Hydrogen Bonding | Hot Paper

Platinum-Catalyzed Hydrofluorination of Alkynes: Hydrogen Bonding to Indolylphosphine Ligands to Provide Fluoride Reactivity

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Dedicated to Holger Braunschweig on the occasion of his 60th birthday.

Abstract: The reaction of the Pt complexes *cis*-[Pt-(CH$_3$)$_2$\{R$_2$P(Ind)\}$_2$] (Ind = 2-(3-methyl)indolyl, R = Ph (**1a**), 4-FC$_6$H$_4$ (**1b**), 4-CF$_3$C$_6$H$_4$ (**1c**)) with HF afforded the fluorido complexes *trans*-[Pt(F(HF)$_2$)(CH$_3$)\{R$_2$P-(Ind)\}$_2$] **2a–c**, which can be converted into *trans*-[Pt(F)-(CH$_3$)\{R$_2$P(Ind)\}$_2$] (**3a–c**) by treatment with CsF. Addition of 3-hexyne to **2a–c** gave alkyne complexes *trans*-[Pt(*C,C*-η^2-C$_2$H$_5$*C*≡*C*C$_2$H$_5$)(CH$_3$)\{R$_2$P(Ind)\}$_2$\{F(HF)$_2$\}] (**4a–c**) at which a fluoride is stabilised as polyfluoride in the coordination sphere by hydrogen bonding to the indolyl-substituted phosphine ligands. Subsequent heating of a solution of **4a** in the presence of PVPHF led to fluoroalkene formation. Selective catalytic hydrofluorination of alkynes to yield (*Z*)-fluoroalkenes were developed. The ability of hydrogen bonding to polyfluoride favours the fluorination step as demonstrated by studies with complexes bearing no indolyl groups at the phosphine ligands.

Introduction

The development of new routes for the selective fluorination of organic molecules is of enormous importance for the production of new materials as well as agricultural and biomedical compounds.[1] Among numerous fluorination reagents, direct fluorination with hydrogen fluoride represents an important method to incorporate fluorine atoms into organic molecules.[2] An approach of particular interest involves selective hydrofluorination reactions of alkynes to give monofluoroalkenes. The latter can be considered as isosteric building blocks to a peptide moiety,[3] and their incorporation led to the development of various bioactive compounds.[4] Often, direct addition of hydrogen fluoride to an alkyne provides the corresponding *gem*-difluoroalkane.[5]
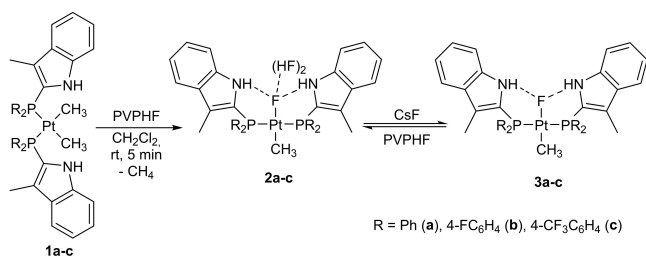
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Pioneering work by Sadighi et al. demonstrated the selective hydrofluorination of alkynes to provide (*Z*)-fluoroalkenes catalysed by Au^I complexes.[6] This work was extended in recent years by the groups of Miller et al., Hammond, Xu et al., Nolan et al., Toste et al., Paquin et al. and Crimmin et al.[7] Ynamides can also be transferred via Cu^I- and Ag^I-catalysed reactions.[8] However, all previous studies on non-activated alkynes are concerned on using Au^I complexes, solely. It has been suggested that electrophilic gold centres play a crucial role to coordinate and activate the alkyne.[9] Note also that recently, Liu and Wang et al. described a hydrofluorination of aryl substituted alkynes with protic tetrafluoroborates to access both the *E* and *Z* isomers of vinyl fluorides.[10] Apart from alkyne hydrofluorination, various other strategies for the synthesis of fluorinated olefins have been described in the literature.[11]

We recently demonstrated the applicability of Pt complexes bearing 2-(3-methyl)indolyl-substituted phosphine ligands to stabilise poly(hydrogen fluoride) anions in the outer coordination sphere.[12] In the present contribution we report on an unprecedented strategy for catalytic hydrofluorination reactions of alkynes on using Pt^{II} complexes bearing cooperating indolyl phosphine ligands. Model reactions provided access to complexes bearing a pendant fluoride in the coordination sphere, which is hydrogen-bonded to indolyl moieties. After alkyne coordination outer-sphere fluorination[13] allows for hydrofluorination steps in the presence of a proton source.

Results and Discussion

Treatment of the dimethyl indolylphosphine complexes *cis*-[Pt(CH$_3$)$_2$\{R$_2$P(Ind)\}$_2$] (Ind = 2-(3-methyl)indolyl, R = Ph (**1a**), 4-FC$_6$H$_4$ (**1b**), 4-CF$_3$C$_6$H$_4$ (**1c**)) with Poly[4-vinylpyridinium poly(hydrogen fluoride)] (PVPHF) led to protonation of one methyl ligand and resulted in the formation of the moisture- and air-stable polyfluorido complexes *trans*-[Pt(F(HF)$_2$)(CH$_3$)\{R$_2$P(Ind)\}$_2$] **2a–c** (Scheme 1). Note that Seppelt et al. also obtained methyl fluoride complexes after treatment of dimethyl platinum complexes with anhydrous HF.[14] The fluoride-bound HF in **2a–c** can be removed by treating the reaction solution with CsF to yield the fluorido complexes *trans*-[Pt(F)(CH$_3$)\{R$_2$P(Ind)\}$_2$] (**3a–c**). Complexes **2a–c** can be recovered upon treating **3a–c** with PVPHF.

Triplet of triplets with ^{195}Pt satellites were found for the fluorido ligands in the ^{19}F NMR spectra of **3a–c** due to

Scheme 1. Formation of platinum fluorido complexes **2a–c** and **3a–c**.

Figure 2. Molecular structure of **2b**. Thermal ellipsoids are drawn at 50% probability level; hydrogen bonds are depicted as magenta dashed lines. Carbon-bound hydrogen atoms were omitted for clarity. Selected distances [Å] and angles [°]: Pt1–F1 2.1466(13), N1···F1 2.609(2), N2···F1 2.604(2); P1-Pt1-F1 90.20(4), N1-H1···F1 155(3), N2-H2···F1 157(3).

Figure 1. Parts of the ^{19}F NMR (bottom) and ^{19}F{^{1}H} NMR spectra (top) of **3b**, coupling constants: $^1J(F,H) = 52$ Hz, $^2J(F,P) = 12$ Hz, $^1J(F,Pt) = 537$ Hz.

coupling with the N*H* protons and the two phosphorus atoms (Figure 1). The observed chemical shifts between −268.0 ppm–−264.0 ppm and the $^2J(F,P)$ coupling constants of 12.1–12.7 Hz are typical values for Pt bound fluorido ligands with phosphine ligands in a mutually *cis* arrangement.[12,13b,c,15] Hydrogen bonding of the indolyl moieties to the fluorido ligands in **3a–c** is revealed by the $^1J(H,F)$ coupling constants (52.8–51.3 Hz, Table S2) in the ^{1}H and ^{19}F NMR spectra, the $^2J(N,F)$ coupling constants (35–36 Hz, Table S2) in the ^{1}H,^{15}N HMBC spectra as well as the strongly downfield shifted signals for the N*H* protons of the indolylphosphine ligands in the ^{1}H NMR spectra (13.09–12.91 ppm).[12,16] For **2a–c** broad signals at similar high field in the ^{19}F NMR spectra were observed, but even at low temperature couplings could not be resolved. Additional signals for the remote bound HF appear at approximately −180 ppm. The amount of pendant HF was determined by treatment of **2a–c** with Et$_3$SiCl to yield Et$_3$SiF, the amount of which was determined by integration in the ^{19}F NMR spectra. The IR spectra of **2a–c** and **3a–c** revealed broad features below 3100 cm$^{−1}$, which can be assigned to the N–H···F moieties. Note, that absorptions of N–H hydrogen bonded fluorides have been reported in a region between 3000–3150 cm$^{−1}$.[17]

Additionally, hydrogen bonding of the 2-(3-methyl)indolyl groups to the fluorido ligand is demonstrated in the molecular structure of *trans*-[Pt(F)(CH$_3$){(4-FC$_6$H$_4$)$_2$P-(Ind)}$_2$] (**3b**), which was determined by single-crystal X-ray diffraction (Figure 2).[18] Electron density which cou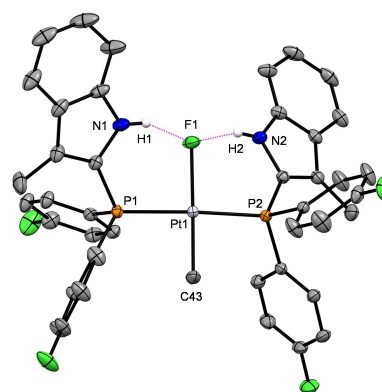ld be assigned to nitrogen bound hydrogen atoms was found in the difference Fourier map and a free refinement was allowed. The Pt(1)–F(1) bond length of 2.1466(13) Å is slightly elongated compared to the bond separations in comparable Pt^{II} fluorido complexes that feature no hydrogen bond donor groups in the ligand sphere (1.9787(14)–2.117(3) Å).[14,15c,g,19]

To assess the lability of the metal–fluorine interaction induced by the hydrogen bonds, **2a–c** were treated with 3-hexyne. The formation of the platinum(II) poly(hydrogen fluorido) alkyne complexes *trans*-[Pt(*C,C*-η^2-C$_2$H$_5$C≡CC$_2$H$_5$)(CH$_3$){R$_2$P(Ind)}$_2${F(HF)$_2$}] (R = Ph (**4a**), 4-FC$_6$H$_4$ (**4b**), 4-CF$_3$C$_6$H$_4$ (**4c**)) was observed (Scheme 2). The amount of bound HF was again determined by treatment of **4a–c** with Et$_3$SiCl. For comparison, the tetrafluoroborate analogue of **4a** *trans*-[Pt(*C,C*-η^2-C$_2$H$_5$C≡CC$_2$H$_5$)(CH$_3$){Ph$_2$P-(Ind)}$_2$(BF$_4$)] (**5a**) was also synthesised by treatment of [PtCl(CH)$_3${Ph$_2$P(Ind)}$_2$][20] with AgBF$_4$ and 3-hexyne (Scheme 2, bottom). However, when the alkyne was added to a solution of the HF-free complexes **3a–c**, no reaction occurred.

In the ^{19}F NMR spectra of **4b** a signal at $\delta = −167.4$ ppm was observed, which appears in a typical region for polyfluoride anions.[12,21] The IR spectrum reveals a strongly
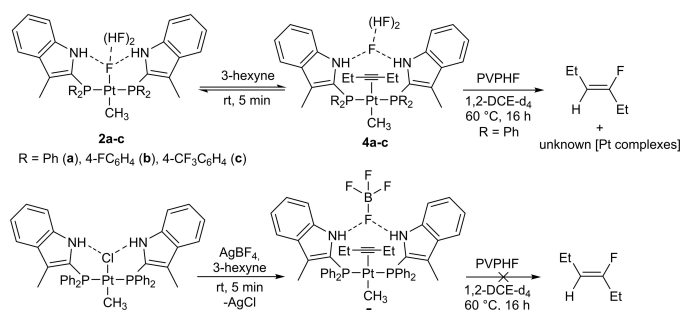
Scheme 2. Formation and reactivities of the alkyne complexes **4a–c** and **5a**.

broadened absorption and red shifted band at 3167 cm^{-1}, which can be attributed to the N–H stretches as part of the hydrogen bonding network.[12,17,22] Additional broad features were detected in the regions of 2700–2500 cm^{-1} and at around 1800 cm^{-1}, which are typical bands for polyfluoride moieties.[17,23] Analytical data for **4a** and **4c** are comparable. For **5a** the ^{19}F NMR spectrum shows a characteristic signal at $\delta = -149.4$ ppm for the tetrafluoroborate anion. For the N–H stretch in **5a** a broad absorption band at $\tilde{v} = 3356$ cm^{-1} was observed, revealing a much lower red shift than observed for **4a–c**.

Crystals of *trans*-[Pt(C,C-η^2-C$_2$H$_5$C≡CC$_2$H$_5$)(CH$_3$){(4-FC$_6$H$_4$)$_2$P(Ind)}$_2${F(HF)}] (**4b′**) suitable for single-crystal X-ray diffraction were obtained from a reaction solution containing **4b** (Figure 3).[18] **4b′** contained an FHF entity bound in the coordination sphere instead of F(HF)$_2$ as found for **4b** in solution. The metal-bound alkyne exhibits a perpendicular orientation to the plane defined by the platinum and phosphorus atoms as well as C28. The alkyne ligand deviates only slightly from linearity, which is a characteristic feature for an electron depleted alkyne ligand,
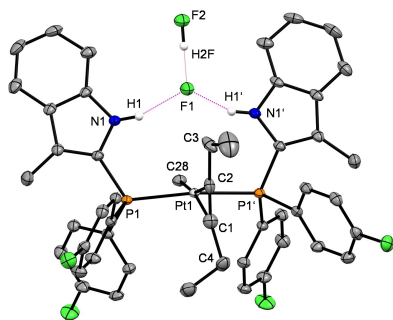

Figure 3. Structure of **4b′**. Thermal ellipsoids are drawn at 50% probability level; hydrogen bonds are depicted as magenta dashed lines. Carbon-bound hydrogen atoms were omitted for clarity. Selected distances [Å] and angles [°]: Pt1–C1 2.319(3), Pt1–C2 2.241(3), Pt1⋯F1 3.530, N1⋯F1 2.666, F1–F2 2.319; C1-Pt1-C2 30.51(12), C1-C2-C3 164.7(4), C2-C1-C4 161.7(3), N1-H1⋯F1 159, F2-H2F⋯F1 179.
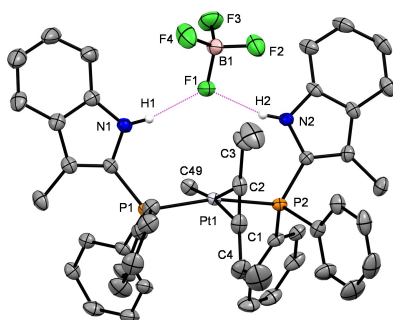

Figure 4. Structure of **5a**. Thermal ellipsoids are drawn at 50% probability level; hydrogen bonds are depicted as magenta dashed lines. Carbon-bound hydrogen atoms and a solvent molecule were omitted for clarity. Selected distances [Å] and angles [°]: Pt1–C1 2.322(5), Pt1–C2 2.244(4), Pt1⋯F1 3.553(3), N1⋯F1 2.999(5), N2⋯F1 2.954(6); C1-Pt1-C2 31.02(19), C1-C2-C3 166.1(5), C2-C1-C4 167.0(5), N1-H1⋯F1 167(6), N2-H2⋯F1 164(7).

caused by a σ-bond to the metal centre, but only weak π-acceptance bonding.[9b] The molecular structure of **5a** shows a similar arrangement of the Pt^{II}-bound alkyne (Figure 4).[18] Importantly, for both structures hydrogen bonding from the 2-(3-methyl)indolyl phosphine ligands provides ion pairing with the poly(hydrogenfluoride) and tetrafluoroborate anions in the outer coordination sphere of **4b′** and **5a**, respectively. The N1⋯F1 separations of 2.666 Å in **4b′** feature hydrogen bonding of medium strength to the fluoride, while the N1⋯F1 (2.999(5) Å) and N2⋯F1 (2.954 (6) Å) distances to the tetrafluoroborate in **5b** indicate weak(er) hydrogen bonding.[24]

The platinum alkyne complexes **4a–c** are stable in solution and no decomposition was observed when they are exposed to moisture or air. Remarkably, heating a solution of **4a** in 1,2-C$_2$D$_4$Cl$_2$ to 60°C in presence of PVPHF for 16 hours resulted in the selective formation of (*Z*-3-fluoro-3-hexene[25] (Scheme 2, top). In contrast, no hydrofluorination was observed when the tetrafluoroborate complex **5a** was heated under the same conditions in presence of PVPHF (Scheme 2, bottom). This observation suggests a considerable influence of the outer coordination sphere bound poly(hydrogen fluoride) anion on the Pt^{II}-mediated hydrofluorination step of the metal-bound alkyne.

Based on these results, catalytic hydrofluorination reactions of 3-hexyne were investigated (Table 1). Experiments with 2.5–10% **1a** as precatalyst and 2 equivalents of Et$_3$N·3HF in 1,2-dichloroethane (1,2-DCE) as solvent at temperatures of 60°C or 80°C for 72 h revealed no catalytic hydrofluorination of 3-hexyne (Table 1, entries 1–4). *ortho*-Chlorobenzoic acid (*o*-Cl-BA) was then added as a soluble co-catalyst, which presumably provides additional protons for a protodemetalation of an intermediate vinyl complex. This resulted in an increased yield of fluoroalkene formation (26% after 72 h, 5% **1a**). A reaction time of 144 h led to a slightly improved yield of 33%. Increasing the precatalyst load to 10% enhanced the fluoroalkene yield further to 65% (Table 1, entries 5–7). Note that the addition of co-catalysts like KHSO$_4$[6,7] or *para*-chlorobenzoic acid (*p*-Cl-BA)[7d] have been described for Au^I-catalysed hydrofluorination reactions. However, due to their insolubility in dichloroethane, the above-mentioned reagents did not provide an adequate improvement of fluoroalkene yields in the Pt catalysed reactions (Table 1, entries 8 and 9). *o*-Dichlorobenzene (*o*-DCB) as solvent gave similar fluoroalkene yields. Chloroform or toluene are also applicable, but yields were lower (Table 1, entries 10–12). A blank reaction without Pt catalyst did not lead to any fluorination of the alkyne. Reactions with PVPHF also showed catalytic conversion, but were more difficult to conduct, because of the heterogeneous reaction mixture. Note, that even by using additives, ^{31}P{^{1}H} NMR spectroscopic studies always revealed the formation of **4a** before heating the reaction mixtures.

The catalytic hydrofluorination of 3-hexyne was further studied, testing the complexes **1b** and **1c** as precatalysts bearing 4-FC$_6$H$_4$ or 4-CF$_3$C$_6$H$_4$ instead of C$_6$H$_5$ substituents at the phosphorus centre (Scheme 3, Table 2, entries 1–3). While **1b** gave similar yields of the fluoroalkene as **1a**, **1c**

Table 1: Screening for the catalytic hydrofluorination of 3-hexyne using cis-[Pt(CH$_3$)$_2$\{Ph$_2$P(C$_9$H$_8$N))$_2$\}] (**1a**) as precatalyst.

Entry	Load [%]	Additive	Solvent	T [°C]	t [h]	Yield [%][a]
1	2.5	*none*	1,2-DCE-d$_4$	60	72	2
2	5	*none*	1,2-DCE-d$_4$	60	72	3
3	5	*none*	1,2-DCE-d$_4$	80	72	4
4	10	*none*	1,2-DCE-d$_4$	60	72	6
5	5	*o*-Cl-BA	1,2-DCE-d$_4$	60	72	26
6	5	*o*-Cl-BA	1,2-DCE-d$_4$	60	144	33
7	10	*o*-Cl-BA	1,2-DCE-d$_4$	60	144	65
8	5	KHSO$_4$	1,2-DCE-d$_4$	60	72	3
9	5	*p*-Cl-BA	1,2-DCE-d$_4$	60	72	9
10	10	*o*-Cl-BA	*o*-DCB-d$_4$	60	144	65
11	10	*o*-Cl-BA	CDCl$_3$	60	144	54
12	10	*o*-Cl-BA	Tol-d$_8$	60	144	38
13	*none*	*o*-Cl-BA	1,2-DCE-d$_4$	60	144	0

[a] Determined from ^{19}F NMR data on using benzotrifluoride as internal standard.
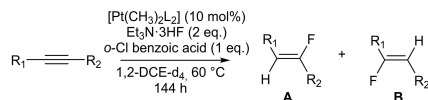
Scheme 3. Catalytic hydrofluorination of alkynes using cis-[Pt(CH$_3$)$_2$L$_2$] as precatalysts (L = Ph$_2$P(Ind) (**1a**), (4-FC$_6$H$_4$)$_2$P(Ind) (**1b**), (4-CF$_3$C$_6$H$_4$)$_2$P(Ind) (**1c**), PPh$_3$, P(4-FC$_6$H$_4$)$_3$, P(4-CF$_3$C$_6$H$_4$)$_3$.

Table 2: Pt^{II}-catalysed hydrofluorination of alkynes.[a]

Entry	Complex	R$_1$	R$_2$	Yield [%][b]	A:B
1	**1a**	Et	Et	65 (67)[c]	–
2	**1b**	Et	Et	64	–
3	**1c**	Et	Et	43	–
4	**3a**	Et	Et	63	–
5	**5a**	Et	Et	19	–
6	cis-[Pt(CH$_3$)$_2$(PPh$_3$)$_2$][27]	Et	Et	42	–
7	cis-[Pt(CH$_3$)$_2$\{P(4-FC$_6$H$_4$)$_3$\}][28]	Et	Et	28	–
8	cis-[Pt(CH$_3$)$_2$\{P(4-CF$_3$C$_6$H$_4$)$_3$\}][28]	Et	Et	11	–
9	**1a**	n-Pr	n-Pr	44	–
10	**1a**	n-Pe	n-Pe	50	–
11	**1a**	Ph	Me	75	2.3:1
12	**1a**	Ph	n-Bu	26	3.5:1
13	**1a**	n-Bu	Me	63	1:1.8
14	**1a**	CO$_2$Et	Me	66	>99:1
15	**1a**	CO$_2$Et	Ph	41	>99:1
16	**1a**	n-Bu	H	54	<1:99

[a] 10% of [Pt(CH$_3$)$_2$L$_2$] (**1**) as precatalysts, 2.0 equiv of Et$_3$N·3HF, 1.0 equiv of *ortho*-chlorobenzoic acid at alkyne concentrations of 0.5 M, reaction time: 144 h. [b] Determined from ^{19}F NMR data on using benzotrifluoride as internal standard. [c] Yield isolated by distillation from a reaction at a 7.5 mmol scale using 1,2-dichlorobenze as solvent for convenience of separation.

showed a more than 20% lower alkyne conversion. The fluorido complex **3a** was also tested as precatalyst resulting in a similar yield of the fluoroalkene as found for **1a**. However, when the tetrafluoroborate complex **5a** was applied, the yield was only 19%, supporting the suggested

impact of the outer-sphere bound poly(hydrogen fluoride) anion for the C–F bond formation step. The influence of the phosphine bound indolyl groups, which stabilise polyfluoride in the outer-sphere by hydrogen bonding, becomes additionally evident, when the reactions were performed with platinum complexes bearing the phosphine ligands PPh$_3$, P(4-FC$_6$H$_4$)$_3$ and P(4-CF$_3$C$_6$H$_4$)$_3$ (Table 2, entries 6–8). In all cases the (Z)-3-fluoro-3-hexene yield was lowered significantly.

The scope of the hydrofluorination reactions was studied on using **1a** as catalytic precursor. The reactivity of dialkyl, alkyl/aryl, alkyl/ester and aryl/ester substituted alkynes, as well as terminal aliphatic and aromatic alkynes were tested (Table 2, entries 1, 9–16). The regioselectivity is higher for electron poor substituted alkynes than for electron rich ones (Table 2, entries 11–15), which is in accordance with the results reported for Au^{I}-catalysed hydrofluorination reactions.[6] Exclusive formation of Markovnikov products was observed for the terminal alkynes. However, when phenylacetylene was used, only traces of the α-fluorostyrene product were detected in the ^{19}F NMR spectrum. Note that α-fluorostyrene undergoes a facile polymerisation behaviour under the given reaction conditions.[26] In all cases no *gem*-difluoroalkanes were detected and *trans*-hydrofluorination was observed, exclusively.

Mechanistically, we assume that initially the alkyne will be bound at a cationic Pt centre. The structure of the active species might resemble complexes **4**, but it does probably not possess any methyl ligand. This assumption is supported by in situ experiments. Thus, the catalytic hydrofluorination of 3-hexyne with **4a**, PVPHF and excess was monitored by NMR spectroscopy. No signals for a methyl ligand or fluorido ligand were observed in the ^{19}F NMR and ^{1}H NMR spectra. In addition, the ^{31}P NMR data reveal the presence of two platinum complexes bearing inequivalent phosphines presumably in a mutually *cis*-coordination. The identity of these complexes is still unknown. However, after alkyne coordination fluoride will be provided in the outer-coordina-

tion sphere by polyfluoride clusters, which interact by hydrogen-bonding with indolyl groups. After a nucleophilic attack a fluorovinyl complex is formed. Subsequently the fluoroalkene is produced after protonation.

Conclusion

In conclusion, Pt polyfluorido complexes were synthesised, which possess indolyl phosphines as cooperating ligands. Hydrogen bonding allows for the generation of electrophilic metal centres, whereas at the same time fluoride is stabilised in the coordination sphere and provided for reactivity. Indeed, model reactions suggest that hydrogen bonding in the outer coordination sphere to polyfluorides favours fluorination reactions of alkynes. Finally, the air-, moisture- and light-insensitive Pt^{II} (poly)fluorido complexes were applied for catalytic hydrofluorination reactions of internal alkynes to yield selectively (Z)-fluoroalkenes using Et$_3$N·3HF as mild HF source. The indolylphosphine-based catalysts are distinct when compared to derivatives that do not facilitate hydrogen-bonding.

Acknowledgements

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

Keywords: Fluorido Complexes · Hydrofluorination · Hydrogen Bonding · Platinum · Polyfluorides

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