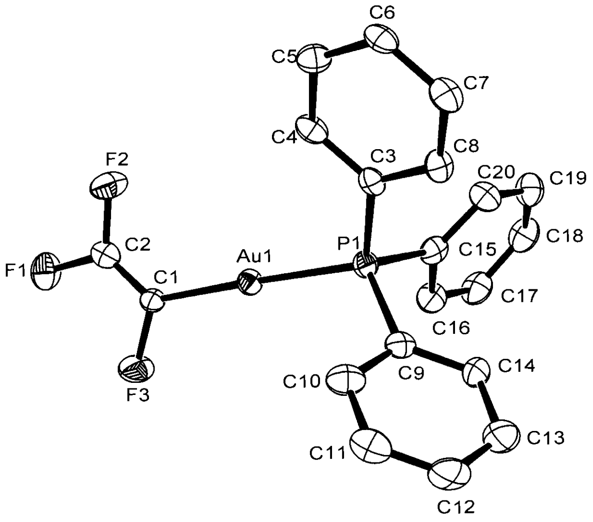


Fig. 4. The molecular structure of $[Au(CF{=}CF_2)PPh_3]$ (**12**), thermal elipsoids are shown at the 30% probability level and hydrogen atoms have been omitted for clarity.

Table 4
Selected bond distances (Å) and angles (°) for $[Au(CF{=}CF_2)PPh_3]$ (**12**)

Au(1)–C(1)	2.028(9)
Au(1)–P(1)	2.272(3)
F(3)–C(1)	1.350(11)
F(1)–C(2)	1.342(15)
F(2)–C(2)	1.304(13)
C(1)–C(2)	1.297(14)
C(1)–Au(1)–P(1)	178.1(3)
C(2)–C(1)–Cl(1)	113.5(9)
Cl(1)–C(1)–Au(1)	117.2(7)
C(1)–C(2)–F(2)	125.7(12)
C(1)–C(2)–F(1)	125.4(10)
F(2)–C(2)–F(1)	108.9(10)

These variations in C–F distances and other geometric parameters led us to try to obtain crystals for analogous perfluorovinyl complexes of the chlorodifluorovinyl complexes reported here with which direct comparisons may be made. The perfluorovinyl-containing analogues were synthesised using a similar method to that described above, but based on CF_3CH_2F (HFC-134a) from which perfluorovinyl lithium may be generated. Unfortunately most of the analogous materials were obtained as liquids or oily solids; it was, however, possible to obtain crystals suitable for structural characterisation for the perfluorovinyl-containing gold complex by the slow evaporation of the solvent from a dilute solution of $[Au(CF{=}CF_2)PPh_3]$ (**12**) in chloroform and hexane.

Solution of the data resulted in a similar structure to that found for the comparable chlorodifluorovinyl-containing complex **11**. That is a near-linear geometry is observed at the gold atom [C1–Au–P = 178.1(3)°] with Au–C1 and Au–P bond distances of 2.028(9) and 2.272(3) Å respectively (Fig. 4, Table 4). In this respect there appears to be little difference in the *trans*-effect of the chlorodifluorovinyl and perfluorovinyl ligands. Within the perfluorovinyl ligand the C=C distance is 1.297(14) Å and the three C–F distances are 1.350(11) [C1–F3], 1.304(13) [C2–F2] and 1.342(15) [C2–F1] Å. There is, therefore, no significant difference between the C=C and C–F bond distances found in the chlorodifluorovinyl and perfluorovinyl moieties in complexes **11** and **12**. The two β-C–F distances differ significantly from each other, and this behaviour is consistent with the parameters obtained for $Hg(CF{=}CF_2)_2$ in both the solid and gas phases via single-crystal X-ray diffraction and gas-phase electron diffraction studies [10]. However, for the gold complexes the effects are reversed; for $Hg(CF{=}CF_2)_2$ the carbon–fluorine bond *cis* to the metal is the longer whereas for both $[Au(CF{=}CF_2)(PPh_3)]$ and $[Au(CCl{=}CF_2)(PPh_3)]$ the opposite situation exists.

Currently it is not possible to assess, in detail, the factors that give rise to the variation in C–F bond lengths within the fluorovinyl groups. This is principally due to the very limited number of examples of such compounds which have been structurally characterised to date. It is, however, obvious on close inspection of the data that there do not appear to be any particularly close intermolecular interactions which may account for these observations. It would also appear, from the data

Table 5
Crystallographic data for complexes **3**, **10**, **11** and **12**

Compound	Hg(CCl=CF$_2$)Cl (**2**)	*Trans*-[Pd(CCl=CF$_2$)$_2$ (PBu$_3$)$_2$] (**9**)	[Au(CCl=CF$_2$) PPh$_3$] (**11**)	[Au(CF=CF$_2$) PPh$_3$] (**12**)
Formula	$C_2Cl_2F_2Hg$	$C_{28}H_{54}Cl_2F_4P_2Pd$	$C_{20}H_{15}AuClF_2P$	$C_{20}H_{15}AuF_3P$
M	333.51	705.95	556.71	540.26
Crystal system	Triclinic	Monoclinic	Monoclinic	Orthorhombic
	$P\bar{1}$	$P2(1)/n$	$P2(1)/c$	$P212121$
Unit cell parameters				
a (Å)	4.239(3)	9.4885(5)	8.7800(19)	11.403(13)
b (Å)	6.146(2)	8.544(5)	13.081(4)	11.736(14)
c (Å)	11.219(7)	22.173(11)	16.631(4)	13.433(17)
α (°)	100.06(3)	90	90	90
β (°)	95.93(5)	98.93(5)	102.105(17)	90
γ (°)	96.24(4)	90	90	90
U (Å^3)	283.8(3)	1775.8(16)	1867.6(8)	1797.6(4)
Z	2	2	4	4
D (g cm^{-3})	3.903	1.320	1.980	1.996
μ(Mo–K$_\alpha$) (mm^{-1})	27.964	0.799	8.124	8.301
Crystal size (mm)	0.20 × 0.10 × 0.05	0.15 × 0.10 × 0.10	0.15 × 0.10 × 0.10	0.30 × 0.25 × 0.20
No. data collected (θ range)	718 (3.39–24.45)	3320 (1.86–24.98)	3509 (2.00–24.96)	1806 (2.30–24.96)
F(000)	288	736	1056	1024
Maximum, minimum transmission	0.992, 0.953	0.9243, 0.8895	0.4972, 0.3754	0.2876, 0.1897
Temperature (K)	293(2)	203(2)	203(2)	203(2)
R_1, wR_2 [$I > 2\sigma(I)$]	0.0725, 0.1686	0.0687, 0.1179	0.0447, 0.1068	0.0315, 0.0.623
R_1 (all data)	0.0804	0.1717	0.0651	0.0411
Maximum, minimum residual electron density (e Å^{-3})	3.034, −2.252	0.594, −0.660	1.646 and −1.440	1.029 and −0.984

obtained for the gold complexes, that the substitution of the halogen on the α-carbon of the fluorovinyl group does not have a major impact on the structure and bond lengths within the remainder of the molecule.

In conclusion, we report a high-yielding, one-pot synthetic method based on CF_3CH_2Cl (HCFC-133a) for the synthesis of chlorodifluorovinyl-containing organometallic complexes via the intermediacy of the lithium reagent Li$^+$CCl=CF$_2$ (**1**). This method provides a reasonably straightforward route to these complexes and we have shown that this route appears to be of general utility. We have prepared and characterised a number of main group and transition metal chlorodifluorovinyl-containing complexes and report the single-crystal X-ray derived structures of three of these; this provides the first crystallographic data for complexes of this type.

3. Experimental

HCFC-133a, HFC-134a (both ICI Klea), butyllithium (2.5 M in hexane, Aldrich) and metal halides were used as supplied after verification of purity. Platinum, palladium and gold starting complexes were prepared from the appropriate halometallate salt (Johnson Matthey) based on literature methods [20]. Diethyl ether and THF were dried by standing over sodium wire for ca. 1 day and subsequently refluxed over sodium–benzophenone under a dinitrogen atmosphere. Hexane was stored over sodium wire prior to use. Fluorine, proton, phosphorus and mercury NMR spectra were recorded on solutions of samples on a Bruker DPX200 instrument at 188.3, 200.2, 81.0 and 35.8 MHz and referenced against $CFCl_3$, TMS, 85% H_3PO_4 and $HgMe_2$ respectively using the high-frequency-positive convention. Elemental analyses were performed by the analytical service in the department. IR spectra were recorded on a Nicolet PC5 or Nexus instrument. All reactions were carried out under anaerobic and anhydrous conditions. All glassware was flame dried prior to use, and moisture-sensitive reagents were handled under an argon atmosphere in a dry-box (Belle Technology, UK). All recorded reaction temperatures are uncorrected temperatures measured using an internal thermocouple.

*3.1. X-ray data for compounds **10**, **11** and **12***

X-ray data for compounds **9**, **11a** and **11b** were collected at low temperature on a Nonius MACH3 diffractometer, details are given in Table 5. The data for complex **3** were collected at room temperature at the EPSRC X-ray service using a Nonius Kappa CCD area detector mounted on a Nonius FR591 diffractometer. The data for all the compounds was solved using direct methods (SHELXS [21]). The structures were refined by full-matrix least-squares on F_o^2, using the program SHELX-97. All data used were corrected for Lorentz-polarisation factors and subsequently for absorption by the ψ-scan method, except for **3**, where the multscan method was used. The non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms in the compounds were included in idealised positions and were refined isotropically. For compound **10** disorder was observed in the chlorodifluorovinyl part of the complex and this was modelled by including two equally occupied split sites for the ligand and refining this isotropically.

3.2. Preparation of bis(chlorodifluorovinyl)mercury (2)

A 250 ml three-neck flask held at -80°C was equipped with a magnetic stirrer, a rubber septum and a silicon oil bubbler and maintained under a positive flow of dinitrogen gas. The flask was charged with pre-cooled diethyl ether (200 ml, -50°C) and liquid HCFC-133a ($d = 1.389$ g cm^{-3}, 0.80 cm^3, 9.36 mmol) was added. Butyllithium (2.5 M in hexane, 7.52 cm^3, 18.8 mmol) was added slowly to the stirred solution over a 0.5 h period. Once addition of the BuLi was complete the reaction temperature was maintained between -55°C and -80°C for 2 h to ensure generation of $CF_2{=}CF^-Li^+$. After lowering the reaction mixture temperature to -110°C mercury(II) chloride (1.26 g, 4.64 mmol), dissolved in THF (200 ml, -80°C), was added slowly. The reaction was left to warm to -35°C over a period of a few hours and then allowed to attain room temperature by removal of the slush bath. The solvent volume was reduced in vacuo to half and hexane (300 ml) was added resulting in the precipitation of lithium salts, from the organic phase. The mixture was allowed to settle before being carefully filtered through a No. 4 sinter under a dinitrogen atmosphere. The solvent was then removed in vacuo to leave a brown liquid which was subsequently washed with hexane (4 × 10cm^3), and vacuum distilled (180–185°C, 10 mmHg) to afford **2** as a clear liquid. Yield 1.61 g, 88%. (Anal. Found: C, 12.9; H, 0.2; Cl, 20.1. $Hg(CCl{=}CF_2)_2$ requires: C, 12.2; H, 0.0; Cl, 18.0%.) δ^{19}F(CDCl$_3$), -75.5 [d, J(FF) = 44, J(HgF) = 247 Hz], -85.2 [d, J(FF) = 44, J(HgF) = 131 Hz]. δ^{199}Hg (CDCl$_3$), 701.8 [dd, J(HgF1) = 251, J(HgF2) = 135 Hz]. ν_{max} (cm^{-1}) (neat liquid) 1686 (C=C), 1258, 992 (C–F).

3.3. Chloro(chlorodifluorovinyl)mercury (3)

In an analogous method to that described for **2**, BuLi 2.5 M (5.9 cm^3, 14.75 mmol) was slowly added to a solution of HCFC-133a (0.63 cm^3, 7.38 mmol) in diethyl ether (180 ml, -80°C). After approximately 2 h $HgCl_2$ (2.00 g, 7.36 mmol), dissolved in THF (250 ml, -80°C), was added slowly to the reaction mixture which was held at -110°C. After the reaction was complete it was worked up as previously described to yield an oily solid material which was washed with hexane to leave a white solid. Yield 2.14 g, 87%. m.p. (uncorrected) 150°C dec. (Anal. Found: C, 7.6; H, 0.0; Cl, 20.8. $Hg(CCl{=}CF_2)Cl$ requires: C, 7.2; H, 0.0; Cl, 21.3%.) δF(CDCl$_3$), -78.4 [d, J(FF) = 40.8, J(HgF) = 416.0 Hz], -83.9 [d, J(FF) = 40.8, J(HgF) = 102.5 Hz]. δ^{199}Hg (CDCl$_3$), 701.8 [dd, J(HgF1) = 414.4, J(HgF2) = 100.7 Hz. ν_{max} (cm^{-1}) (CHCl$_3$ solution) 1699 (C=C), 1273, 995 (C–F).

3.4. Trimethyl(chlorodifluorovinyl)tin (4)

In a similar procedure to that outlined above, cold liquid HCFC-133a (0.86 cm^3, 10.0 mmol) in hexane (150 ml) was added to butyllithium (2.5 M in hexane, 8.0 cm^3, 20.0 mmol) over a 0.5 h period. After 2 h the temperature of the reaction mixture was lowered to -100°C and trimethyltinchloride (1 M in CH$_2$Cl$_2$, 10.0 cm^3, 10.0 mmol) was added slowly. After warming to room temperature the solvent volume was reduced and hexane was added. The mixture was filtered under a dinitrogen atmosphere and the volatile organic solvents were removed in vacuo. Trap to trap distillation under reduced pressure (0.2 mmHg) resulted in the separation of the product as a clear liquid. Yield 2.12 g, 81%. Mass spec., EI, $m/z = 262$ (M$^+$, 5%), 165 (Me$_3$Sn$^+$, 10%). δ^{19}F (CDCl$_3$), -72.0 [d, J(FF) = 42 Hz, J(SnF) = 6.4 Hz], -87.2 [d, J(FF) = 42 Hz]. δ^1H (CDCl$_3$), 0.39 [s, J(^{117}SnH) = 56.1 Hz, J(^{119}SnH) = 58.6 Hz]. ν_{max} (cm^{-1}) (neat liquid) 1685 (C=C), 1244, 982 (C–F).

3.5. Triethyl(chlorodifluorovinyl)tin (5)

A preparative route similar to that for **4** outlined above was used. BuLi (2.5 M, 8.4 cm^3, 21 mmol) was added to a solution of HCFC-133a (0.90 cm^3, 10.5 mmol) in diethyl ether (60 cm^3, -80°C). After 2 h Et$_3$SnBr (3.00 g, 10.5 mmol) dissolved in diethyl ether (60 cm^3, -80°C) was added slowly to the reaction mixture which was held at -110°C. The reaction was left to warm slowly to room temperature overnight. Hexane (100 cm^3) was added and the solution was filtered. The solvents were removed on a rotary evaporator to leave a light brown coloured liquid. Distillation at 182°C/0.2 mmHg resulted in the separation of the product as a clear liquid. Yield 2.68 g, 84%. (Anal. Found: C, 33.7; H, 5.3. $Et_3Sn(CCl{=}CF_2)$ requires: C, 31.7; H, 5.0%.) δ^{19}F (CDCl$_3$), -72.2 [d, J(FF) = 46 Hz], -87.2 [d, J(FF) = 46 Hz, J(SnF) = 14 Hz]. ν_{max} (cm^{-1}) (neat liquid) 1686 (C=C), 1243, 980 (C–F).

3.6. *Tributyl(chlorodifluorovinyl)tin* (***6***)

A preparative route similar to that for **4** outlined above was used. BuLi (2.5 M, 12.0 cm^3, 30 mmol) was added to a solution of HCFC-133a (1.30 cm^3, 15.2 mmol) in diethyl ether (60 cm^3, −80°C). After 2 h Bu_3SnCl (5.00 g, 15.4 mmol) dissolved in diethyl ether (100 cm^3, −80°C) was added slowly to the reaction mixture which was held at −110°C. The reaction was left to warm slowly to room temperature overnight. Hexane (100 cm^3) was added and the solution was filtered. The solvents were removed on a rotary evaporator to leave a light brown coloured liquid. Distillation at 242°C/0.2 mmHg resulted in the separation of the product as a clear liquid. Yield 4.88 g, 84%. (Anal. Found: C, 44.5; H, 6.9; Cl, 8.1. $Bu_3Sn(CCl{=}CF_2)$ requires: C, 43.4; H, 7.0; Cl, 9.2%.) δ ^{19}F ($CDCl_3$), −72.2 [d, J(FF) = 47 Hz], −87.2 [d, J(FF) = 47, J(SnF) = 20 Hz]. ν_{max} (cm^{-1}) (neat liquid) 1680 (C=C), 1240, 980 (C–F).

3.7. *Tetrakis(chlorodifluorovinyl)tin* (***7***)

A preparative route similar to that for **4** outlined above was used. BuLi (2.5 M, 63.6 cm^3, 159 mmol) was added over a 3 h period to a solution of HCFC-133a (6.8 cm^3, 79.7 mmol) in diethyl ether (150 cm^3, −80°C). After 2 h $SnCl_4$ (5.00 g, 19.2 mmol) dissolved in THF (100 cm^3, −80°C) was added slowly to the reaction mixture which was held at −110°C. The reaction was left to warm slowly to room temperature overnight. Hexane (100 cm^3) was added and the solution was filtered. The solvents were removed on a rotary evaporator to leave a light brown coloured liquid. Distillation at 120°C/0.2 mmHg resulted in the separation of the product as a clear liquid. Yield 7.52 g, 77%. (Anal. Found: C, 20.1; H, 0.1; Cl, 26.9. $Sn(CCl{=}CF_2)_4$ requires: C, 18.9; H 0.0; Cl, 27.9%.) δ ^{19}F ($CDCl_3$), −66.8 [d, J(FF) = 20 Hz, J(SnF) = 69 Hz], −79.2 [d, J(FF) = 20 Hz]. ν_{max} (cm^{-1}) (neat liquid) 1678 (C=C), 1271, 1001 (C–F).

3.8. *tris(Chlorodifluorovinyl)antimony* (***8***)

A preparative route similar to that for **4** outlined above was used. BuLi (2.5 M, 14.5 cm^3, 36.3 mmol) was added to a solution of HCFC-133a (1.55 cm^3, 18.2 mmol) in diethyl ether (60 cm^3, −80°C). After 2 h SbI_3 (3.00 g, 5.98 mmol) dissolved in THF (60 cm^3, −80°C) was added slowly to the reaction mixture which was held at −110°C. The reaction was left to warm slowly to room temperature overnight. Hexane (80 cm^3) was added and the solution was filtered. The solvents were removed on a rotary evaporator to leave a brown coloured liquid. Distillation at 195°C/40 mmHg resulted in the separation of the product as a clear liquid. Yield 1.72 g, 69%. (Anal. Found: C, 18.0; H 0.0; Cl, 25.9%. $Sb(CCl{=}CF_2)_3$ requires: C, 17.4; H, 0.0; Cl, 25.7%.) δ ^{19}F ($CDCl_3$), −67.8 [d, J(FF) = 23 Hz], −79.5 [d, J(FF) = 23 Hz]. ν_{max} (cm^{-1}) (neat liquid) 1680 (C=C), 1271, 992 (C–F).

3.9. *[bis(Tributylphosphine)bis(chlorodifluorovinyl)nickel]* (***9***)

[bis(Tributylphosphine)nickeldichloride] was prepared by the reaction of nickel dichloride with two equivalents of tributylphosphine in ethanol. In a 250 ml round bottom flask equipped as described previously BuLi (2.5 M, 1.6 cm^3, 4 mmol) was added to a solution of HCFC-133a (0.17 cm^3, 2 mmol) in diethyl ether (180 cm^3, −80°C). After 2 h $[NiCl_2(PBu_3)_2]$ (0.53 g, 1 mmol) dissolved in THF(25 cm^3, −80°C) was added slowly to the reaction mixture the temperature of which was held at −110°C. The reaction was left to warm slowly to room temperature overnight. Hexane (100 cm^3) was added and the solution was filtered. The solvents were removed on a rotary evaporator to leave a light yellow coloured oil. Yield 0.24g, 36%, m.p. (uncorrected) 84–88°C, dec. (Anal. Found: C, 51.7; H, 8.4; F, 10.9. $[Ni(PBu_3)_2(CCl{=}CF_2)Cl]$ requires: C, 51.1; H, 8.2; F, 11.5%.) δP{^{1}H}($CDCl_3$), 10.3 ppm [d, J(PF) = 6.5 Hz]. δ ^{19}F ($CDCl_3$) −72.8 [dt, J = 6.5, 75 Hz], −96.6 [d, J = 75 Hz]. ν_{max} (cm^{-1}) (nujol mull) 1684 (C=C), 1197, 954 (C–F).

3.10. *trans-[bis(Tributylphosphine)bis-(chlorodifluorovinyl)palladium]* (***10***)

Trans-[bis(tributylphosphine)palladiumdichloride] was prepared by the reaction of disodium tetrachloropalladate with two equivalents of tributylphosphine in water. In a 250 ml round bottom flask equipped as described previously BuLi (2.5 M, 8.8 cm^3, 22 mmol) was added to a solution of HCFC-133a (0.95 cm^3, 11 mmol) in diethyl ether (180 cm^3, −80°C). After 2 h $[(PBu_3)_2PdCl_2]$ (3.00 g, 5.2 mmol) dissolved in THF (25 cm^3, −80°C) was added slowly to the reaction mixture which was held at −110°C. The reaction was left to warm slowly to room temperature overnight after which hexane (100 cm^3) was added and the solution was filtered. The solvents were removed on a rotary evaporator to leave a light yellow–brown coloured solid. Yield 2.75 g, 75%, m.p. (uncorrected) 91–93°C, dec. (Anal. Found: C, 47.9; H, 7.6; F, 10.4. $[Pd(PBu_3)_2(CCl{=}CF_2)_2]$ requires: C, 47.6; H, 7.7; Cl, 10.0; F, 10.8%.) δP{^{1}H}($CDCl_3$), 9.4 [quintet, J = 5 Hz]. δ ^{19}F ($CDCl_3$), −77.5 [ddt, J = 72, 25, 5 Hz], −95.8 [ddt, J = 72, 25, 5 Hz]. ν_{max} (cm^{-1}) (nujol mull) 1686 (C=C), 1202, 955 (C–F).

3.11. [Triphenylphosphine(chlorodifluorovinyl)gold] (**11**)

Triphenylphosphinegold chloride was prepared by the reaction of sodium tetrachloroaurate with triphenylphosphine in ethanol [20]. In a 250 ml round bottom flask equipped as described previously BuLi (2.5 M, 4.9 cm^3, 12.3 mmol) was added to a solution of HCFC-133a (0.52 cm^3, 6.1 mmol) in diethyl ether (180 cm^3, −80°C). After 2 h [$AuCl(PPh_3)$] (3.02 g, 6.1 mmol) dissolved in THF (25 cm^3, −80°C) was added slowly to the reaction mixture which was maintained at −110°C. The reaction was left to warm slowly to room temperature overnight. Hexane (100 cm^3) was added and the solution was filtered. The solvent2s were removed on a rotary evaporator to leave a light brown coloured solid. Yield 2.54 g, 75%. (Anal. Found: C, 43.0; H, 3.0; F, 6.7. [$Au(PPh_3)$]-($CCl{=}CF_2$)] requires: C, 43.2; H, 2.7; F, 6.8%.) $\delta\,^{31}P$-$\{^1H\}$($CDCl_3$), 42.5 ppm [m]. $\delta\,^{19}F$ ($CDCl_3$), −79.1 [dd, $J=$ 53, 18 Hz], −89.9 [d, $J=53$ Hz]. ν_{max} (cm^{-1}) (nujol mull) 1670 (C=C), 1219, 963 (C–F).

3.12. [Triphenylphosphine(perfluorovinyl)gold] (**12**)

This compound was prepared in a similar way to that described above for **12**. BuLi (2.5 M, 5.2 cm^3, 12 mmol) was added to a solution of HFC-134a ($d=1.21$ g cm^{-1}, 0.5 cm^3, 6 mmol) in diethyl ether (180 cm^3, −80°C). After 2 h [$AuCl(PPh_3)$] (2.97 g, 6.0 mmol) dissolved in THF (25 cm^3, −80°C) was added slowly to the reaction mixture which was held at −110°C. The reaction was left to warm slowly to room temperature overnight, hexane (100 cm^3) was added and the solution was filtered. The solvents were removed on a rotary evaporator to leave an off-white coloured solid. Yield 1.95 g, 60%, m.p. (uncorrected) 86–88°C, dec. (Anal. Found: C, 44.4; H, 4.1; F, 10.9. [$Au(PPh_3)(CF{=}CF_2)$] requires: C, 44.5; H, 2.8; F, 10.6%.) $\delta\,^{31}P\{^1H\}$ ($CDCl_3$) 42.2 ppm [m]. $\delta\,^{19}F$ ($CDCl_3$), −95.5 [ddd, $J=14, 35, 87$ Hz], −127.3 [ddd, $J=4, 87, 99$ Hz], −177.0 ppm [ddd, $J=35, 69, 99$ Hz]. ν_{max} (cm^{-1}) (nujol mull) 1698 (C=C), 1248, 1100, 986 (C–F).

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Database as supplementary publication numbers CCDC 144498–144501. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge, CB2 1E2, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We acknowledge ICI Klea for the donation of CFC-replacements, Johnson Matthey for the loan of metal salts, the Royal Society for a research grant and the EPSRC for the provision of grants for UMIST's NMR (GR/L52246) and FT-IR/Raman (GR/M30135) facilities, also for access to the X-ray structural database, and to the national X-ray Crystallography Data Collection Service, for compound **3**.

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