Platinum Indolylphosphine Fluorido and Polyfluorido Complexes: An Interplay between Cyclometallation, Fluoride Migration, and Hydrogen Bonding

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Abstract: The reaction of [PtCl₂(COD)]⁻ (COD = 1,5-cyclooctadiene) with diisopropyl-2-(3-methylindolophosphine) (IPrP₂(C₆H₁₃N)) led to the formation of the platinum(II) chlorido complexes, cis-[PtCl₂/IPrP₂(C₆H₁₃N)]⁻ (1) and trans-[PtCl₂/IPrP₂(C₆H₁₃N)]⁻ (2). The cis-complex 1 reacted with NEt₃ yielding the complex cis-[PtCl₂(iPr₉-P(Pr(C₆H₁₃N)][iPr₂P(C₆H₁₃N)]) (3) bearing a cyclometalated κ²-(P,N)-phosphine ligand, while the isomer 2 with a trans-configuration did not show any reactivity towards NEt₃. Treatment of 1 or 3 with (CH₃)₂NF (TMAF) resulted in the formation of the twofold cyclometalated complex cis-[Pt(iPr₉-P(Pr(C₆H₁₃N)](HF)₄ (4). The molecular structures of the complexes 1–4 were determined by single-crystal X-ray diffraction. The fluorido complexes cis-[PtF(iPr₉-P(Pr(C₆H₁₃N)][iPr₂P(C₆H₁₃N)])(HF)₄ (5–(HF)₄) was formed when complex 4 was treated with different hydrogen fluoride sources. The Pt(II) fluorido complex 5-(HF)₄ exhibits intramolecular hydrogen bonding in its outer coordination sphere between the fluorido ligand and the NH group of the 3-methylindolyl moiety. In contrast to its chlorido analogue 3, complex 5-(HF)₄ reacted with CO or the ynamide 1-(2- phenylethenyl)-2-pyrolidinone to yield the complexes trans-[Pt(CO)(iPr₉-P(Pr(C₆H₁₃N)][iPr₂P(C₆H₁₃N)])(F(HF))₄ (7) and a complex, which we suggest to be cis-[Pt(C=C(CH₃)OCN(C₆H₅))][(iPr₉-P(Pr(C₆H₁₃N)][F(HF))₄ (9), respectively. The structure of 9 was assigned on the basis of DFT calculations as well as NMR and IR data. Hydrogen bonding of HF and NH to fluorido was proven to be crucial for the existence of 7 and 9.

Introduction

Fluorido complexes of late transition metals gain increasing attention,[1] in part because of their ability to open up original routes for metal-mediated fluorination reactions.[1h,1j,2] In addition, they can also play a distinct role in C–F or C–H activation reactions.[3–5] However, late transition metal fluorido complexes tend to be unstable, which is often explained by the mismatch of a soft Lewis acid with a hard Lewis base, but also with an unfavourable p(π)-a(π) repulsion.[4] The first examples of platinum(II) fluorido complexes were already described in the early 1970s.[4,5] Platinum fluorido complexes came again into focus in recent years.[6–8] Wendt et al., Vigalok et al. and recently Beyzavi, Shahsavari et al. described the preparation of Pt(II) fluorido complexes by a F/I exchange reaction with AgF.[6a–8] Platinum fluorido complexes were also obtained by reaction of hydrogen fluoride sources with platinum hydrido or dimethyl complexes, as shown by Perutz et al. and Seppelt et al., respectively.[6a,6d] Braun et al. revealed that Pt alkyne complexes react with N-Fluorobenzenesulfonyl fluoride (NFSI) or XeF₂ to give platinum fluoride and fluorovinyl complexes.[6d,6h] Vigalok et al., Puddephatt et al. and Haghighi et al. reported on the formation of Pt(II) fluorido complexes using XeF₂, NFSI or Selectfluor (N-chloromethyl-N-fluorotriethylenediammonium bis(tetrafluoroborate)).[6d,6e,6h,6l] Love et al. demonstrated Pt(II) mediated C–F bond activation reactions generating Pt(IV) fluorido complexes,[6b,c,f,6g] while Finze, Braunschweig and Bickelhaupt et al. presented the formation of a trifluorophosphine platinum (II) fluorido complex by P–F bond activation of PF₃.[6f]

Hydrogen bonding is discussed as an important factor to enable fluorination reactions by increasing the effective nucelophilicity of the fluoride, due to a lowering of its basicity.[7] Richmond et al. reported on the potential of transition metal fluorido complexes to act as hydrogen bond acceptors.[7] The ability of transition metal fluorido complexes to undergo strong hydrogen bonding with hydrogen fluoride to result in the formation of bifluorido complexes is well described.[7m,a,8] NH or OH groups were also employed as hydrogen bond donors for transition metal fluorides.[7h,i,k,l] Thus, Crabtree et al. probed intramolecular hydrogen bonding of a ligand appended amino group to an iridium(III) fluorido complex.[7c,d,b] Gray et al. reported on a cyclometalated Iridium(III) fluorido complex exhibiting intramolecular hydrogen bonding to an adjacent pyrazole ligand.[7b] Szmyczak et al. demonstrated a remarkable
Results and Discussion

Synthesis of platinum(ii) chlorido complexes with 3-methyl-2-indolylphosphine ligands

Treatment of \( [\text{PtCl}_2(\text{COD})] \) with two equivalents of \( \text{IPr},\text{P}(\text{C}_9\text{H}_8\text{N}) \) led to the formation of the platinum(ii) complexes cis-\( [\text{PtCl}_2(\text{iPr},\text{P}(\text{C}_9\text{H}_8\text{N}))] \) (1) and trans-\( [\text{PtCl}_2(\text{iPr},\text{P}(\text{C}_9\text{H}_8\text{N}))] \) (2) in a ratio of 4.5 : 5.5 (Scheme 1). Complex 2 could be removed from the crude product mixture by washing the solid with a CHCl\(_3\)/\( \text{MeOH} \) mixture (1:3), resulting in 1 as a colourless solid. The complex trans-\( [\text{PtCl}_2(\text{iPr},\text{P}(\text{C}_9\text{H}_8\text{N}))] \) (2) was synthesised independently by reaction of \( \text{K}_2\text{PtCl}_4 \) with two equivalents of \( \text{iPr},\text{P}(\text{C}_9\text{H}_8\text{N}) \) in ETOH/H\(_2\)O, following a modified procedure for the formation of trans-\( [\text{PtCl}_2(\text{IPr},\text{P}(\text{C}_9\text{H}_8\text{N}))] \). When the complex cis-\( [\text{PtCl}_2(\text{iPr},\text{P}(\text{C}_9\text{H}_8\text{N}))] \) (1) was treated with an excess of NEt\(_3\), cyclometallation and the formation of cis-\( [\text{PtCl}_2(\text{iPr},\text{P}(\text{C}_9\text{H}_8\text{N}))](\text{IPr},\text{P}(\text{C}_9\text{H}_8\text{N})) \) (3) was observed (Scheme 1). Complex 3 was also obtained directly by adding a solution of \( \text{iPr},\text{P}(\text{C}_9\text{H}_8\text{N}) \) together with NEt\(_3\) to a suspension of \( [\text{PtCl}_2(\text{COD})] \) in THF. However, complex 2 bearing the phosphines in a trans position did not show any reactivity towards NEt\(_3\). This might be because a chlorido ligand in the trans position to the phosphine is more liable than the one trans to a chlorido ligand.

All complexes were characterised by \( ^1\text{H} \) NMR and \( ^{31}\text{P}(^1\text{H}) \) NMR spectroscopy as well as IR-spectroscopy. A comparison of selected NMR and IR data is shown in Table 1. The \( ^{31}\text{P}(^1\text{H}) \) NMR spectra of the complexes 1 and 2 reveal a singlet with \( ^{199}\text{Pt} \) satellites for the phosphorus atoms of the phosphine ligands. The values of the \( J(Pt,Pt) \) coupling constants (3580 Hz for 1 and 2490 Hz for 2) are consistent with the cis or trans arrangement of the phosphine ligands. The \( ^{31}\text{P} \) NMR spectrum of 3
exhibits two doublets with $^{195}$Pt satellites at $\delta = 17.5$ ppm ($\gamma(P,P) = 14.0$ Hz, $\gamma(P,Pt) = 3231$ Hz) and $\delta = -7.8$ ppm ($\gamma(P,P) = 14.0$ Hz, $\gamma(P,Pt) = 3083$ Hz). Note, that the signal of the $\kappa^2-P,N$ bound phosphine ligand appears high field shifted. The $\gamma(P,P)$ coupling constants are typical for platinum complexes bearing phosphine ligands in a mutually $cis$ coordination.\(^{13,14}\) The $^1H$ NMR spectra of 1, 2, and 3 show each a broad signal for the NH group in a region of $\delta = 8.22$–$8.68$ ppm. The resonances of the NH protons show for all complexes a downfield shift compared to the data for the free phosphine, which is consistent with hydrogen bonding interactions to the chlorido ligands.\(^{13,14}\) The IR spectrum of cis-[PtCl$_2$(i-Pr$_2$P(C$_6$H$_3$N)$_2$)] (1) reveals two characteristic N–H stretching frequencies at $\nu$(NH) = 3333, 3278 cm$^{-1}$. The ATR IR spectra of trans-[PtCl$_2$(i-Pr$_2$P(C$_6$H$_3$N)$_2$)] (2) and cis-[PtCl$_2$($\kappa^2$-P,N)-i-Pr$_2$P(C$_6$H$_3$N)]/[i-Pr$_2$P(C$_6$H$_3$N)] (3) show only a single broad absorption band at $\nu$(NH) = 3396 cm$^{-1}$ and 3413 cm$^{-1}$, respectively. Comparison to the N–H absorption frequencies of the phosphine iPr$_2$P(C$_6$H$_3$N) (3423 cm$^{-1}$) revealed shifts to lower frequencies together with broadened absorption bands, which is consistent for the presence of hydrogen bonding in solid state.\(^{11}\)

The molecular structures of the complexes cis-[PtCl$_2$(i-Pr$_2$P(C$_6$H$_3$N)$_2$)] (1), trans-[PtCl$_2$(i-Pr$_2$P(C$_6$H$_3$N)$_2$)] (2) and cis-[PtCl$_2$($\kappa^2$-P,N)-i-Pr$_2$P(C$_6$H$_3$N)]/[i-Pr$_2$P(C$_6$H$_3$N)] (3) were obtained by X-ray crystallography, and they are depicted in the Figures 1–4. Selected bond lengths, angles and atomic distances are given in the captions of the corresponding Figures. Electron density for nitrogen bound hydrogen atoms were found in the difference Fourier maps and a free refinement was allowed. The molecular structures of 1 and 2 exhibit a slightly distorted square-planar coordination of the two $\kappa^2$-(P)-phosphine and chlorido ligands in a mutually cis and trans coordination, respectively. For both structures, the asymmetric unit contains one half of the molecule. The Pt–P bond length of complex 1 (2.2890(9) Å) features a smaller value than the Pt–P bond length in complex 2 (2.3428(7) Å), while the opposite trend is seen for the Pt–Cl bond lengths (2.3561(9) Å for 1, 2.3050(6) Å for 2), resulting from the larger trans-influence of the phosphine ligands. The Pt–P and P–Cl bond lengths are in good agreement with other analogous iPr$_2$P(C$_6$H$_3$N) complexes.\(^{15,16}\)
Reactivity of Pt chlorido complexes towards TMAF

Anhydrous tetramethylammonium fluoride (TMAF) is frequently used for nucleophilic fluorination reactions, because of its ability to deliver a rather nucleophilic fluoride. TMAF was also applied for the synthesis of several fluorido complexes starting from their halido precursors. TMAF the formation of the complex cis-[Pt(cis-2-(P,N)-Pr\(_2\)P(C\(_2\)H\(_5\)N)]) (4) was observed (Scheme 1). The \(^{19}\)F NMR spectrum of the reaction mixture revealed the formation of the GHF anion, which exhibits the characteristic doublet at \(\delta = -151\) ppm with a \(J(\text{F,H})\) coupling constant of 122 Hz. No reaction of trans-[PtCl\(_2\)(iPr\(_2\)P(C\(_2\)H\(_5\)N))] (2) towards TMAF was observed.

Complex 4 could be separated from the tetramethylammonium salts by extraction of the crude product with toluene. The \(^{31}\)P[H] NMR spectrum of 4 exhibits a high field shifted singlet with \(^{195}\)Pt satellites at \(\delta = -10.1\) ppm with a \(J(\text{P,Pr})\) coupling constant of 2784 Hz. The molecular structure of complex 4 in the solid state was determined by X-ray crystal structure determination (Figure 5). Complex 4 exhibits a distorted square-planar coordination geometry with two bidentate \((P,N)\)-phosphine ligands in a mutually cis arrangement. The P(1)-Pt(1) and P(2)-Pt(2) bond lengths show almost the same values, which is also observed for the N(1)-Pt(1)/N(2)-Pt(2) bond lengths (2.2498(6) Å/2.2450(6) Å and 2.126(2) Å/2.128(2) Å, respectively). As a consequence of the two cyclometalated Pt\(_{\text{cis}}\) (P,N)-phosphine ligands, the P(1)-Pt(1)-N(1) and P(2)-Pt(1)-N(2) angles exhibit small values of 69.95(5)° and 69.39(5)°, respectively. Therefore, the P(1)-Pt(1)-P(2) (110.16(2)°) as well as the N(1)-Pt(1)-N(2) (111.52(7)°) bond angles are increased.

The formation of 4 from the (di-)chlorido platinum(ii) precursors 1 or 3 with TMAF might proceed via two different pathways. One conceivable pathway involves an initial deprotonation of the 3-methylindole moiety by fluoride followed by the cyclometallation and release of chloride. The second possible route consists of an Cl/F exchange at the Pt(ii) centre and a subsequent HF elimination, which might again be supported by a fluoride base. For both steps FHF\(^{-}\) would be formed, the signal of which was observed in the \(^{19}\)F NMR spectrum.

Figure 5. Structure of cis-[Pt(cis-2-(P,N)-Pr\(_2\)P(C\(_2\)H\(_5\)N)]) (4). Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms were omitted for clarity. Selected distances (Å) and angles (°): P(1)-P(1) 2.2498(6); P(2)-P(2) 2.2450(6); P(1)-N(1) 2.126(2); P(1)-N(2) 2.128(2); P(1)-P(1)-P(2) 110.16(2); P(1)-Pt(1)-N(2) 111.52(7).

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Reactivity of 4 towards hydrogen fluoride sources

To investigate a possible ring-opening at complex 4, the reactivity towards the HF sources Et₄N·3HF or polymer supported poly[4-vinylpyridinium poly(hydrogen fluoride)] (PVPhF) was studied. After treatment of a solution of complex 4 with a ten-fold excess of the hydrogen fluoride sources, the formation of the Pt(μ) fluorido complex cis-[PtF{P(η²-N,P)-Pr,P-(C₅H₄N)}/(Pr,P(C₅H₄N))]:[HF] (5·(HF)₄) was observed (Scheme 2). To determine the amount of pendant HF, a solution of complex 5·(HF)₄ was treated with ten equivalents of Et₄SiCl. A full conversion to complex 1 as well as the formation of Et₄SiF was detected. The signal for Et₄SiF in the ^19F NMR spectrum was integrated towards an internal standard (C₅F₅) revealing values between 3.8 and 4.1 HF equivalents. The ^31P(^1H) NMR spectrum of the fluorido complex 5·(HF)₄ exhibits two signals for the two different phosphine ligands. The resonance on δ = 19.6 ppm displays as a doublet of doublets with ^195Pt satellites with coupling constants of J(P,Pr) = 16.5 Hz, J(P,F) = 11.3 Hz and J(P,Pr,Pr) = 3311 Hz and can be assigned to the phosphorus atom in the cis position to the fluorido ligand. The doublet of doublets with ^195Pt satellites at δ = -18.0 ppm, exhibiting coupling constants of J(P,Pr) = 16.5 Hz, J(P,F) = 146.8 Hz and J(P,Pr,Pr) = 3081 Hz is allocated to the phosphorus atom trans to the fluorido ligand. The ^19F(^1H) NMR spectrum revealed a doublet of doublets with ^195Pt satellites at δ = -281.5 ppm with coupling constants of J(F,P) = 146.8 Hz, J(F,Pt) = 11.3 Hz and J(F,Pt,Pr) = 283 Hz (Figure 6). The chemical shift as well as the observed J(F,P) and J(F,Pt) coupling constants are typical for a platinum bound fluorido ligand with phosphorus nuclei in a trans or cis arrangement. In the ^19F NMR spectrum the signal gets broadened to a doublet with ^195Pt satellites, in part due to the coupling to the NH proton and HF. Additionally, a broad signal for remaining (HF)₄ was found at δ = -181.7 ppm. The ^1H NMR spectrum of 5·(HF)₄ displays a doublet at δ = -9.18 ppm with a coupling constant of J(F,H) = 5.8 Hz, indicating hydrogen bonding from the NH group to the fluorido ligand. The signal collapses to a singlet in the ^1H(^19F) NMR spectrum. Complex 5·(HF)₄ was treated with CsF for 5 min to remove excess of HF. Indeed, the formation of the fluorido complex cis-[PtF{P(η²-N,P)-Pr,P-(C₅H₄N)}/(Pr,P(C₅H₄N))]:[HF] (5·(HF)₄) was observed, but also its precursor complex cis-[PtF{P(η²-N,P)-Pr,P-(C₅H₄N)}/(Pr,P(C₅H₄N))]:[HF] (4) in a ratio of 1:1 as evidenced by the ^19F(^1H) NMR spectrum. For complex 5 the ^19F(^1H) NMR spectrum displays a doublet of doublets with ^195Pt satellites at δ = -282.5 ppm revealing coupling constants of J(F,P) = 127.5 Hz, J(F,Pt) = 7.4 Hz and J(F,Pt,Pr) = 180 Hz (Figure 7). In the ^19F NMR spectrum the signal appears as a doublet of doublets due to additional coupling with the NH proton exhibiting a J(F,H) coupling constant of 26.7 Hz. For the NH proton a doublet is found at δ = 10.64 ppm (J(H,F) = 26.7 Hz) in the ^1H NMR spectrum, which collapses to a singlet in the ^1H(^19F) NMR spectrum. Note that the values of the J(F,P) and J(F,Pt) coupling constants decreased after the removal of

Scheme 2. Formation of the Pt(μ) fluorido complex cis-[PtF{P(η²-N,P)-Pr,P-(C₅H₄N)}/(Pr,P(C₅H₄N))]:[HF] (5·(HF)₄), its reactivity towards CsF, CO and the rearrangement reaction to the fluorophosphine complex cis-[Pt(2-C₅H₄N)P(η²-N,P)-Pr,P-(C₅H₄N)][Pr,P(C₅H₄N)] (6).

Figure 6. Part of the ^19F NMR spectrum (bottom) and the ^1H(^19F) NMR spectrum (top) of cis-[PtF{P(η²-N,P)-Pr,P-(C₅H₄N)}/(Pr,P(C₅H₄N))]:[HF] (5·(HF)₄) revealing coupling constants of J(F,P) = 146.8 Hz, J(F,Pt) = 11.3 Hz, J(P,Pr) = 283 Hz. Note that part of the ^19Pt satellites is hidden by the main signal.

Figure 7. Part of the ^19F NMR spectrum (bottom) and the ^1H(^19F) NMR spectrum (top) of HF free cis-[PtF{P(η²-N,P)-Pr,P-(C₅H₄N)}/(Pr,P(C₅H₄N))] (5) revealing coupling constants of J(F,H) = 26.7 Hz, J(F,P) = 126.5 Hz, J(F,Pt) = 7.3 Hz and J(F,Pt,Pr) = 180 Hz.

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HF, which might indicate that the bond has less s-orbital character. However, a larger $\mathcal{J}(\text{F}, \text{H})$ coupling constant was found, which indicates a stronger hydrogen bond from the NH proton to the fluoro ligand.

At room temperature a solution of fluoro complex $5 \cdot (\text{HF})_4$ was not stable and after 30 minutes the formation of the complex $\text{cis-}[\text{Pt}(\text{C}(\text{C}_2\text{H}_6)_2\text{N})\{\text{C}(\text{P},\text{N})-\text{iPr,Pr}^1\text{P}(\text{C}(\text{C}_2\text{H}_6)_2\text{N})]\{\text{Pr}^1\text{P,F}}]$ (6) bearing a fluorphosphine ligand was observed by a dyotropic rearrangement (Scheme 2). The ratio $5 \cdot (\text{HF})_4 : 6$ was found to be 1:1.5 after approximately 90 minutes after addition of HF (as indicated by the signal intensity in the $^{195}$Pt NMR spectrum). Note, that this rearrangement reaction was not observed for the HF free complex $5$ after 90 minutes. However, after 24 h complex $6$ was detected in small amount with a ratio $5 : 6$ of 4.5:1. A complete conversion to complex $6$ was not achieved, since at the same time decomposition to yield a fluorphosphonium cation started, which was detected in the corresponding $^{19}$F NMR spectrum as a doublet of triplets at $\delta = -98.6$ ppm ($\mathcal{J}(\text{F}, \text{P}) = 1042.2$ Hz, $\mathcal{J}(\text{F}, \text{H}) = 6.8$ Hz) as well as in the $^{195}$Pt NMR spectrum as a doublet at $\delta = -80.4$ ppm ($\mathcal{J}(\text{P}, \text{F}) = 1042.2$ Hz). Comparable $\mathcal{J}(\text{F}, \text{P})$ coupling constants are described in the literature for other fluorphosphonium salts.[28]

The $^{19}$F NMR spectrum of $6$ displays a doublet of doublet of triplets with $^{195}$Pt satellites at $\delta = -143.7$ ppm revealing coupling to both phosphorus nuclei ($\mathcal{J}(\text{F}, \text{P}) = 854.8$ Hz, $\mathcal{J}(\text{F}, \text{H}) = 59.6$ Hz), the CH protons of the proximal isopropyl groups with a coupling constant of $\mathcal{J}(\text{F}, \text{H}) = 14.1$ Hz as well as coupling to the platinum centre with a coupling constant of $\mathcal{J}(\text{P}, \text{F}) = 401$ Hz. The signal collapses to a doublet of doublets with $^{195}$Pt satellites in the $^{19}$F/$^1$H NMR spectrum (Figure 8). The $^{19}$Pt/$^1$H NMR spectrum features a strongly downfield shifted doublet of doublets with $^{195}$Pt satellites for the fluorphosphine ligand at $\delta = 179.9$ ppm with coupling constants of $\mathcal{J}(\text{F}, \text{P}) = 854.8$ Hz, $\mathcal{J}(\text{F}, \text{H}) = 9.3$ Hz and $\mathcal{J}(\text{P}, \text{F}) = 3991$ Hz. Comparable data for fluorphosphine ligands have been described by Schmutzler et al. as well as Perutz, Braun et al. for platinum(ii) complexes, Macgregor, Grushin et al. for rhodium(i) complexes and Mistleit et al. for iridium(i) complexes.[28] For the phosphorus atom of the cyclometalated phosphine, a doublet of doublets with $^{195}$Pt satellites is found at $\delta = 7.0$ ppm with coupling constants of $\mathcal{J}(\text{F}, \text{P}) = 59.6$ Hz, $\mathcal{J}(\text{P}, \text{P}) = 9.3$ Hz. The small $\mathcal{J}(\text{P}, \text{Pt})$ coupling constant of 1498 Hz gives an additional indication for a phosphorus atom trans-bound to an $\sigma$-donor ligand.[30]

Reactivity of cis-$[\text{PtF}(\text{C}(\text{P},\text{N})-\text{iPr,Pr}^1\text{P}(\text{C}(\text{C}_2\text{H}_6)_2\text{N})]\{\text{Pr}^1\text{P,F}}]$ towards CO.

Next, the reactivity of complex $5 \cdot (\text{HF})_4$ towards carbon monoxide was studied to estimate the binding properties of the fluoride ligand. Exposure of an in situ formed solution of complex $5 \cdot (\text{HF})_4$ to an atmosphere of CO resulted in the formation of the complex trans-$[\text{Pt(CO)}(\text{C}(\text{P},\text{N})-\text{iPr,Pr}^1\text{P}(\text{C}(\text{C}_2\text{H}_6)_2\text{N})][\text{iPr}^1\text{P,F}(\text{C}(\text{C}_2\text{H}_6)_2\text{N})]$ (7) (Scheme 2). Apparently, an insertion of a CO molecule into the Pt–N bond occurred in addition to CO coordination at the Pt centre, resulting in a five membered carbamoyl metallacycle. The presence of an excess of HF, which forms a poly(hydrogen fluoride) anion, is necessary for the generation and stabilisation of the fluoride anion and, therefore, complex $7$ in solution. Accordingly, addition of CsF to complex $7$ resulted in a second cyclometallation yielding trans-$[\text{Pt}(\text{C}(\text{P},\text{N})-\text{iPr,Pr}^1\text{P}(\text{C}(\text{C}_2\text{H}_6)_2\text{N})][\text{iPr}^1\text{P,F}(\text{C}(\text{C}_2\text{H}_6)_2\text{N})]$ (8) as the only product (Scheme 2). Note that an independent reaction of complexes $3$ and $4$ with CO did not show any conversion.

The $^{19}$Pt/$^1$H NMR spectra of $7$ and $8$ feature downfield shifted signals with $^{195}$Pt satellites at $\delta = 55.7$, 31.8 ppm and 47.8 ppm, respectively. In the $^1$H NMR spectrum a broad signal at $\delta = 10.82$ ppm is observed, which can be assigned to $\text{F(HF)}_x$ anion.[27b] For the NH proton a signal at $\delta = 10.61$ ppm is observed featuring a downfield shift through hydrogen bonding with the poly(hydrogen fluoride) anion.[31] The IR spectrum of complex $7$ features a very intense absorption band at $\nu = 2108$ cm$^{-1}$, which can be attributed to the CO stretch of the CO ligand. Another band is observed at 1654 cm$^{-1}$ resulting from the CO stretch of the carbamoyl group. Comparable stretching frequencies have been reported for other cationic Pt(ii) carbonyl/carbamoyl complexes.[31] Additionally, a broad absorption band could be identified at $\nu = 1797$ cm$^{-1}$, which can be assigned to the stretching vibrations of the poly(hydrogen fluoride) anion.[31] The IR spectrum of $8$ displayed an absorption band at $\nu = 1664$ cm$^{-1}$, which is assigned to the CO stretch of the carbamoyl group. The molecular structure of trans-$[\text{Pt}(\text{C}(\text{P},\text{N})-\text{iPr,Pr}^1\text{P}(\text{C}(\text{C}_2\text{H}_6)_2\text{N})][\text{iPr}^1\text{P,F}(\text{C}(\text{C}_2\text{H}_6)_2\text{N})]$ (8) was also determined by X-ray crystal structure determination (Figure 9). It features a slightly distorted square-planar coordination of the cyclometalated phosphine ligand, as represented by the C1-Pt1-P1 angle of 85.51(9)$^\circ$. The P1-Pt1 length of 2.2833(8) Å is comparable with the P–Pt distance found for the trans complex $2$. The Pt–C1 bond length is found to be 2.056(3) Å. A C1-O1 bond length of 1.219(4) Å and a N1-C1 1.442(4) Å is observed for the carbamoyl group. Similar bond lengths were reported for other platinum carbamoyl complexes.[31]
Reactivity of cis-[PtF\(_2\)\(\{\kappa^2-(P,N)-iPrP(C,H,N)\}\)] (5·(HF)) towards an Ynamide

Additionally, the reactivity of the platinum fluoroido complex 5·(HF)\(_2\) towards alkenes and amino substituted alkenes (ynamides) was studied. In the past several examples for the transition metal catalysed hydrogen fluorination of alkenes and ynamides were reported. However, these reactions are limited solely to Au(11) complexes and to some extent on Ag(i)/Cu(i) complexes as catalytic precursors.\(^{[13b,27b]}\)

Initially, an in situ generated reaction solution of complex 5·(HF)\(_2\) was treated with diphenylacetylene or phenylacetylene, but no reactions with the substrates were observed and the rearrangement reaction to give complex 6 took place. However, a reaction of in situ formed complex 5·(HF)\(_2\) with one equivalent of 1-(2-phenylethynyl)-2-pyrrolidinone led to the selective formation of a Pt(\(\alpha\))-carbon donor ligand in the trans position.\(^{[28]}\)

In the \(^{19}F\) NMR spectrum, a signal at \(\delta = -174.3\) ppm was detected, which indicates the presence of a poly(hydrogen fluoride) entity.\(^{[27,37]}\) The corresponding signal in the \(^1H\) NMR spectrum can be found at \(\delta = 10.77\) ppm. Most likely this suggests the presence of an \((HF)_n\)\(_\alpha\) anion.\(^{[27]}\) For the nitrogen bound proton a resonance signal is found at \(\delta = -10.22\) ppm. The signal of the NH proton appears strongly downfield shifted suggesting hydrogen bonding with the poly(hydrogen fluoride) anion.\(^{[28]}\)

Furthermore, the \(^1H\) NMR spectrum displays six signals which could be assigned via a \(^1H,^1H\) COSY NMR experiment to the three CH moieties of the pyrrolidinone backbone. For the two carbon atoms of the Pt-C=\(C\) moiety two doublets of doublets were detected in the \(^{13}C(1\ H)\) NMR at 160.3 (C \(\alpha\) to Pt) and 123.9 ppm (C \(\alpha\) to Pt). The \(^1H/\(^13C\) HMBC spectrum of 9 reveals cross peaks at 10.22/\(-245\) (d/s), \(195/\(-87\) Hz, N-H) and at 3.24/-163 (s/s), 3.13/-163 (s/s) ppm. The latter signal at \(-163\) ppm can be assigned to the nitrogen of the pyrrolidinone backbone. Note that the \(^1C\) chemical shift of free 1-(2-phenylethynyl)-2-pyrrolidinone was detected at \(-269\) ppm (Figure S42). A signal for the platinum bound nitrogen atom could not be detected.

The IR spectrum of complex 9 displays a broad absorption band at 3263 cm\(^{-1}\) which can be attributed to the N–H stretch (Figure 10). As it was already described for complex 7 a broad absorption band was detected at \(\tilde{\nu} = 1801\) cm\(^{-1}\) for the stretching vibrations of the poly(hydrogen fluoride) anion.\(^{[28]}\)

Further data were obtained from liquid injection field desorption/ionisation mass spectrometry (LIFDI-MS). The mass spec-

![Scheme 3. Reactivity of the fluoroido complex 5·(HF)\(_2\) towards 1-(2-phenylethynyl)-2-pyrrolidinone.](image)

![Figure 9. Structure of trans-[Pt(t\(\kappa^2-(P,C)\)-\(\kappa^2-iPrP(C,H,N)\))] (8).](image)

![Figure 10. IR spectrum of cis-[Pt(C=\(\kappa^2-(P,N)-iPrP(C,H,N)\))] (6·(HF)) (9).](image)
trum revealed a peak at m/z = 873.507 which can be assigned to the complex cation [M]⁺ (calcd. 873.339).

To gain further insight into the activation of the ynamide, the tosylate (OTs⁻ = H₂C₆H₄SO₃⁻) complex cis-[Pt{x²-(P,N)}-iPr,P-(C₆H₅N)][iPr,P(C₆H₅N)]OTs] (10) (Scheme 4) was treated with 1-(2-phenylethynyl)-2-pyrrolidinone to give cis-[Pt(C(Ph)OCN(C₆H₅))][x²-(P,N)-iPr,P(C₆H₅N)][iPr,P(C₆H₅N)]OTs] (11). Compound 10 was prepared from 4 on treatment with HOTs. Complex 11 revealed comparable data to complex 8 (Figure 13).

Selected experimental NMR and IR data for the complexes 9 and 11, and calculated data for alternative metallaketeniminiums and alkyne complexes; Figure 13 shows the corresponding calculated structures.

**Table 2.**

| Structure   | Compound | δ[^1]C[^3]N[^3]NHMBC | δ[^1]C[^3]N[^3]C                  | Normal mode[^3]C                  | Normal mode[^3]C                  |
|-------------|----------|----------------------|---------------------------------|-----------------------------------|-----------------------------------|
| Experimental | 9        | 160.3 123.9 170.3    | -163 -245 -                    | - - -                             | - - -                             |
|             | 11       | 159.9 123.6 170.9    | -163 -243 -                    | - - 1688                         | - - 1688                         |
| COSMO(DCM)  | 9-1      | 82 82 190           | -274 -246 -225 -2046           | 1991 1770                        | 1722                             |
|             | 9-2      | 93 164 183          | -255 -258 -232 -              | - - -                             | - - -                             |
|             | 9-3      | 175 142 178         | -168 -258 -230               | 1722                             | 1722                             |
|             | 11-1     | 86 116 189          | -267 -242 -234-2015           | - - -                             | - - -                             |
|             | 11-2     | 86 141 193          | -259 -247 -243 -231          | 2021 1745                        | 1722                             |
|             | 11-3     | 173 138 181         | -168 -254 -236               | - - -                             | - - -                             |

[a] Molecular and atomic labels are depicted in Figure 13; [b] Fully relativistic 4c-mdKS/PBEP/Dyall-VTZ/GLO-III/GLO-II calculations at MARU-BP86-D3(BJ)/def2-TZVPP/COSMO(DCM) optimized structures. References: TMS ([^1]C), CH₃NO₂ ([^3]N); [c] Harmonic vibrational frequency analyses at MARU-BP86-D3(BJ)/def2-TZVPP/COSMO(DCM) optimized structures.
The ynamide itself shows a strong band for the ethynyl triple bond at $\nu = 2265$ cm\(^{-1}\) (experimental: $\tilde{\nu} = 2240$ cm\(^{-1}\)). Upon formation of the keteniminium tosylate contact ion pair, a weaker but nevertheless distinct band at $\tilde{\nu} = 2011$ cm\(^{-1}\) for the asymmetric CCN stretching vibration is observed, accompanied by a considerable blue shift of the CO band of about 130 cm\(^{-1}\). Importantly, the presence of the tosylate anion in close vicinity to the CCN moiety does not affect the CCN band significantly. Comparison with the corresponding IR band of the free keteniminium cation shows that the impact of the anion on the CCN stretching vibration within the contact ion pair unit is merely about 30 cm\(^{-1}\) (Table S1), with little effect on its intensity. It is only upon covalent bond formation between one of the tosylate oxygen atoms and the $\alpha$-N carbon atom, and hence a concomitant C–C bond formation, that the CCN band vanishes from the spectrum. At the same time the CO band is significantly shifted back again to lower frequencies by about 150 cm\(^{-1}\). These results evidently suggest that a similarly strong interaction, like a 1,2-addition type reaction, is likely the cause for the absence of a CCN band in the experimental spectra of the platinum ynamide complexes. Note, however, that unlike the product from the metal-free conversion of the ynamide into the Pt–N bond of 10 (affording 11–10, Table S3), addition of the anion at the $\alpha$-N carbon atom of the keteniminium moiety in 11–2 (structures 11–6 and 11–7 in Table S3), cyclisation of 11–2 involving the keteniminium and the indolyl ligand (11–8 and 11–9 in Table S3), and intra-ligand cyclisation of the keteniminium moiety in 11–2, leading to 11–3 (Figure 13). From a purely thermochemical point of view, the latter structure is more stable when compared to the corresponding metallaketeniminium or metallacyclopropene isomers. Note, that this does not imply that they are all necessarily kinetically accessible under the experimental conditions. However, metallaketeniminium or metallacyclopropene structures are likely formed immediately upon initial ynamide coordination, serving as starting point for subsequent transformations.

Closer inspection of the computed IR data of all isomers provides further evidence for the structural characteristics of 11. Firstly, in accordance with the results from the reaction of 1-(2-phenylethynyl)-2-pyrrolidinone with TsOH, only the spectra of 1-(2-phenylethynyl)-2-pyrrolidinone (MARIJ-BP86-D3(BJ)/def2-TZVP results).

Analyses of the structural and conformational space of 11 naturally shows a more complicated stereochemical situation, which is mainly caused by the high flexibility of the ynamide and the anion in terms of their (mutual) structural arrangements within the metal complex. In general, the computed isomers can be divided into two categories: structures which feature a metallaketeniminium or metallacyclopropene motif, that is, a coordinated alkyn (11–1–11–2 in Figure 13), and structures exhibiting a vinyl binding motif from 1,2 addition at the ynamide. This involves structures resulting from insertion of the ynamide into the Pt–N bond of 10 (affording 11–10, Table S3),
significantly high-frequency-shift for the nitrogen atom N1 of the ynamide upon coordination. This particularly characteristic feature is only seen for the keteniminium moiety after ring closure in isomers 11–3. The same considerations hold for the derivatives with polyfluorido moieties instead of a tosylate (9–1–9–3, Table 2).

Inter- and intramolecular (electro-)cyclisation reactions using keteniminium salts as intermediates are seeing widespread use in organic chemistry, and corresponding synthesis procedures involving complexes of late transition metals are common. These also involve intramolecular trapping of (metallated) keteniminium ions, which further supports the identification of 11–3 as platinum-bound cyclic keteniminium species.

Additionally, the plausibility of the intra-ligand cyclisation mechanism was corroborated by modeling of the corresponding free energy profile (Scheme S2). The overall reaction proceeds strongly exergonically, by $-71 \text{kJ mol}^{-1}$, and the computed barrier for cyclisation of $66 \text{kJ mol}^{-1}$ is fully consistent with a process at room temperature. In line with the observed reversibility of complex formation upon treatment of 9 with CsF (Scheme 3), calculations show that the free ligand of 9 easily rearranges to the significantly more stable alkyne structure, with a barrier for ring opening of only $34 \text{kJ mol}^{-1}$ (Scheme S2).

**Conclusion**

In conclusion, we described the formation of various platinum (II) complexes bearing $\kappa^1$-$\{P\}$ and $\kappa^2$-$\{P,N\}$ bound disopropyl-2-(3-methyl)indolyl phosphate ligands and their reactivity towards fluorides as well as hydrogen fluoride. The metal bound fluorides can induce cyclometallation, migrate to phosphorus and engage in hydrogen bonding to NH units or generate polyfluoride moieties. The reaction of cis-[PtCl$_3$(iPr$_2$P(C$_6$H$_5$N))$_2$] (1) and cis-[PtCl$_3$(x$_2$-$\{P,N\}$)-iPr$_2$P(C$_6$H$_5$N)], cis-[PtCl$_3$(x$_2$-$\{P,N\}$)-iPr$_2$P(C$_6$H$_5$N)] with polyfluoride moieties instead of a tosylate (9–1–9–3, Table 2).

**Experimental Section**

Full details of experimental procedures, complex synthesis and characterisation, NMR data, IR data and crystallographic data as well as computational details can be found in the Supporting Information.

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**Conflict of Interest**

The authors declare no conflict of interest.

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