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Hydrogen Bonding in Platinum Indolylphosphine Polyfluorido and Fluorido Complexes

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Abstract: The reaction of the Pt complexes *cis*-[Pt(CH_3)(Ar)-{Ph_2P(Ind)}$_2$] (Ind = 2-(3-methyl)indolyl, Ar = 4-*t*BuC_6H_4 (**1 a**), 4-$CH_3C_6H_4$ (**1 b**), Ph (**1 c**), 4-FC_6H_4 (**1 d**), 4-ClC_6H_4 (**1 e**), 4-$CF_3C_6H_4$ (**1 f**)) with HF afforded the polyfluorido complexes *trans*-[Pt(F(HF)$_2$)(Ar){Ph_2P(Ind)}$_2$] **2 a–f**, which can be converted into the fluoride derivatives *trans*-[Pt(F)(Ar){Ph_2P(Ind)}$_2$] (**3 a–f**) by treatment with CsF. The compounds **2 a–f** and **3 a–f** were characterised thoroughly by multinuclear NMR spectroscopy. The data reveal hydrogen bonding of the fluorido ligand with HF molecules and the indolylphosphine ligand. Polyfluorido complexes **2 a–f** show larger $|^1J(F,Pt)|$, but lower $^1J(H,F)$ coupling constants when compared to the fluorido complexes **3 a–f**. Decreasing $^1J(P,Pt)$ coupling constants in **2 a–f** and **3 a–f** suggest a *cis* influence of the aryl ligands in the following order: 4-*t*BuC_6H_4 (**a**) ≈ 4-$CH_3C_6H_4$ (**b**) < Ph (**c**) ≪ 4-FC_6H_4 (**d**) < 4-ClC_6H_4 (**e**) < 4-$CF_3C_6H_4$ (**f**). In addition, the larger *cis* influence of aryl ligands bearing electron-withdrawing groups in the *para* position correlates with decreasing magnitudes of $|^1J(F,Pt)|$ coupling constants. The interpretation of the experimental data was supported by quantum-chemical DFT calculations.

Introduction

In the last two decades fluorido complexes of late transition metals attracted an increasing interest,[1] in part due to their ability to establish novel routes for metal-mediated fluorination,[1h,i,l,r,2] but they can also play a distinct role in C–F and C–H bond activation reactions.[1j,n,3] Initial studies on the synthesis of Pt(II) fluorido complexes were reported in the early 1970's.[1a,4] They then came back into focus at the begin of the millennium.[1d,e,5] Strategies reported for the formation of platinum fluorido complexes include Cl/F exchange reactions with AgF,[1d,e,5l] fluorination with XeF_2[5d,i] as well as with NFSI or Selectfluor,[5m,n] C–F,[5b,c, f] P–F[5k] or S–F[1p,6] bond activation reactions, and conversions involving hydrogen fluoride.[4a,5a,g,7] The potential of transition metal fluorido complexes to act as hydrogen bond acceptors[1k,8] is of certain interest to control reactivity, for example by modulating the *effective nucleophilicity* of the fluoride through lowering its basicity,[9] or by stabilisation of the fluoride in the outer ligand-sphere.[7,10] A familiar route for the generation of bifluorido and polyfluorido complexes showing intermolecular hydrogen bonding to the fluorido ligand consists of the utilisation of hydrogen fluoride as potential hydrogen bond donor molecule.[1m,5a,11] Furthermore, several examples of complexes were described, where functional ligands - bearing NH or OH groups - form intramolecular hydrogen bonds to fluorido ligands in the outer ligand-sphere. Recently, we reported on Pt(II) (poly-)fluorido complexes featuring 2-(3-methyl)indolyl substituted phosphines as cooperating ligands, which stabilise (poly)fluorides by intramolecular hydrogen bonding in the outer ligand sphere.[7] The hydrogen bonds of NH groups to the fluorido ligand provided unprecedented reactivities.[12]

Most notably, the strength of a metal-ligand bond is affected by the *trans influence* of the *trans* coordinated ligand. For platinum complexes there is a well described correlation between Pt–P bond lengths and $^1J(P,Pt)$ coupling constants[13] that enabled the early estimation of a ligand's *trans-influence*.[13b,14] However, recent studies of complexes of the type *trans*-[Pt(X)(Y)(PPh_3)$_2$] also emphasised the presence of a non-negligible *cis-influence*, i.e. a weakening of the Pt–P bonds in the *cis* positions.[15]

Herein, we report on the formation of the platinum fluorido complexes *trans*-[Pt(F)(Ar){Ph_2P(Ind)}$_2$] (**3 a-f**) (Ar = 4-*t*BuC_6H_4 (**3 a**), 4-$CH_3C_6H_4$ (**3 b**), Ph (**3 c**), 4-FC_6H_4 (**3 d**), 4-ClC_6H_4 (**3 e**), 4-$CF_3C_6H_4$ (**3 f**), Ind = 2-(3-methyl)indolyl) bearing indolylphosphine ligands as well as aryl ligands, which differ by their substitution pattern at the *para* position. The complexes were studied thoroughly by multinuclear NMR and IR-spectroscopy

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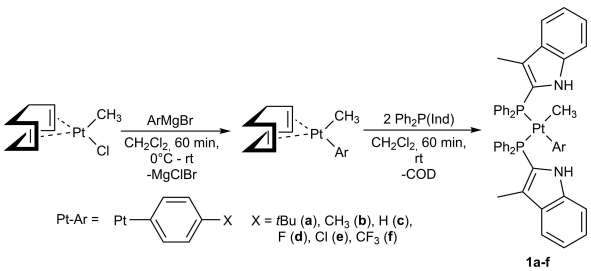
as well as by single crystal X-ray diffraction. NMR data revealed a notable influence of the various aryl ligands on the ^{1}J(P,Pt) coupling constants, which show a correlation with the $|^{1}J(F,Pt)|$ coupling constants as well as with the chemical shifts for the indolyl N*H* proton and the fluorido ligand in the ^{1}H, ^{19}F and ^{1}H/^{15}N HMBC NMR spectra.

Results and Discussion

The Pt(II) methyl aryl complexes *cis*-[Pt(CH_3)(Ar){Ph_2P(Ind)}$_2$] (Ar = 4-*t*BuC_6H_4 (**1 a**), 4-$CH_3C_6H_4$ (**1 b**), Ph (**1 c**), 4-FC_6H_4 (**1 d**), 4-ClC_6H_4 (**1 e**), 4-$CF_3C_6H_4$ (**1 f**)) were synthesised by reactions of [Pt(Ar)(CH_3)(COD)] (Ar = 4-*t*BuC_6H_4, 4-$CH_3C_6H_4$,[16] Ph,[17] 4-FC_6H_4,[18] 4-ClC_6H_4, 4-$CF_3C_6H_4$) with two equivalents of diphenyl-2-(3-methyl)indolylphosphine (Ph_2P(Ind)) (Scheme 1). The 1,5-cyclooctadiene platinum (II) precursor complexes were formed by treating [Pt(Cl)(CH_3)(COD)][19] (COD = 1,5-cyclooctadiene) with the appropriate aryl Grignard reagents in THF at 0 °C. Complexes **1 a-f** were characterised by ^{1}H NMR, ^{31}P{^{1}H} NMR as well as IR spectroscopy, and selected NMR and IR data are listed in Table 1.

The ATR IR spectra of **1 a-f** each exhibit two medium-intensity absorption bands between 3444–3449 cm^{-1} and 3361–3370 cm^{-1}, respectively, which can be assigned to the N–H stretch of the indolyl groups. Each complex exhibits one broadened and red shifted absorption band, compared to the absorption band of the free phosphine ligand precursor (3445 cm^{-1}), which indicates hydrogen bonding in the solid state.[20] The ^{1}H NMR spectra of **1 a–f** display two signals for the N*H* protons of the indolyl moiety between 9.03–8.88 and 8.44–8.52 ppm. Both, the IR and ^{1}H NMR data for the indolyl NH-group resemble data reported for similar Pt(II) dimethyl indolylphosphine complexes.[12] For the platinum bound methyl ligand a multiplet with ^{195}Pt satellites was observed at δ = 0.49–0.52 ppm with ^{2}J(H,Pt) coupling constants of 67–68 Hz, which are typical values for platinum methyl complexes.[21] The ^{31}P{^{1}H} NMR spectra of **1 a**, **1 b** and **1 d–f** exhibit two doublets with ^{195}Pt satellites revealing ^{2}J(P,P) coupling constants < 15 Hz, which are characteristic for phosphorus nuclei in a mutually *cis* position.[22] For complex **1 c**, two overlapping signals with ^{195}Pt satellites were detected at δ = 9.1 ppm. However the ^{195}Pt satellites clearly showed ^{2}J(P,P) coupling constants of 9.9 Hz. For all complexes, ^{1}J(P,Pt) coupling constants between 1594–1669 Hz and 1867–1899 Hz were observed, which are typical values for a phosphorus nuclei in the *trans* position to an aryl or a methyl ligand, respectively.[21,23] Note, that for the Pt–P bond *trans* to the aryl ligand complexes, **1 a–c** exhibit lower ^{1}J(P,Pt) coupling constants than **1 d–f**, which is consistent with a larger *trans* influence of the more electron rich *t*BuC_6H_4, $CH_3C_6H_4$ and Ph ligands compared to the 4-FC_6H_4, 4-ClC_6H_4 and 4-$CF_3C_6H_4$ ligands featuring electron withdrawing para substituents.[13b,14a, b, 23d, 24]



Scheme 1. Syntheses of platinum methyl aryl complexes **1 a–f.**

Table 1. Selected NMR and IR data of complexes **1 a–f.**

Complex	^{1}H NMR[a] δ(N*H*) [ppm]	δ(Pt-C*H*$_3$) [ppm]	^{2}J(H,Pt) [Hz]	^{31}P{^{1}H} NMR[a] δ [ppm]	^{1}J(P,Pt) [Hz]	IR data $\tilde{\nu}$ (N–H) [cm^{-1}]
1 a	9.02	0.49	68	9.3	1594	3445 3365
	8.52			9.1	1898	
1 b	8.88	0.50	68	9.4	1615	3449 3370
	8.44			8.6	1888	
1 c	8.99	0.51	68	9.1	1607	3444 3363
	8.51			9.1	1891	
1 d	8.93	0.51	67	9.1	1664	3448 3366
	8.50			9.0	1867	
1 e	8.90	0.49	67	9.0	1670	3444 3368
	8.47			8.8	1870	
1 f	8.99	0.51	67	9.1	1669	3444 3361
	8.46			8.8	1876	

[a] all spectra were recorded using CD_2Cl_2 as solvent.

Furthermore, the molecular structures of *cis*-[Pt(CH_3)(4-FC_6H_4){Ph_2P(Ind)}$_2$] (**1 d**) and *cis*-[Pt(CH_3)(4-ClC_6H_4){Ph_2P(Ind)}$_2$] (**1 e**) were determined by single-crystal X-ray diffraction analysis. Colourless crystals of **1 d** and **1 e** were obtained by slow evaporation of a concentrated solution in CH_2Cl_2 at room temperature. Selected bond lengths and angles are listed in the captions of Figure 1. For **1 d** the asymmetric unit contains two independent molecules, which show only minor differences of the bond lengths and angles. Therefore, only the structure of one molecule will be discussed.

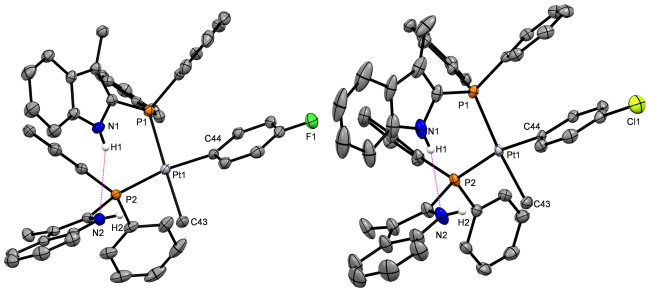
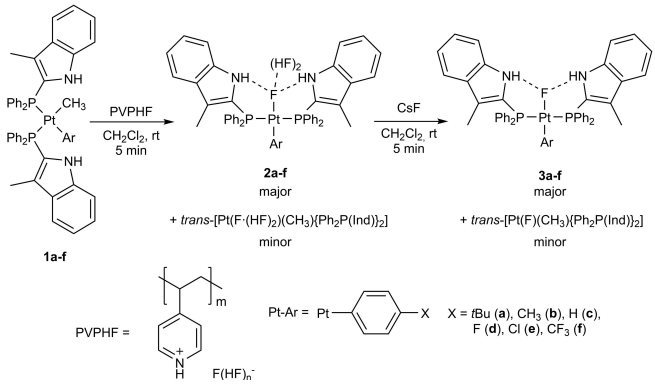


Figure 1. Molecular structure of *cis*-[Pt(CH_3)(4-FC_6H_4){Ph_2P(Ind)}$_2$] (**1 d**) (left) and *cis*-[Pt(CH_3)(4-ClC_6H_4){Ph_2P(Ind)}$_2$] (**1 e**) (right). Thermal ellipsoids are drawn at 50 % probability level, the intermolecular hydrogen bond is depicted as a magenta dashed line. The second molecular structure of **1 d**, the solvent molecule and carbon bound hydrogen atoms were omitted for clarity. Selected bond lengths, distances [Å] and bond angles [°] of **1 d**: Pt1-P1 2.3022(7), Pt1-P2 2.3255(7), Pt1-C43 2.113(3), Pt1-C44 2.055(3), P1-Pt1-P2 96.09(2), C43-Pt1-C44 84.90(11), P1-Pt1-C44 91.85(7), P2-Pt1-C43 87.44(8). Selected bond lengths, distances [Å] and bond angles [°] of **1 e**: Pt1-P1 2.3105(8), Pt1-P2 2.3208(8), Pt1-C43 2.109(3), Pt1-C44 2.044(3), P1-Pt1-P2 102.82(3), C43-Pt1-C44 82.65(12), P1-Pt1-C44 88.78(8), P2-Pt1-C43 85.55(9).

Both complexes, **1 d** and **1 e**, possess a slightly distorted square-planar coordination geometry of the two phosphines, the aryl and methyl ligands bound to Pt. They exhibit P1 – Pt1 – P2 bond angles of 96.09(2) and 102.82(3), while the C43 – Pt1 – C44 bond angle between the methyl and aryl ligand are smaller with values of 84.90(11) and 82.65(12), respectively. For each complex the Pt1 – P1 bond length in a *trans* position to the methyl ligand is slightly shorter (2.3022(7) for **1 d**, 2.3105(8) for **1 e**) compared to the Pt1 – P2 bond length that is located *trans* to the aryl ligand (2.3255(7) (**1 d**), 2.3208(8) (**1 e**)). The Pt1 – P1, Pt1 – P2 and the platinum methyl Pt1 – C43 bond lengths (2.113(3) (**1 d**), 2.109(3) (**1 e**)) as well as the platinum aryl Pt1 – C44 bond length (2.055(3) (**1 d**), 2.044(3) (**1 e**)) are in good accordance with the literature.[21b,23b,25] Additionally, both structures exhibit intramolecular hydrogen bonding from one NH group of an 2-(3-methyl)indolyl moiety to the nitrogen atom of the second indolyl unit.

Recently, it has been reported that protonolysis of platinum dimethyl complexes bearing indolyl substituted phosphine ligands with HF sources led to the formation of the Pt(II) methyl (poly-)fluorido complexes *trans*-[Pt(F·(HF)$_2$)(CH$_3$){R$_2$P(Ind)}$_2$]. The fluorido derivatives *trans*-[Pt(F)(CH$_3$){R$_2$P(Ind)}$_2$] were generated by subsequently removing the pendant HF with CsF as a base (R = Ph, 4-FC$_6$H$_4$, 4-CF$_3$C$_6$H$_4$).[12]



Scheme 2. Formation of platinum (poly)fluorido complexes **2 a**–**f** and **3 a**–**f**.

Intrigued by these results we investigated whether protonolysis of the methyl ligand is also feasible for the Pt(II) methyl aryl complexes **1 a**–**f**. Indeed, when solutions of **1 a**–**f** in dichloromethane were treated with an excess HF on using poly[4-vinylpyridinium poly(hydrogen fluoride)] (PVPHF; 38–42 wt% HF) as HF source, an immediate gas evolution was observed. NMR spectroscopic investigations revealed the formation of the platinum (poly)fluorido complexes *trans*-[Pt(F·(HF)$_2$)(Ar){Ph$_2$P(Ind)}$_2$] **2 a**–**f** as the main products. However, cleavage of the Pt–Ar bond was also observed and therefore *trans*-[Pt(F(HF)$_2$)(CH$_3$){Ph$_2$P(Ind)}$_2$][12] was detected as minor product. Although the amount of the latter varied, the largest amount of the Pt fluorido methyl complexes was determined to be 20% (based on signal integration from the ^{31}P{^{1}H} NMR spectrum) (Scheme 2). The amount of pendant HF at **2 a**–**f** was determined by treatment of the reaction solutions with Et$_3$SiCl to yield Et$_3$SiF, the amount of which was determined by integration in the ^{19}F NMR spectra. When the reaction solutions of the polyfluorido complexes were stirred over anhydrous CsF for five minutes, the fluorido complexes *trans*-[Pt(F)(Ar){Ph$_2$P(Ind)}$_2$] **3 a**–**f** (major) as well as *trans*-[Pt(F)(CH$_3$){Ph$_2$P(Ind)}$_2$] (minor) were obtained (Scheme 2).

The fluorido complexes **3 a**–**f** were characterised thoroughly by ^{1}H, ^{19}F, ^{31}P{^{1}H} NMR as well as ^{1}H/^{15}N HMBC NMR spectroscopy. For the polyfluorido complexes **2 a**–**f** broad signals were observed at room temperature and therefore ^{1}H, ^{19}F and ^{31}P{^{1}H} NMR were measured at −30 °C. Selected NMR data are listed in Table 2.

The ^{1}H NMR spectra of **3 a**–**f** each exhibit a downfield shifted doublet signal at δ = 12.93–12.76 ppm, which can be assigned to the N*H* proton of the indolyl moieties. The N*H* groups undergo hydrogen bonding to the fluorido ligand, which is in accordance with the downfield shift, but is also revealed by the ^1J(H,F) coupling constants of 48–50 Hz.[7,12] The signals collapse into singlets in the corresponding ^{1}H{^{19}F} NMR spectra. Additional data for **3 a**–**f** were obtained from ^{1}H/^{15}N HMBC NMR spectra. The ^2J(N,F) coupling constants decrease slightly from 34 Hz for **3 a** to 31 Hz for **3 f**. The values are characteristic for a ^{15}N-^{19}F spin-spin coupling across a N*H*···F hydrogen bond,[26] while the ^{15}N chemical shifts as well as the ^1J(N,H) coupling constants are typical for indoles.[27]

Table 2. Selected NMR data for the fluorido complexes **3 a**–**f** [a] and polyfluorido complexes **2 a**–**f**.[a,b]

	^{1}H NMR[a]		^{19}F NMR[a]		^{1}H/^{15}N HMBC NMR[c]			^{31}P{^{1}H} NMR[a]		
complex	δ (N*H*) [ppm]	^1J(H,F) [Hz]	δ (Pt-F) [ppm]	$\lvert ^1J$(F,Pt)$\rvert$ [Hz]	δ (*N*H) [ppm]	^1J(N,H) [Hz]	^2J(N,F) [Hz]	δ [ppm]	^1J(P,Pt) [Hz]	^2J(P,F) [Hz]
3 a	12.93 11.79	50	−273.6	567	−238	97	34	5.8	3176	13.1
2 a		38	−267.7	639	–	–	–	7.1	3164	13.4
3 b	12.91 11.84	50	−274.0	564	−238	97	34	5.1	3172	13.0
2 b		40	−269.8	626	–	–	–	6.2	3156	13.8
3 c	12.88 11.87	50	−275.2	559	−238	97	33	5.5	3162	13.7
2 c		40	−270.0	620	–	–	–	6.7	3149	14.2
3 d	12.80 12.01	49	−278.3	521	−239	97	33	5.1	3112	13.6
2 d		41	−274.3	583	–	–	–	6.0	3099	13.3
3 e	12.76 12.05	49	−278.7	519	−239	97	32	4.9	3103	13.7
2 e		42	−275.1	570	–	–	–	5.6	3091	13.4
3 f	12.71 11.92	48	−280.0	515	−239	97	31	5.5	3090	13.5
2 f		40	−275.9	569	–	–	–	6.3	3080	13.7

[a] all spectra were recorded using CD_2Cl_2 as solvent. [b] all spectra were recorded at 243 K.

The ^{19}F NMR spectra of **3a-f** revealed a triplet of triplets with ^{195}Pt satellites for the fluorido ligands due to coupling with the N*H* protons and the two phosphorus nuclei (Figure 2, top). The observed chemical shifts between δ = -267.7 ppm – -280.0 ppm and the ^{2}J(F,P) coupling constants of 13–14 Hz are typical values for Pt fluorido complexes bearing phosphine ligands in a *cis* position.[1e,p,4c,5a,c,f,h,j,k, 6–7,28] The observed $|^{1}J(F,Pt)|$ coupling constants (567-517 Hz) have comparable values to those reported for the fluorido complexes *trans*[-Pt(F)(CH_3){R_2P-(Ind)}$_2$] (R=Ph, 4-FC_6H_4, 4-$CF_3C_6H_4$).[12]

For the polyfluorido complexes **2a–f** the ^{1}J(H,F) coupling constants to the indolyl moiety show smaller values (38–42 Hz) and the chemical shifts of the N*H* protons appear at higher field between δ = 11.79-12.05 ppm when the data are compared to those of **3a–f**. These observations are consistent with those for comparable Pt(II) (poly)fluorido complexes.[12]

Note that for **2a–f** only broad signals with ^{195}Pt satellites were detected in the ^{19}F NMR spectra at −30 °C and cooling to −70 °C or −90 °C did not resolve any additional coupling (Figure 2, bottom). The absolute values of the (negative, see below) $|^{1}J(F,Pt)|$ coupling constants in the polyfluorido complexes **2a–f** are larger (639–569 Hz) when compared to these for the fluorido complexes **3a–f** (515-567 Hz). An increase of the absolute values of the $|^{1}J(F,Pt)|$ coupling constants upon coordination of HF was also observed for the fluorido complexes *cis*-[Pt(F){κ^2-(*P*,*N*)-*i*$Pr_2P(C_9H_7N)$}{*i*Pr_2P(Ind)}][7] and *trans*[Pt-(F)(CH_3){R_2P(Ind)}$_2$] (R=Ph, 4-FC_6H_4, 4-$CF_3C_6H_4$).[12]

The ^{31}P{^{1}H} NMR spectra of **3a–f** and **2a–f** each disclose a doublet with ^{195}Pt satellites, due to coupling of the two phosphorus nuclei to the fluorido ligand. The ^{1}J(P,Pt) coupling constants of **3a–f** and **2a–f** reveal typical values for Pt(II) complexes bearing a carbon bound σ-donor ligand and two phosphine ligands in a mutually *trans* coordination.[12,24, 29]

The IR spectra of the fluorido complexes **2a–f** and **3a–f** featured broad absorption bands 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}.[30] However, due to overlapping with C–H absorption bands, no distinct band maxima could be determined. For **2a–f** 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.[30–31]

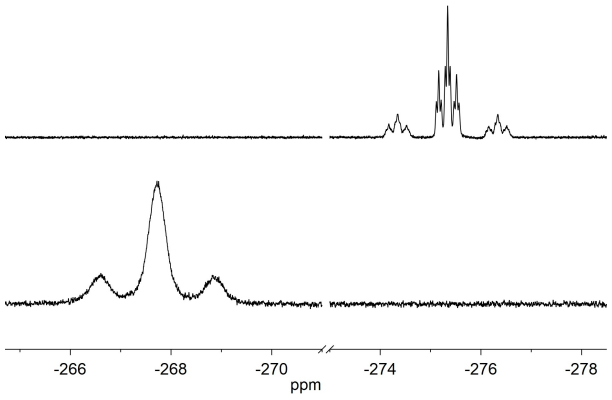


Figure 2. Sections of the ^{19}F NMR NMR spectra of **2a** (bottom) and **3a** (top), revealing coupling constants of $|^{1}J(F,Pt)|$ = 639 Hz for **2a** and $^{1}J(F,H)$ = 50 Hz, $^{2}J(F,P)$ = 13 Hz, $|^{1}J(F,Pt)|$ = 567 Hz for **3a**.

Overall, the NMR data of the complexes **2a–f** and **3a–f** reveal several interesting trends. The ^{1}J(P,Pt) coupling constants decrease continuously in the series from **2a** to **2f** as well as **3a** to **3f** from 3164 Hz to 3080 Hz and 3176 Hz to 3090 Hz, respectively. As only the substituent in the *para*-position of the aryl ligand differs, this corresponds to a larger *cis*-influence of the aryl ligands featuring electron withdrawing substituents, weakening somewhat the Pt–P bonds.[15,32] Indeed, analysis of the DFT optimised structures for **2a-f** and **3a-f** reveals a successive lengthening of the average Pt–P bonds with increasing electronegativity of the substituent in the *para*-position of the aryl ligand. The computed ^{1}J(P,Pt) couplings for **3a–f** (Tables S3, S4 in Supporting Information) do not show an as clear trend, but with (at least) one HF molecule hydrogen-bonded to the fluoride, the distinction between electron-donating substituents (**3a–3c**) and electron-withdrawing ones (**3d–3f**) becomes clearer, as it does for **2a–2f** (Tables S3, S4), i.e. with two HF molecules present. Similar to the effect of HF coordination, explicit hydrogen-bonding by two CH_2Cl_2 solvent molecules leads to an increase of the ^{1}J(P,Pt) couplings, although to a lesser extent (excluding **3a**·$(CH_2Cl_2)_2$ from the analysis). Overall, the *cis* influence of the aryl ligands follows the order: 4-*t*BuC_6H_4 (**a**) ≈ 4-$CH_3C_6H_4$ (**b**) < Ph (**c**) ≪ 4-FC_6H_4 (**d**) < 4-ClC_6H_4 (**e**) < 4-$CF_3C_6H_4$ (**f**). This trend is inverse to the *trans* influence of the aryl ligands observed for **1a–f**, which is also consistent with the literature.[15,32]

Furthermore, the N*H* chemical shift in the ^{1}H NMR spectra as well as ^{1}J(H,F) coupling constants suggest a weakening of the N*H*···F hydrogen bond by additional fluoride bound HF molecules in the polyfluorido complexes **2a–f**. However, the absolute values of $|^{1}J(F,Pt)|$ coupling constants are larger for the polyfluorido complexes **2a–f** than for the fluorido complexes **3a–f**. In addition, decreasing ^{1}J(P,Pt) coupling constants for the sequences **2a** to **2f** as well as for **3a** to **3f** correlate with high-frequency shifts of the signal for the fluorido ligand and smaller $|^{1}J(F,Pt)|$ coupling constant in the ^{19}F NMR spectra; i.e. more electronegative aryl ligands show smaller $|^{1}J(F,Pt)|$ couplings.

For the $|^{1}J(F,Pt)|$ coupling constants of the fluorido complexes **3a–f** it is important to note that the computations show them to have negative signs (Table S3, S4). This is consistent with the smaller fluorine s-character in the F–Pt bond compared to phosphorus and similar to, for example, ^{1}J(C–F) couplings.[34] As for the $|^{1}J(F,Pt)|$ coupling constants, the computations give overall negative couplings at the given BHLYP DFT level, even more so when including two CH_2Cl_2 solvent molecules hydrogen-bonded to the platinum-bound fluorine. Assuming a negative sign, the experimental data indicate less negative ^{1}J(F,Pt) values in the series **3a** (−567 Hz) to **3f** (−515 Hz). Again, the calculations on non-solvated **3a–3f** do not capture the trend correctly, while computations with explicit microsolvation by two CH_2Cl_2 molecules distinguish between more negative couplings for **3a–3c** and less negative ones for **3d-3f** (Tables S3, S4). However, then the absolute values are over-

estimated, even more when for **2a**–**2f** (Tables S3, S4). Therefore, we have to assume that the systematic DFT error can be about −200 Hz to −300 Hz. Computationally, the *trans* influence is clearly to some extent coupled to all the inter- and intramolecular hydrogen bonds present, rendering NMR analyses more complex. One complication for **3a**–**3f** is obviously due to charge-assisted CH···F hydrogen bonds to the CH_2Cl_2 solvent (see above). Some of us have recently analyzed such interactions in detail using similar microsolvated cluster models[35] and found them to be substantial whenever NPA charges that are more negative than −0.6 on fluorine are present. This is clearly the case for the platinum fluorides studied here (Tables S1, S2). The various hydrogen-bonding interactions likely also prevent a more accurate representation of the subtle substituent effects for the present systems. In the case of **2a**–**2f** our modelling includes two explicit HF molecules (Tables S3, S4). In solution we have to expect, however, that these HF molecules are also microsolvated by CH···F hydrogen bonding with CH_2Cl_2, generating further complications.

Overall, more hydrogen bonding to the Pt-bound fluoride, either by HF or by the CH_2Cl_2 solvent, clearly provides more negative $|^1J(F,Pt)|$ couplings, even though the magnitudes are not easy to reproduce computationally. This is consistent with experimental observations for the fluorido methyl complex *trans*-[Pt(F)(CH_3)(Ph_3P)$_2$], which does not exhibit any hydrogen bonding to the fluorido ligand and which exhibits a $|^1J(F,Pt)|$ coupling constant of 361 Hz that is lowered by 150–200 Hz compared to **3a**–**f**. On the other hand, the methyl fluorido complex *trans*-[Pt(F)(CH_3){Ph_2P(Ind)}$_2$], featuring hydrogen bonding from indolylphosphine ligands to the fluorido ligand, exhibits a $|^1J(F,Pt)|$ coupling constant of 546 Hz that is comparable with those found for **3a**–**f**.[12,36]

Furthermore, the molecular structures of **3a**, **3c** and **3d** were determined by single crystal X-ray diffraction (Figure 3, Table 3). In all cases electron density which could be assigned to nitrogen bound hydrogen atoms were found in the difference Fourier map and a free refinement was allowed. For complex **3d**, the molecule is located on a mirror plane and the asymmetric unit consists only of one half of the molecule. All structures reveal a slightly distorted square-planar coordination of the ligands, with the two phosphine ligands in a mutually *trans* position, exhibiting hydrogen bonds from their indolyl N*H* groups to the fluorido ligand. The Pt−P bond lengths of **3a** (2.3124(4), 2.3220(4) Å) and **3c** (2.3118(5), 2.3188(6) Å) are slightly shorter than those of **3d** (2.3254(7) Å), which is in accordance with the trend of the observed ^1J(P,Pt) coupling constants.[13d] Generally, all Pt–P bond lengths are in accordance with similar data for Pt(II) fluorido complexes reported previously.[1d,12]

The Pt–F bond lengths of **3a** (2.1361(9) Å) and **3c** (2.1386(13) Å) are slightly longer compared to **3d** (2.125(3) Å) which might result from the larger *trans* influence of the 4-*t*Bu and Ph ligands, respectively. However, all Pt−F bond lengths are elongated compared to Pt(II) fluorido complexes that feature no hydrogen bonding to the fluorido ligand in the coordination sphere (1.9787(14)-2.117(3) Å).[1d,e,4d,5g,k] A Pt–F bond length of 2.1466(13) Å was observed for the molecular structure of the fluorido complex *trans*-[Pt(F)(CH_3){(4-FC_6H_4)$_2$P-(Ind)}$_2$] that also features indolylphosphine ligands.[12] The N···F distances of **3a** (2.591(1), 2.610(1) Å), **3c** (2.620(3), 2.619(2) Å) and **3d** (2.588 Å) suggest hydrogen bonding of medium strength to the fluorido ligand.[10b,12,37] The F–Pt–P–N dihedral angles of **3a** and **3c** reveal relative small values of −12.89(4)° and 19.86(4)° as well as 18.31(6)° and −19.06(6)°, respectively, resulting in a favoured alignment of the N–H···F bond. The indolyl moieties in **3d** appear to be more twisted, expressed by a larger dihedral F–Pt–P–N angle of 28.72°. This might be due to crystal packing effects associated with short contact interactions of a proximal CH group of a 4-fluorophenyl ligand to the fluorido ligand of a second molecule, as well as C–H-π-interactions between phosphine ligands. However, all fluorido complexes **3a**, **3c** and **3d** reveal smaller dihedral F–Pt–P–N angles when compared to the Cl–Pt–P–N angles of the chlorido analogue *trans*-[Pt(Cl)(Ph){Ph_2P(Ind)}$_2$] (**4**) (Cl1-Pt1-P1-N1 61.94(4)°, Cl1-Pt1-P2-N2 51.37(4)°), which is very likely explained by the sterically more demanding chlorido ligand (Figure 4).

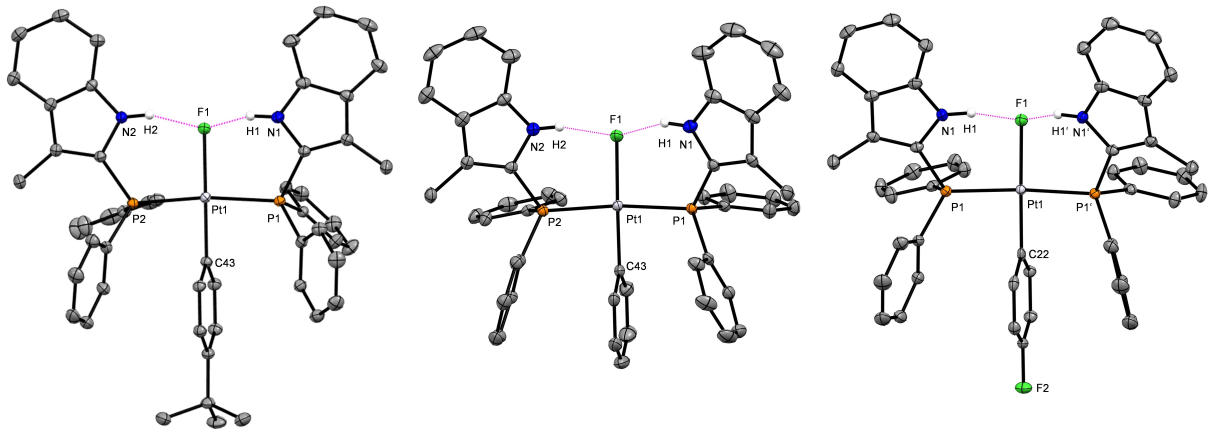


Figure 3. Molecular structures of *trans*-[Pt(F)(4-*t*BuC_6H_4){Ph_2P(Ind)}$_2$] (**3a**) (left), *trans*-[Pt(F)(Ph){Ph_2P(Ind)}$_2$] (**3c**) (middle) and *trans*-[Pt(F)(4-FC_6H_4){Ph_2P(Ind)}$_2$] (**3d**) (right). Thermal ellipsoids are drawn at 50% probability level, the intermolecular hydrogen bonds are depicted as magenta dashed lines. Carbon bound hydrogen atoms and the solvent molecules were omitted for clarity.

Table 3. Selected bond lengths, distances [Å] and bond angles [°] of **3a**, **3c** and **3d**.

complex	Pt1-P1 Pt1-P2	Pt1-F1	Pt1-C(Aryl)	N1···F1 N2···F1	P1-Pt1-F1 P2-Pt1-F1	P1-Pt1-P2(P1′) F1-Pt1-C(Aryl)	P1-Pt1-C(Aryl) P2-Pt1-C(Aryl)	N1-H1···F1 N2-H2···F1	F1-Pt1-P1-N1 F1-Pt1-P2-N2
3a	2.3124(4)	2.1361(9)	1.9990(14)	2.591(1)	93.23(3)	171.165(12)	86.27(4)	160(2)	−12.89(4)
	2.3220(4)			2.610(1)	93.89(3)	178.06(4)	86.27(4)	152(3)	19.86(4)
3c	2.3118(5)	2.1386(13)	2.012(2)	2.620(3)	92.23(4)	173.614(19)	87.21(6)	158(3)	18.31(6)
	2.3188(6)			2.619(2)	93.94(4)	177.00(8)	86.71(6)	164(3)	−19.06(6)
3d	2.3254(7)	2.125(3)	1.991(5)	2.588	92.10(2)	174.97(4)	88.01(2)	160	28.72
	–			–	–	175.45(15)	–	–	–

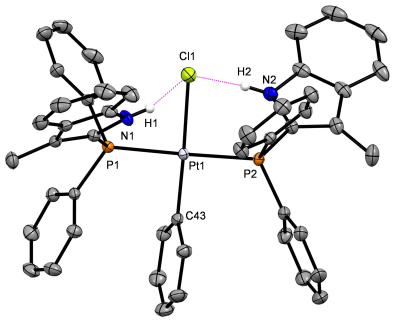


Figure 4. Molecular structure of *trans*-[Pt(Cl)(Ph){Ph_2P(Ind)}$_2$] (**4**). Thermal ellipsoids are drawn at 50% probability level, the intermolecular hydrogen bond is depicted as a magenta dashed line. Carbon bound hydrogen atoms and the solvent molecule were omitted for clarity. Selected bond lengths, distances [Å] and bond angles [°]: Pt1-P1 2.2978(5), Pt1-P2 2.2960(5), Pt1-Cl1 2.4314(6), Pt1-C43 2.0219(18), N1···Cl1 3.241(2), N2···Cl1 3.168(2), P1-Pt1-Cl1 87.740(18), P2-Pt1-Cl1 89.154(19), P1-Pt1-P2 169.154(16), P1-Pt1-C1 90.55(5), P2-Pt1-C1 92.96(5), Cl1-Pt1-C1 177.05(5), N1-H1···Cl1 147(2), N2-H2···Cl1 147(2), Cl1-Pt1-P1-N1 61.94(4), Cl1-Pt1-P2-N2 51.37(4).

Both N*H* groups of the indolyl moieties form hydrogen bonds to the chlorido ligand with typical N···Cl distances of 3.241(2) Å and 3.168(2) Å.[7,29,38] Complex **4** was synthesised by treatment of [Pt(Cl)(Ph)(COD)] with Ph_2P(Ind).

Conclusion

In conclusion, we describe the formation of the platinum fluorido and polyfluorido complexes *trans*-[Pt(F)(Ar){Ph_2P(Ind)}$_2$] **3a-f** and *trans*-[Pt(F·(HF)$_2$)(Ar){Ph_2P(Ind)}$_2$] **2a-f** bearing electronically different aryl ligands (Ar = 4-*t*BuC_6H_4 (**1a**), 4-$CH_3C_6H_4$ (**1b**), Ph (**1c**), 4-FC_6H_4 (**1d**), 4-ClC_6H_4 (**1e**), 4-$CF_3C_6H_4$ (**1f**)), as well as 2-(3-methyl)indolyl (Ind) substituted phosphine ligands that allow for generation of intramolecular hydrogen bonding to the platinum bound fluoride. The complexes were analysed thoroughly by multinuclear NMR spectroscopy and in part by single crystal X-ray diffraction. X-ray data revealed a lower *trans* influence for aryl ligands with electron withdrawing substituents in the *para* position, but simultaneously a larger *cis* influence was observed. The *cis* influence was mirrored by the NMR ^1J(P,Pt) coupling constants,[15] whereas the *trans* influence is not mirrored by the $|^1J(F,Pt)|$ coupling constants. In addition, the $|^1J(F,Pt)|$ coupling constants were found to be smaller for fluorido complexes **3a–f** compared to polyfluorido complexes **2a–f**. Moreover, intramolecular hydrogen bonding of the fluorido ligand to the indolyl N*H* moiety seems to be slightly weaker in the polyfluorido systems **2a–f** based on N*H* chemical shifts and ^1J(H,F) coupling constants. DFT calculations suggest that, due to the high negative charge on the platinum-bound fluoride, hydrogen bonding by HF, but also by the dichloromethane solvent molecules to the fluoride have a considerable influence on the NMR parameters, complicating their quantitative description by DFT methods.

Experimental Section

All manipulations (if not otherwise mentioned) were carried out under argon using standard Schlenk techniques or in an argon-filled glovebox (MBRAUN). THF and *n*-hexane were dried and purified by distillation from SOLVONA® and stored under argon over molecular sieves. *n*-Pentane was purified using a two-column solid-state purification system (MBRAUN). Dichloromethane and CD_2Cl_2 were purified by distillation from CaH_2 and stored over molecular sieves. [Pt(Cl)(CH_3)(COD)][19] and $Ph_2P(Ind)$[39] were prepared according to the literature.

Poly[4-vinylpyridinium poly(hydrogen fluoride)] (PVPHF; 38–42 wt% HF) and 1-bromo-4-*tert*-butylbenzene were obtained from Sigma-Aldrich and were used without further purification. 4-Bromobenzotrifluoride was obtained from abcr GmbH and was used without further purification. p-Tolylmagnesium bromide (0.5 M in Et_2O), phenylmagnesium bromide (1.6 M in cyclopentyl methyl ether), 4-fluorophenylmagnesium bromide (2 M in Et_2O) and 4-chlorophenylmagnesium bromide (1 M in THF/toluene) were obtained from Acros Organics. The NMR spectra were recorded on a Bruker Avance 500, Bruker Avance 400, Bruker Avance 300, or a Bruker DPX 300 spectrometer. The ^{1}H NMR chemical shifts were referenced to residual $CDHCl_2$ at $\delta = 5.32$ ppm. The $^{13}C\{^1H\}$ NMR spectra were referenced to CD_2Cl_2 at $\delta = 54.00$ ppm. The ^{15}N NMR chemical shifts were referenced to external CH_3NO_2 at $\delta = 0.00$ ppm. The ^{19}F NMR chemical shifts were referenced to external $CFCl_3$ at $\delta = 0.00$ ppm. The $^{31}P\{^1H\}$ NMR chemical shifts were referenced to external H_3PO_4 at $\delta = 0.00$ ppm.

Structure determination of complexes 1 d, 1 e, 3 a, 3 c, and 3 d: Colourless crystals of **1 d**·0.5CH_2Cl_2, **1 e**, **3 a**·CH_2Cl_2, **3 c**·0.5 CH_2Cl_2 and **3 d** were obtained by slow evaporation of the solvent from a dichloromethane solution at room temperature. The diffraction data were collected at a Bruker D8 Venture diffractometer at 100 K using Mo-K_α ($\lambda = 0.71073$ Å) radiation. Multi-scan absorption corrections implemented SADABS were applied to the data.[40] The structures were solved by intrinsic phasing method (SHELXT 2014/5)[41] and refined by full-matrix least-squares methods on F^2 (SHELXL 2016/4 or SHELXL-2018/3).[42] The nitrogen-bound hydrogen atoms were found in the difference electron density maps and freely refined. All other hydrogen atoms were placed at calculated positions and refined using a riding model.

Deposition Number(s) 2166083 (for **1 d**·0.5 CH_2Cl_2), 2166086 (for **1 e**), 2166098 (for **3 a**·CH_2Cl_2), 2166090 (for **3 c**·0.5 CH_2Cl_2), 2166111 (for **3 d**) and 2170875 (for **4**) contain(s) the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

General procedure for the synthesis of [Pt(Ar)(CH_3)(COD)] (Ar = 4-*t*BuC_6H_4, 4-$CH_3C_6H_4$,[16] Ph,[17] 4-FC_6H_4,[18] 4-ClC_6H_4, 4-$CF_3C_6H_4$): The reactions were carried out under Argon, but the work-ups were done under air. In a Schlenk flask [PtCl(CH_3)(COD)] (0.71 g, 2.00 mmol) was dissolved in dry CH_2Cl_2 (20 mL) and solution was cooled to 0 °C followed by dropwise addition of the appropriate Grignard reagent ArMgBr (4.40 mmol) (Ar = 4-*t*BuC_6H_4, 4-$CH_3C_6H_4$, Ph, 4-FC_6H_4, 4-ClC_6H_4, 4-$CF_3C_6H_4$). The reaction mixture was stirred for 30 min and then cooled to −78 °C. 2-Propanol (2 mL) was added to quench excess of the Grignard. The mixture was allowed to warm up to room temperature. Water was added (50 mL) and the mixture was stirred vigorously for 5 min. The two phases were allowed to separate and the lower organic phase was collected. The aqueous phase was extracted with dichloromethane (2×25 mL). The combined organic phases were washed with water (2×50 mL) and dried over anhydrous $MgSO_4$. After filtration, all volatiles were removed *in vacuo* yielding pale yellow to brownish solids. Potential brownish-dark colouring of the solids can be removed by filtration over a pad of silica or Florisil®. The obtained solids were finally washed with small portions of cold *n*-pentane and dried *in vacuo* to give [Pt(Ar)(CH_3)(COD)] as colourless or off-white solids. The complexes obtained by this way can be used without further purification. Yields: 84–94 %.

Analytical data for [Pt(4-*t*BuC_6H_4)(CH_3)(COD)]: ^{1}H NMR (300.1 MHz, CD_2Cl_2): δ = 7.31–7.05 (m, 4H, Ar*H*), 6.91 (m, 2H, Ar*H*), 5.09 (m + sat, ^2J(H,Pt) = 39 Hz, 2H, C*H*), 4.83 (m + sat., ^2J(H, Pt = 39 Hz, 2H, C*H*), 2.43 (m, 8H, CH_2), 1.29 (s, 9H, C(CH_3)$_3$), 0.78 ppm (s + sat., ^2J(H, Pt) = 83 Hz, 3H, Pt-CH_3). $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2): δ = 155.1 (s + sat, J(C,Pt) = 1097 Hz, Pt-C_{ar}), 145.6 (s + sat., J(C,Pt) = 13 Hz, C_{ar}), 134.8 (s + sat., J(C,Pt) = 38 Hz, C_{ar}H), 125.1 (s + sat, J(C,Pt) = 76 Hz, C_{ar}H), 102.7 (s + sat., J(C,Pt) = 50 Hz, C*H*), 102.2 (s + sat., J(C,Pt) = 52 Hz, C*H*), 34.4 (s, $C(CH_3)_3$), 31.8 (s, $C(CH_3)_3$), 30.7 (s, CH_2), 30.2 (s, CH_2), 21.1 (s, CH_3), 6.9 (s + sat., J(C,Pt) = 778 Hz, Pt-CH_3). Anal. Calcd for $C_{19}H_{28}Pt$: C, 50.54; H, 6.25. Found: C, 50.66; H, 6.28.

Analytical data for [Pt(4-$CH_3C_6H_4$)(CH_3)(COD)][16]: ^{1}H NMR (300.1 MHz, CD_2Cl_2): δ = 7.13 (m + sat, ^2J(H,Pt) = 68 Hz, 2H, Ar*H*), 6.91 (m, 2H, Ar*H*), 5.07 (m + sat, ^2J(H,Pt) = 39 Hz, 2H, C*H*), 4.79 (m + sat., ^2J(H, Pt = 39 Hz, 2H, C*H*), 2.41 (m, 8H, CH_2), 0.75 ppm (s + sat., ^2J(H, Pt) = 83 Hz, 3H, Pt-CH_3). $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2): δ = 155.0 (s + sat, J(C,Pt) = 1097 Hz, Pt-C_{ar}), 135.0 (s + sat., J(C,Pt) = 38 Hz, C_{ar}H), 132.2 (s + sat., J(C,Pt) = 13 Hz, C_{ar}), 129.0 (s + sat, J(C,Pt) = 77 Hz, C_{ar}H), 102.7 (s + sat., J(C,Pt) = 50 Hz, C*H*), 102.3 (s + sat., J(C,Pt) = 52 Hz, C*H*), 30.7 (s, CH_2), 30.2 (s, CH_2), 21.1 (s, CH_3), 6.8 (s + sat., J(C,Pt) = 778 Hz, Pt-CH_3).

Analytical data for [Pt(Ph)(CH_3)(COD)][17]: ^{1}H NMR (300.1 MHz, CD_2Cl_2): δ = 7.24 (m + sat, 2H, ^2J(H,Pt) = 68 Hz, Ar*H*), 7.05 (m, 2H, Ar*H*), 6.85 (m, 1H, Ar*H*), 5.09 (m + sat, ^2J(H,Pt) = 40 Hz, 2H, C*H*), 4.80 (m + sat., ^2J(H, Pt = 39 Hz, 2H, C*H*), 2.43 (m, 8H, CH_2), 0.76 ppm (s + sat., ^2J(H, Pt) = 83 Hz, 3H, Pt-CH_3). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ = 158.5 (s + sat, J(C,Pt) = 1094 Hz, Pt-C_{ar}), 134.9 (s + sat., J(C,Pt) = 36 Hz, C_{ar}H), 127.8 (s + sat, J(C,Pt) = 76 Hz, C_{ar}H), 122.9 (s + sat., J(C,Pt) = 12 Hz, C_{ar}), 102.1 (s + sat., J(C,Pt) = 50 Hz, C*H*), 101.7 (s + sat., J(C,Pt) = 51 Hz, C*H*), 30.2 (s, CH_2), 29.8 (s, CH_2), 6.8 (s + sat., J(C,Pt) = 772 Hz, Pt-CH_3).

Analytical data for [Pt(4-FC_6H_4)(CH_3)(COD)][18]: ^{1}H NMR (500.1 MHz, CD_2Cl_2): δ = 7.23 (m + sat, 2H, ^2J(H,Pt) = 68 Hz, Ar*H*), 6.84 (m, 2H, Ar*H*), 5.09 (m + sat, ^2J(H,Pt) = 40 Hz, 2H, C*H*), 4.79 (m + sat., ^2J(H, Pt = 39 Hz, 2H, C*H*), 2.43 (m, 8H, CH_2), 0.77 ppm (s + sat., ^2J(H, Pt) = 82 Hz, 3H, Pt-CH_3). $^{13}C\{^1H\}$ NMR (125.8 MHz, CD_2Cl_2): δ = 160.5 (d + sat., J(C,F) = 239.0 Hz, J(C,Pt) = 17 Hz, C_{ar}-F), 153.3 (d + sat, J(C,F) = 3.5 Hz, J(C,Pt) = 1112 Hz, Pt-C_{ar}), 135.7 (d + sat., J(C,F) = 5.5 Hz, J(C,Pt) = 44 Hz, C_{ar}H), 114.6 (d + sat., J(C,F) = 18.2 Hz, J(C,Pt) = 84 Hz, C_{ar}H), 102.7 (s + sat., J(C,Pt) = 52 Hz, C*H*), 30.7 (s, CH_2), 30.3 (s, CH_2), 6.6 (s + sat., J(C,Pt) = 768 Hz, Pt-CH_3). $^{19}F\{^1H\}$ NMR (470.6 MHz, CD_2Cl_2): δ = −123.4 ppm (s + sat., ^5J(F, Pt) = 26 Hz, Ar-*F*).

Analytical data for [Pt(4-ClC_6H_4)(CH_3)(COD)]: ^{1}H NMR (300.1 MHz, CD_2Cl_2): δ = 7.22 (m + sat, ^2J(H,Pt) = 67 Hz, 2H, Ar*H*), 7.05 (m, 2H, Ar*H*), 5.09 (m + sat, ^2J(H,Pt) = 40 Hz, 2H, C*H*), 4.77 (m + sat., ^2J(H, Pt = 38 Hz, 2H, C*H*), 2.43 (m, 8H, CH_2), 0.74 ppm (s + sat., ^2J(H, Pt) = 82 Hz, 3H, Pt-CH_3). $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2): δ = 157.4 (s + sat, J(C,Pt) = 1110 Hz, Pt-C_{ar}), 136.4 (s + sat., J(C,Pt) = 42 Hz, C_{ar}H), 128.7 (s + sat., J(C,Pt) = 17 Hz, C_{ar}), 127.9 (s + sat, J(C,Pt) = 82 Hz, C_{ar}H), 103.0 (s + sat., J(C,Pt) = 53 Hz, C*H*), 102.7 (s + sat., J(C,Pt) = 51 Hz, C*H*), 30.6 (s, CH_2), 30.3 (s, CH_2), 6.3 (s + sat., J(C,Pt) = 765 Hz, Pt-CH_3). Anal. Calcd for $C_{15}H_{19}ClPt$: C, 41.91; H, 4.46. Found: C, 41.96; H, 4.47.

Analytical data for [Pt(4-$CF_3C_6H_4$)(CH_3)(COD)]: ^{1}H NMR (300.1 MHz, CD_2Cl_2): δ = 7.42 (m + sat, ^2J(H,Pt) = 68 Hz, 2H, Ar*H*), 7.29 (m, 2H, Ar*H*), 5.14 (m + sat, ^2J(H,Pt) = 40 Hz, 2H, C*H*), 4.78 (m + sat., ^2J(H, Pt = 38 Hz, 2H, C*H*), 2.44 (m, 8H, CH_2), 0.74 ppm (s + sat., ^2J(H, Pt) = 82 Hz, 3H, Pt-CH_3). $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2): δ = 165.8 (s + sat,

J(C,Pt) = 1106 Hz, Pt-C_{ar}), 135.6 (s + sat., J(C,Pt) = 39 Hz, C_{ar}H), 125.7 (q, J(C,F) = 271.1 Hz, CF_3), 124.9 (q, J(C,F) = 31.6 Hz, C_{ar}H), 124.1 (q + sat, J(C,F) = 3.8 Hz, J(C,Pt) = 79 Hz), 103.5 (s + sat., J(C,Pt) = 53 Hz, *C*H), 102.8 (s + sat., J(C,Pt) = 51 Hz, *C*H), 30.7 (s, *C*H_2), 30.3 (s, *C*H_2), 5.9 (s + sat., J(C,Pt) = 761 Hz, Pt-*C*H_3). ^{19}F NMR (470.6 MHz, CD_2Cl_2): δ = −62.4 ppm (*CF*$_3$). Anal. Calcd for $C_{16}H_{19}F_3Pt$: C, 41.47; H, 4.13. Found: C, 41.62; H, 4.24.

Synthesis of *cis*-[Pt(Me)(4-*t*BuC$_6$H$_4$){PPh$_2$(Ind)}$_2$] (1 a): A solution of diphenyl-2-(3-methyl)indolylphosphine (662 mg, 2.10 mmol) in CH_2Cl_2 (10 mL) was added to a solution of [Pt(4-*t*BuC_6H_4)(CH_3)(COD)] (452 mg, 1.00 mmol) in CH_2Cl_2 (10 mL) while stirring. The resulting solution was stirred for another hour. The solvent was then removed *in vacuo* to yield an off-white solid. The crude product was washed with pentane (5×5 mL) and the solid was dried *in vacuo*, affording **1 a** as a colourless powder. Yield 737 mg (76%). IR (ATR, diamond): $\tilde{\nu}$ = 3445 cm^{-1} (medium, broad, N–H), 3365 cm^{-1} (medium, broad, N–H). ^{1}H NMR (400.1 MHz, CD_2Cl_2): δ = 9.02 (s, 1H, NH), 8.52 (s, 1H, NH), 7.58 (d, ^3J(H,H) = 7.9 Hz, 1H, ArH), 7.45 (d, ^3J(H,H) = 7.7 Hz, 1H, ArH), 7.41 (d, ^3J(H,H) = 8.2 Hz, 1H, ArH), 7.31 (dd, ^3J(H,H) = 8.2 Hz, ^3J(H,H) = 6.9 Hz, 1H ArH), 7.23 (m, 3H, ArH), 7.17 (m, 4H, ArH), 7.11-7.02 (m, 14H, ArH), 6.96 (m, 4H, ArH), 6.72 (d, ^3J(H,H) = 8.3 Hz, 2H, ArH), 6.68 (d, ^3J(H,H) = 8.2 Hz, 1H, ArH), 2.03 (s, 3H, $ArCH_3$), 1.90 (s, 3H, $ArCH_3$), 1.17 (s, 9H, C(CH_3)$_3$), 0.49 (m + sat., ^2J(H,Pt) = 68 Hz, 3H, Pt-CH_3). ^{31}P{^{1}H} NMR (162.0 MHz, CD_2Cl_2): δ = 9.3 (d + sat., ^2J(P,P) = 9.8 Hz, ^1J(Pt,P) = 1594 Hz), 9.1 ppm (d + sat., ^2J-(P,P) = 9.8 Hz, ^1J(Pt,P) = 1898 Hz). Anal. Calcd for $C_{50}H_{46}N_2P_2Pt$: N, 2.88; C, 65.35; H, 5.38. Found: N, 2.89; C, 65.55; H, 5.34.

Synthesis of *cis*-[Pt(Me)(4-MeC$_6$H$_4$){PPh$_2$(Ind)}$_2$] (1 b): A solution of diphenyl-2-(3-methyl)indolylphosphine (687 mg, 2.18 mmol) in CH_2Cl_2 (10 mL) was added to a solution of [Pt(4-$CH_3C_6H_4$)(CH_3)(COD)] (446 mg, 1.09 mmol) in CH_2Cl_2 (10 mL) while stirring. The resulting solution was stirred for another hour. The solvent was then removed *in vacuo* to yield an off-white solid. The crude product was washed with pentane (5×5 mL) and the solid was dried *in vacuo*, affording **1 b** as a colourless powder. Yield 873 mg (86%). IR (ATR, diamond): $\tilde{\nu}$ = 3449 cm^{-1} (medium, broad, N–H), 3370 cm^{-1} (medium, broad, N–H). ^{1}H NMR (400.1 MHz, CD_2Cl_2): δ = 8.99 (s, 1H, NH), 8.48 (s, 1H, NH), 7.59 (d, ^3J(H,H) = 7.9 Hz, 1H, ArH), 7.45 (d, ^3J(H,H) = 8.1 Hz, 1H, ArH), 7.40 (d, ^3J(H,H) = 8.2 Hz, 1H, ArH), 7.30 (m, 1H, ArH), 7.21 (m, 7H, ArH), 7.13 (m, 7H, ArH), 7.05 (m, 7H, ArH), 6.97 (m, 4H, ArH), 6.71 (d, ^3J(H,H) = 7.9 Hz, 1H, ArH), 6.54 (d, ^3J(H,H) = 7.2 Hz, 2H, ArH), 2.07 (s, 3H, $ArCH_3$), 1.97 (d, ^4J(H,P) = 1.2 Hz, 3H, $ArCH_3$), 1.92 (d, ^4J(H,P) = 1.3 Hz, 3H, $ArCH_3$), 0.50 ppm (dd + sat., ^3J(H,P) = 9.6 Hz, ^3J(H,P) = 6.5 Hz, ^2J(Pt,H) = 68 Hz, 3H, CH_3). ^{31}P{^{1}H} NMR (162.0 MHz, CD_2Cl_2): δ = 9.4 (d + sat., ^2J(P,P) = 9.8 Hz, ^1J(Pt,P) = 1615 Hz), 8.6 ppm (d + sat., ^2J(P,P) = 9.8 Hz, ^1J(Pt,P) = 1888 Hz). Anal. Calcd for $C_{50}H_{46}N_2P_2Pt$: N, 3.01; C, 64.44; H, 4.98. Found: N, 2.89; C, 64.27; H, 5.20.

***cis*-[Pt(CH_3)(Ph){PPh$_2$(Ind)}$_2$] (1 c)**: A solution of diphenyl-2-(3-methyl)indolylphosphine (1.24 g, 3.92 mmol) in CH_2Cl_2 (20 mL) was added to solution of [Pt(Ph)(CH_3)(COD)] (0.74 g, 1.87 mmol) in CH_2Cl_2 (15 mL) while stirring. The resulting solution was stirred for another hour. The solvent was then removed *in vacuo* yielding the crude product as an off-white solid which was recrystallised from CH_2Cl_2/*n*-hexane (5 mL/60 mL) at 0 °C. The solid was collected by filtration, washed with *n*-pentane (3×5 mL) and dried *in vacuo* to yield **1 c** as a colourless powder. Yield 1.33 g (77%). IR (ATR, diamond): $\tilde{\nu}$ = 3444 cm^{-1} (medium, broad, N–H), 3363 cm^{-1} (medium, broad, N–H). ^{1}H NMR (400.1 MHz, CD_2Cl_2): δ = 8.98 (br s, 1H, NH), 8.50 (br s, 1H, NH), 7.58 (d, ^3J(H,H) = 8.0 Hz, 1H, ArH), 7.46 (d, ^3J(H,H) = 7.2 Hz, 1H, ArH), 7.40 (d, ^3J(H,H) = 8.2 Hz, 1H, ArH), 7.30 (m, 1H, ArH), 7.23 (m, 5H, ArH), 7.17 (m, 4H, ArH), 7.11 (m, 7H, ArH), 7.05 (m, 5H, ArH), 6.97 (m, 4H, ArH), 6.69 (m, 3H, ArH), 6.54 (m, 1H, ArH), 2.02 (d, ^4J(H,P) = 1.1 Hz, 3H, $ArCH_3$), 1.91 (d, ^4J(P,H) = 1.1 Hz, 3H, $ArCH_3$), 0.51 ppm (dd + sat., ^3J(H,P) = 9.3 Hz, ^3J(H,P) = 6.5 Hz, ^2J(H,Pt) = 68 Hz, 3H, CH_3). ^{31}P{^{1}H} NMR (162.0 MHz, CD_2Cl_2): δ = 9.1 (d + sat., ^2J(P,P) = 9.9 Hz, ^1J(P,Pt) = 1607 Hz), 9.1 ppm (d + sat., ^2J(P,P) = 9.9 Hz, ^1J(P,Pt) = 1891 Hz). Anal. Calcd for $C_{49}H_{44}N_2P_2Pt$: N, 3.05; C, 64.12; H, 4.83. Found: N, 2.77; C, 63.75; H, 5.14.

Synthesis of *cis*-[Pt(Me)(4-ClC$_6$H$_4$){PPh$_2$(Ind)}$_2$] (1 e): A solution of diphenyl-2-(3-methyl)indolylphosphine (659 mg, 2.09 mmol) in CH_2Cl_2 (10 mL) was added to a solution of [Pt(4-ClC_6H_4)(CH_3)(COD)] (451 mg, 1.05 mmol) in CH_2Cl_2 (10 mL) while stirring. The resulting pink solution was stirred for another hour. The solvent was then removed *in vacuo* to yield an off-white solid. The crude product was washed with pentane (5×5 mL) and the solid was dried *in vacuo*, affording **1 e** as a colourless powder. Yield 950 mg (95%). IR (ATR, diamond): $\tilde{\nu}$ = 3444 cm^{-1} (medium, broad, N–H), 3368 cm^{-1} (medium, broad, N–H). ^{1}H NMR (400.1 MHz, CD_2Cl_2): δ = 8.90 (s, 1H, NH), 8.47 (s, 1H, NH), 7.59 (d, ^3J(H,H) = 8.2 Hz, 1H, ArH), 7.48 (d, ^3J(H,H) = 7.5 Hz, 1H, ArH), 7.39 (d, ^3J(H,H) = 8.2 Hz, 1H, ArH), 7.31 (m, 1H, ArH), 7.26-6.97 (m, 25H, ArH), 6.70 (d, ^3J(H,H) = 7.7 Hz, 1H, ArH), 6.64 (m, 2H, ArH), 2.10 (d, ^4J(H,P) = 1.2 Hz 3H, $ArCH_3$), 1.94 (d, ^4J(P,H) = 1.2 Hz, 3H, $ArCH_3$), 0.49 ppm (dd + sat., ^3J(H,P) = 9.3 Hz, ^3J(H,P) = 6.4 Hz, ^2J(H,Pt) = 68 Hz, 3H, CH_3). ^{31}P{^{1}H} NMR (162.0 MHz, CD_2Cl_2): δ = 9.0 (d + sat., ^2J(P,P) = 10.5 Hz, ^1J(P,Pt) = 1670 Hz), 8.8 ppm (d + sat., ^2J(P,P) = 10.5 Hz, ^1J(P,Pt) = 1870 Hz). Anal. Calcd for $C_{49}H_{43}ClN_2P_2Pt$: N, 2.94; C, 61.80; H, 4.55. Found: N, 2.75; C, 61.55; H, 4.70.

Synthesis of *cis*-[Pt(Me)(4-CF$_3$C$_6$H$_4$){PPh$_2$(Ind)}$_2$] (1 f): A solution of diphenyl-2-(3-methyl)indolylphosphine (306 mg, 0.97 mmol) in CH_2Cl_2 (5 mL) was added to a solution of [Pt(4-$CF_3C_6H_4$)(CH_3)(COD)] (227 mg, 0.49 mmol) in CH_2Cl_2 (5 mL) while stirring. The resulting solution was stirred for another hour. The solvent was then removed *in vacuo* to yield the crude product as a yellow powder. This was washed with pentane (5×5 mL) and dried *in vacuo* to yield **1 f** as a pale-yellow powder. Yield 338 mg (70%). IR (ATR, diamond): $\tilde{\nu}$ = 3449 cm^{-1} (medium, broad, N–H), 3370 cm^{-1} (medium, broad, N–H). ^{1}H NMR (400.1 MHz, CD_2Cl_2): δ = 8.88 (s, 1H, NH), 8.45 (s, 1H, NH), 7.60 (d, ^3J(H,H) = 7.8 Hz, 1H, ArH), 7.48 (m, ^3J(H,H) = 8.5 Hz, 1H, ArH), 7.40 (m, ^3J(H,H) = 8.2 Hz, 1H, ArH), 7.34-7.17 (m, 10H, ArH), 7.08 (m, 12H, ArH), 6.97 (m, 4H, ArH), 6.86 (d, ^3J(H,H) = 7.6 Hz, 2H, ArH), 6.69 (m, 1H, ArH), 2.14 (d, ^4J(H,P) = 1.3 Hz, 3H, $ArCH_3$), 1.95 (d, ^4J(H,P) = 1.3 Hz, 3H, $ArCH_3$), 0.51 (dd + sat., ^3J(H,P) = 9.2 Hz, ^3J(H,P) = 6.3 Hz, ^2J(H,Pt) = 67 Hz, 3H, CH_3). ^{19}F NMR (282.4 MHz, CD_2Cl_2): δ = −62.2 ppm (s, CF_3). ^{31}P{^{1}H} NMR (162.0 MHz, CD_2Cl_2): δ = 9.1 (d + sat., ^2J(P,P) = 11.0 Hz, ^1J(P,Pt) = 1877 Hz), 8.77 ppm (d + sat., ^2J(P,P) = 11.0 Hz, ^1J(P,Pt) = 1669 Hz). Anal. Calcd for $C_{50}H_{43}F_3N_2P_2Pt$: N, 2.84; C, 60.91; H, 4.40. Found: N, 2.63; C, 60.70; H, 4.71.

General procedure for the formation of fluorido complexes *trans*-[Pt(F·(HF)$_2$)(Ar){Ph$_2$P(Ind)}$_2$] (2 a-f) and *trans*-[Pt(F)(Ar){Ph$_2$P(Ind)}$_2$] (3 a-f) (Ar = Ph (a), 4-FC$_6$H$_4$ (b), 4-ClC$_6$H$_4$ (c), 4-CH$_3$C$_6$H$_4$) (d), 4-CF$_3$C$_6$H$_4$) (e), 4-(CH$_3$)$_3$CC$_6$H$_4$) (f)): Solutions of *cis*-[Pt(CH_3)(Ar){R_2P-(Ind)}$_2$] (**1 a–f**) (0.15 mmol) in CD_2Cl_2 or CH_2Cl_2 (2 mL) were added into PFA-tubes containing PVPHF (150 mg; 38–42 wt% HF). Immediate gas evolution was overserved, and the mixtures were stirred for further 5 minutes. The respective solutions were then filtered from the polymer into PFA-Inliners and analysed by NMR-spectroscopy revealing the formation of **2 a–f**. Afterwards, the reaction solutions of **2 a–f** were added into a Schlenk flask loaded with anhydrous CsF (100 mg) and the mixtures were vigorously stirred for 5 minutes. After filtration of the solvent were removed *in vacuo* to give pale-yellow solids, which were dissolved in CD_2Cl_2 (0.7 mL) and analysed by NMR spectroscopy revealing the formation of **3 a–f**. Colourless crystals of **3 a**·CH_2Cl_2, **3 c**·0.5 CH_2Cl_2 and **3 d** were obtained by slow evaporation of the solvent from a dichloromethane solution at room temperature and were isolated by filtration. **3 a**·CH_2Cl_2 was dried under an argon stream yielding **3 a**·CH_2Cl_2 (84 mg, 53%) as colourless crystals. **3 c**·0.5 CH_2Cl_2 and **3 d** were dried in vacuo to give **3 c** (94 mg, 68%) and **3 d** (67 mg, 48%) as a colourless solid.

Selected analytical data:

***trans*-[Pt(F·(HF)$_2$)(4-*t*BuC$_6$H$_4$){Ph$_2$P(Ind)}$_2$] (2 a)**: ^{1}H NMR (300.1 MHz, CD_2Cl_2, 243 K) δ = 11.79 ppm (d, ^1J(H,F) = 38.1 Hz). ^{19}F NMR (282.4 MHz, CD_2Cl_2, 243 K): δ = −171.8 (br s, HF), −267.7 ppm (br s + sat, $|^1J(F,Pt)|$ = 639 Hz, Pt–F). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, 243 K): δ = 7.1 ppm (d + sat, ^2J(P,F) = 13.4 Hz, ^1J(P,Pt) = 3164 Hz).

***trans*-[Pt(F·(HF)$_2$)(4-CH$_3$C$_6$H$_4$){Ph$_2$P(Ind)}$_2$] (2 b)**: ^{1}H NMR (300.1 MHz, CD_2Cl_2, 243 K) δ = 11.84 ppm (d, ^1J(H,F) = 39.8 Hz). ^{19}F NMR (282.4 MHz, CD_2Cl_2, 243 K): δ = −171.5 (br s, HF), −269.8 ppm (br s + sat, $|^1J(F,Pt)|$ = 626 Hz, Pt–F). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, 243 K): δ = 6.2 ppm (d + sat, ^2J(P,F) = 13.8 Hz, ^1J(P,Pt) = 3156 Hz).

***trans*-[Pt(F·(HF)$_2$)(Ph){Ph$_2$P(Ind)}$_2$] (2 c)**: ^{1}H NMR (300.1 MHz, CD_2Cl_2, 243 K) δ = 11.87 ppm (d, ^1J(H,F) = 39.9 Hz). ^{19}F NMR (282.4 MHz, CD_2Cl_2, 243 K): δ = −177.8 (br s, HF), −270.0 ppm (br s + sat, $|^1J(F,Pt)|$ = 620 Hz, Pt–F). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, 243 K): δ = 6.7 ppm (d + sat, ^2J(P,F) = 14.2 Hz, ^1J(P,Pt) = 3149 Hz).

***trans*-[Pt(F·(HF)$_2$)(4-FC$_6$H$_4$){Ph$_2$P(Ind)}$_2$] (2 d)**: ^{1}H NMR (300.1 MHz, CD_2Cl_2, 243 K) δ = 12.01 ppm (d, ^1J(H,F) = 41.4 Hz). ^{19}F NMR (282.4 MHz, CD_2Cl_2, 243 K): δ = −126.0 (m, Ar–F), −171.4 (br s, HF), −274.3 ppm (br s + sat, $|^1J(F,Pt)|$ = 583 Hz, Pt–F). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, 243 K): δ = 6.0 ppm (d + sat, ^2J(P,F) = 13.3 Hz, ^1J(P,Pt) = 3099 Hz).

***trans*-[Pt(F·(HF)$_2$)(4-ClC$_6$H$_4$){Ph$_2$P(Ind)}$_2$] (2 e)**: ^{1}H NMR (300.1 MHz, CD_2Cl_2, 243 K) δ = 12.05 ppm (d, ^1J(H,F) = 42.0 Hz). ^{19}F NMR (282.4 MHz, CD_2Cl_2, 243 K): δ = −173.5 (br s, HF), −275.1 ppm (br s + sat, $|^1J(F,Pt)|$ = 570 Hz, Pt–F). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, 243 K): δ = 5.6 ppm (d + sat, ^2J(P,F) = 13.4 Hz, ^1J(P,Pt) = 3091 Hz).

***trans*-[Pt(F·(HF)$_2$)(4-CF$_3$C$_6$H$_4$){Ph$_2$P(Ind)}$_2$] (2 f)**: ^{1}H NMR (300.1 MHz, CD_2Cl_2, 243 K) δ = 11.92 ppm (d, ^1J(H,F) = 40.0 Hz). ^{19}F NMR (282.4 MHz, CD_2Cl_2, 243 K): δ = −62.4 (s, CF_3), −173.1 (br s, HF), −275.9 ppm (br s + sat, $|^1J(F,Pt)|$ = 569 Hz, Pt–F). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, 243 K): δ = 6.3 ppm (d + sat, ^2J(P,F) = 13.7 Hz, ^1J(P,Pt) = 3080 Hz).

***trans*-[Pt(F)(4-*t*BuC$_6$H$_4$){Ph$_2$P(Ind)}$_2$] (3 a)**: ^{1}H NMR (300.1 MHz, CD_2Cl_2) δ = 12.93 ppm (d, ^1J(H,F) = 50.0 Hz). ^{1}H,^{15}N HMBC (300.2 MHz/30.4 MHz, CD_2Cl_2): δ = 12.9/−238 ppm (dd/dvt, ^1J(H,F) = 50 Hz, ^1J(NH) = 97 Hz/^2J(N,F) = 34 Hz, *N* = 8 Hz). ^{19}F NMR (282.4 MHz, CD_2Cl_2): δ = −273.6 ppm (tt + sat, ^1J(F,H) = 50 Hz, ^2J(F,P) = 13 Hz, $|^1J(F,Pt)|$ = 567 Hz). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2): δ = 5.8 ppm (d + sat, ^2J(P,F) = 13.1 Hz, ^1J(P,Pt) = 3176 Hz). Anal. Calcd for $C_{52}H_{49}FN_2P_2Pt{\cdot}CH_2Cl_2$: N, 2.64; C, 59.89; H, 4.84. Found: N, 2.91; C, 59.95; H, 4.84.

***trans*-[Pt(F)(4-CH$_3$C$_6$H$_4$){Ph$_2$P(Ind)}$_2$] (3 b)**: ^{1}H NMR (300.1 MHz, CD_2Cl_2) δ = 12.91 ppm (d, ^1J(H,F) = 50.1 Hz). ^{1}H,^{15}N HMBC NMR (300.2 MHz/30.4 MHz, CD_2Cl_2): δ = 12.9/−238 ppm (dd/dvt, ^1J(H,F) = 50 Hz, ^1J(NH) = 97 Hz/^2J(N,F) = 34 Hz, *N* = 8 Hz). ^{19}F NMR (282.4 MHz, CD_2Cl_2): δ = −274.0 ppm (tt + sat, ^1J(F,H) = 50 Hz, ^2J(F,P) = 13 Hz, $|^1J(F,Pt)|$ = 564 Hz). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2): δ = 5.1 ppm (d + sat, ^2J(P,F) = 13.0 Hz, ^1J(P,Pt) = 3172 Hz).

***trans*-[Pt(F)(Ph){Ph$_2$P(Ind)}$_2$] (3 c)**: ^{1}H NMR (300.1 MHz, CD_2Cl_2) δ = 12.88 ppm (d, ^1J(H,F) = 49.6 Hz). ^{1}H,^{15}N HMBC NMR (300.2 MHz/30.4 MHz, CD_2Cl_2): δ = 12.8/−238 ppm (dd/dvt, ^1J(H,F) = 50 Hz, ^1J(NH) = 97 Hz/^2J(N,F) = 33 Hz, *N* = 9 Hz). ^{19}F NMR (282.4 MHz, CD_2Cl_2): δ = −275.2 ppm (tt + sat, ^1J(F,H) = 50 Hz, ^2J(F,P) = 14 Hz, $|^1J(F,Pt)|$ = 559 Hz). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2): δ = 5.5 ppm (d + sat, ^2J(P,F) = 13.7 Hz, ^1J(P,Pt) = 3162 Hz). Anal. Calcd for $C_{48}H_{41}FN_2P_2Pt$: N, 3.04; C, 62.54; H, 4.48. Found: N, 3.07; C, 62.58; H, 4.50.

***trans*-[Pt(F)(4-FC$_6$H$_4$){Ph$_2$P(Ind)}$_2$] (3 d)**: **^{1}H NMR** (300.1 MHz, CD_2Cl_2) δ = 12.80 ppm (d, ^1J(H,F) = 48.9 Hz). ^{1}H,^{15}N HMBC NMR (300.2 MHz/30.4 MHz, CD_2Cl_2): δ = 12.8/−239 ppm (dd/dvt, ^1J(H,F) = 49 Hz, ^1J(NH) = 97 Hz/^2J(N,F) = 33 Hz, *N* = 8 Hz). ^{19}F NMR (282.4 MHz, CD_2Cl_2): δ = −126.0 (m, Ar–F) −278.3 ppm (tt + sat, ^1J(F,H) = 49 Hz, ^2J(F,P) = 14 Hz, $|^1J(F,Pt)|$ = 521 Hz, Pt–F). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2): δ = 5.1 ppm (dd + sat, ^2J(P,F) = 13.6 Hz, *J*(P,F) = 2.0 Hz, ^1J(P,Pt) = 3112 Hz). Anal. Calcd for $C_{48}H_{40}F_2N_2P_2Pt$: N, 2.98; C, 61.34; H, 4.29. Found: N, 3.09; C, 61.47; H, 4.30.

***trans*-[Pt(F)(4-ClC$_6$H$_4$){Ph$_2$P(Ind)}$_2$] (3 e)**: ^{1}H NMR (300.1 MHz, CD_2Cl_2) δ = 12.76 ppm (d, ^1J(H,F) = 48.6 Hz). ^{1}H,^{15}N HMBC NMR (300.2 MHz/30.4 MHz, CD_2Cl_2): δ = 12.8/−239 ppm (dd/dvt, ^1J(H,F) = 49 Hz, ^1J(NH) = 97 Hz/^2J(N,F) = 32 Hz, *N* = 8 Hz). ^{19}F NMR (282.4 MHz, CD_2Cl_2): δ = −278.7 ppm (tt + sat, ^1J(F,H) = 48 Hz, ^2J(F,P) = 14 Hz, $|^1J(F,Pt)|$ = 519 Hz, Pt–F). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2): δ = 4.9 ppm (d + sat, ^2J(P,F) = 13.7 Hz, ^1J(P,Pt) = 3103 Hz).

***trans*-[Pt(F)(4-CF$_3$C$_6$H$_4$){Ph$_2$P(Ind)}$_2$] (3 f)**: ^{1}H NMR (300.1 MHz, CD_2Cl_2) = 12.71 ppm (d, ^1J(H,F) = 47.9 Hz). ^{1}H,^{15}N HMBC NMR (300.2 MHz/30.4 MHz, CD_2Cl_2): δ = 12.7/−239 ppm (dd/dvt, ^1J(H,F) = 48 Hz, ^1J(NH) = 97 Hz/^2J(N,F) = 31 Hz, *N* = 8 Hz). ^{19}F NMR (282.4 MHz, CD_2Cl_2): δ = −62.6, (s, CF_3), −280.0 ppm (tt + sat, ^1J(F,H) = 48 Hz, ^2J(F,P) = 14 Hz, $|^1J(F,Pt)|$ = 515 Hz, Pt–F). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2): δ = 5.5 ppm (d + sat, ^2J(P,F) = 13.5 Hz, ^1J(P,Pt) = 3090 Hz).

Synthesis of *trans*-[Pt(Cl)(Ph){Ph$_2$P(Ind)}$_2$] (4): A solution of diphenyl-2-(3-methylindolyl)phosphine (0.15 g, 0.48 mmol) in CH_2Cl_2 (5 mL) was added to a stirring solution of [Pt(Cl)(Ph)(COD)] (0.10 g, 0.24 mmol) in DCM (5 mL). The resulting mixture was stirred for two hours. The solvent was removed *in vacuo* to yield the crude product as a colorless powder. This solid was recrystallised from a solution of CH_2Cl_2/*n*-hexane (20 mL/60 mL) and the product was left to precipitate overnight. The solution was then filtered off and a colourless solid was obtained, which was washed with pentane (3 × 5 mL) and then dried *in vacuo* to yield **4** as a colourless solid. Yield 0.14 g (62 %). IR (ATR, diamond): $\tilde{\nu}$ = 3297 cm^{-1} (strong, sharp, N–H) ^{1}H NMR (500.1 MHz, CD_2Cl_2): δ = 10.11 (s, 2H, NH), 7.57 (dd, ^3J(H,H) = 8.0 Hz, *J*(H,P) = 0.6 Hz, 2H, ArH), 7.45-7.38 (m, 9H, ArH), 7.38-7.33 (m, 5H, ArH), 7.2 9–7.22 (m, 10H, ArH), 7.14-7.09 (m, 2H, ArH), 6.80 (m + sat., ^3J(H,H) = 8.0 Hz, ^4J(H,P) = 1.2 Hz, *J*(Pt,H) = 57 Hz, 2H, ArH, *ortho*), 6.27 (t, ^3J(H,H) = 7.3 Hz,1H, ArH, *para*), 6.15 (t, ^3J(H,H) = 7.6 Hz, 2H, ArH, *meta*), 1.78 (br s, 6H, $ArCH_3$). ^{31}P{^{1}H} NMR (202.5 MHz, CD_2Cl_2): δ = 8.25 (br s + sat., ^1J(Pt,P) = 3066 Hz). Anal. Calcd for $C_{48}H_{41}ClN_2P_2Pt$: N, 2.99; C, 61.44; H, 4.40. Found: N, 2.81, C, 61.75, H, 4.34.

Computational Details: All structure optimizations have been performed with the Turbomole program, version 7.5.1,[43] using the PBE[44] functional in conjunction with def2-TZVP[45] basis sets for all atoms. In all calculations the multipole-accelerated resolution-of-identity approximation (MARIJ)[46] as well as D3[47] empirical dispersion corrections with Becke-Johnson damping (BJ)[48] was employed. In addition to gas phase calculations, all structures were subsequently optimized using the COSMO[49] continuum solvent model, employing a relative permittivity ε = 8.9 for dichloromethane (DCM, CH_2Cl_2) as solvent. Based on the optimized structures, NMR nuclear spin-spin coupling constants were calculated using the AMS program package, release version 2022.1.[50] These calculations were performed at the two-component (2c) quasi-relativistic ZORA[51] all-electron DFT level, employing the BHLYP[52] functional in conjunction with a locally dense basis set scheme with all-electron QZ4P-J[53] basis set for the coupling atoms and otherwise all-electron TZ2P-J[53] basis sets for the remaining atoms, and a Becke grid of quality 4.[54] Further electronic structure analyses at BHLYP/def2-TZVP level used the NBO 7.0.7[55] program linked to the Gaussian 16 program, revision A.03.[56] In this way, atomic charges from natural population analyses (NPA),[57] atomic hybridizations from natural localized molecular orbital (NLMO)[57] analyses, and Wiberg bond indices (WBI)[58] were obtained.

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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 supplementary material of this article.

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