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Liquid injection field desorption/ionization of transition metal fluoride complexes

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ABSTRACT

Metal fluoride complexes that are extremely sensitive to air and water have been characterized by liquid injection field desorption/ionization (LIFDI) mass spectrometry. Dilute solutions of fluoride complexes of nickel, rhodium, titanium, zirconium and ruthenium in toluene and tetrahydrofuran were examined by LIFDI methods on a time-of-flight mass spectrometer. All the spectra of nickel, titanium and zirconium complexes exhibited the molecular ion as base peak. The ruthenium and rhodium complexes showed $[M-HF]^+$ as base peaks but the molecular ions were easily detected. The nickel complexes do not provide useful mass spectra by EI or ESI methods. Only the titanium and zirconium species showed evidence of the fluoride ligands in the ESI spectra. Two new nickel fluoride complexes are formed by C–F activation reactions with 2,3,5,6-tetrafluoro-4-dimethylaminopyridine and 2,3,5,6-tetrafluoro-4-methoxypyridine yielding *trans*-$NiF\{2-C_5NF_3(4-NMe_2)\}(PEt_3)_2$ and *trans*-$NiF\{2-C_5NF_3(4-OMe)\}(PEt_3)_2$, respectively. The crystal structure of *trans*-$NiF\{2-C_5NF_3(4-NMe_2)\}(PEt_3)_2$ shows typical square planar coordination at nickel with an Ni–F distance of 1.8521(9) Å.

1. Introduction

Transition metal fluoride complexes have several characteristics that are significantly different from their analogues with heavier halides. The realization that they have special properties has led to a surge of interest in the last few years. They are prone to rearrangements involving other ligands especially phosphines [1,2], they are highly polar and readily form complexes with hydrogen bond donors and halogen bond donors [3–5], they are capable of C–F reductive elimination in special circumstances [4,6]. They may be formed with the aid of a wide variety of fluorinating agents such as XeF_2, $Et_3N{\cdot}3HF$ and AgF [1,4,7,8], but a method of particular interest to us has been C–F oxidative addition [9–21].

Characterization of metal fluoride complexes is greatly assisted by ^{19}F NMR spectroscopy. For late transition metal fluoride complexes, an upfield resonance is observed that is in a region quite distinct from that of organic fluorine. In contrast, mass spectrometric characterization has proved extremely troublesome, because of loss of fluoride or loss of HF. Electrospray ionization (ESI), although a soft technique, cannot be used to characterize late transition metal fluorides. Most fluoride complexes are neutral molecules and require protonation or association with Na^+/K^+ to observe, but in practice as for other halide complexes, the metal fluoride bond is too labile [22]. Electron impact (EI) has been used occasionally to characterize fluoride complexes but the molecular ion was very weak and the compound showed decomposition [2]. Fast atom bombardment (FAB) has also met with very limited success. Recently, we found that Liquid Injection Field Desorption Ionization (LIFDI) yielded high quality mass spectra for some platinum complexes with conspicuous parent ions [23]. In this paper, we demonstrate that LIFDI in association with a time-of-flight mass spectrometer is generally applicable to the characterization of air-sensitive transition metal fluoride complexes.

Field desorption (FD) is a soft ionization technique of interest for inorganic chemists as it is capable of analysing involatile compounds of low to medium polarity, but it was formerly considered as experimentally very demanding [24]. Nevertheless, it has been used successfully to analyse transition metal complexes with weakly bonded ligands [24,25]. Mass spectra produced by FD show little or no fragmentation and are dominated by molecular radical cations $M^{+\bullet}$ while protonated molecules are formed less often [26]. In the FD technique, the analyte is applied as a thin film directly to the emitter, or small crystals of solid materials are placed onto the emitter. Slow heating of the emitter then begins, and application of the field causes the desorption of intact molecular ions from the regions of high electric field gradient [24].

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The recently developed LIFDI technique [27,28] can now be conducted much faster and more easily. Neutral transition metal complexes often ionize without fragmentation and do not undergo protonation or ion attachment. Transfer of air/moisture sensitive analyte solutions is carried out from a vial (loaded in the glove box) to the FD emitter in the ion source through a fused silica capillary under an inert atmosphere without breaking the vacuum [26].

2. Experimental

2.1. Mass spectrometry

The LIFDI measurements were performed on a Waters Micromass GCT Premier orthogonal time-of-flight instrument set to one scan per second with resolution power of 6000 FWHM and equipped with a LIFDI probe from LINDEN GmbH. The design is very similar to that described by Gross et al. [28]. Toluene was used for tuning the instrument. The polyethylene glycol probe was kept at ambient temperature with the emitter potential at 12 kV. Activated tungsten wire LIFDI emitters (13 μm tungsten from LINDEN) were ramped manually up to 100 mA for the emitter heating current during the experiment. Repeated short baking at 90 mA was used to clean up the emitter after each experiment. Solutions of the analytes (ca. 1 mg mL^{-1}) were made up in toluene or THF (a low freezing solvent is required in order to prevent freezing in the capillary) in the glove box and transferred to a small vial. Transfer from the vial to the emitter is carried out by capillary. The spectra were calibrated with polyethylene glycols. The theoretical isotope patterns for mass spectra were calculated using "Fluorine chemistry mass spec simulator" [29]. Mass peaks are quoted for ^{48}Ti, ^{58}Ni, ^{90}Zr and ^{102}Ru.

2.2. Synthesis

The following compounds were prepared by literature syntheses: 2,3,5,6-tetrafluoro-4-methoxypyridine [30], 2,3,5,6-tetrafluoro-4-dimethylaminopyridine [30], $Ni(PEt_3)_2(C_5F_4N)F$ (**3**) [2], $Ni(PEt_3)_2(C_5F_3HN)F$ (**4**) [2], $Ni(PEt_3)_2(C_6F_5)F$ (**5**) [2], $(Cp^*)_2TiF_2$ (**6**) [31], $Ru(PPh_3)_3(CO)(H)F$ (**8**) [32] and $Rh(PPh_3)_3F$ (**9**) [1].

Trans-NiF{2-C₅NF₃(4-NMe₂)}(PEt₃)₂ (1). 2,3,5,6-Tetrafluoro-4-dimethylaminopyridine (0.258 g, 1.33 mmol) was added to the cloudy red–purple suspension of $Ni(COD)_2$ (0.3 g, 1.1 mmol) and PEt_3 (295 mg, 2.5 mmol) in hexane and stirred for 2 h. The color of the solution changed to yellow. Volatiles were removed under vacuum and the oily residue was dissolved in hexane and filtered through a cannula. The filtrate was concentrated under vacuum to 2 mL and was crystallized at −25 °C for 2 h to give $NiF\{C_5NF_3(NMe_2)\}(PEt_3)_2$. Yield 0.548 g (1.12 mmol, 97%) MS (LIFDI from toluene solution) m/z 488 $[M^+]$ 100%. Anal. Calcd. for $C_{19}H_{36}F_4N_2NiP_2$: C, 46.65; H, 7.42; N, 5.73. Found: C, 46.52; H, 7.40; N, 5.55. ^1H NMR (C_6D_6): δ 1.23 (m, 18H, CH_3), 1.42 (bm, 12H, CH_2), 2.8 (t, J_{FH} = 2.3 Hz, 6H, NMe_2). ^{19}F NMR (C_6D_6): δ −367.74 (t, J = 47.9 Hz, 1F), −91.28 (t, J = 28.5 Hz, 1F), −121.15 (d, J = 24.5 Hz, 1F) −164.33 (d, J = 28.7 Hz, 1F) ^{31}P NMR(C_6D_6): δ 12.79 (d, J_{PF} = 47.4 Hz).

Trans-NiF{2-C₅NF₃(4-OMe)}(PEt₃)₂ (2). 2,3,5,6-Tetrafluoro-4-methoxypyridine (240 μL, 1.33 mmol) was added to the cloudy red–purple suspension of $Ni(COD)_2$ (0.3 g, 1.0 mmol) and PEt_3 (291 mg, 2.4 mmol) in hexane and stirred for 2 h. The color of the solution changed to yellow. Volatiles were removed under vacuum and the oily residue was dissolved in hexane and filtered through a cannula. The filtrate was concentrated to 2 mL and was crystallized at −25 °C for 72 h to yield $NiF\{2\text{-}C_5NF_3(OMe)\}(PEt_3)_2$. Yield 0.2 g (0.52 mmol 48%). Anal. Calcd. for $C_{18}H_{33}F_4NNiOP_2$: C, 45.44; H, 7.43; N, 3.01. Found: C, 45.44; H, 7.43; N, 3.04.

IR (KBr disc, cm^{-1}) 3405(b), 2969(s), 2936(s), 2876(w), 1605(s), 1572(w), 1552(w), 1524(bw), 1485.7(s), 1460.8(s), 1453.0(s), 1432.9(s), 1418.3(s), 1393.5(s), 1377(s), 1256(w), 1100.6(s), 1031.3(s), 1003.5(w), 911(w), 810.4(s), 763.8(s), 725.0(s), 709.6(w), 679.9(w), 632.1(w), 514.1(w), 490.4(w).

^1H NMR (C_6D_6): δ 1.19 (m, CH_3), 1.36 (b, CH_2), 3.73 (s, OMe). ^{19}F NMR (C_6D_6): δ −368.78 (t, J_{PF} = 45.7 Hz, 1F), −170.11 (d, J_{FF} = 28.5 Hz, 1F) −128.33 (d, J_{FF} = 28.0 Hz, 1F), −88.71 (t, J_{FF} = 28.5 Hz, 1F). ^{31}P NMR(C_6D_6): δ 13.05 (d, J_{PF} = 48.1 Hz).

MS (LIFDI from toluene solution) m/z 475 $[M]^+$ 100%.

$(Cp^*)_2TiF_2$ (6) [31]. MS (LIFDI from toluene solution) m/z 356 $[M^+]$ 100%.

MS (ESI from CH_3CN solution) m/z 395, $[M+K]^+$, 379 $[M+Na]^+$, 337 $[M-F]^+$

$(Cp^*)_2ZrF_2$ (7). The synthesis followed the method for $(Cp^*)_2TiF_2$ [31]. A two-necked round bottomed flask was charged with bis(pentamethylcyclopentadienyl)zirconium dichloride (0.295 g, 0.64 mmol), sodium fluoride (0.81 g, 19.2 mmol) and methanol (25 mL). The mixture was refluxed for three hours under argon. The reaction mixture was allowed to cool to the room temperature and filtered. The solvent was pumped off under vacuum. The resultant solid compound was recrystallized from hexane yield 0.15 g (60%).

MS (LIFDI from toluene solution) m/z 398 $[M^+]$ 100%.
MS (ESI from CH_3CN solution) m/z 437 $[M+K]^+$, 421 $[M+Na]^+$.
MS (ESI from $CHCl_3$ solution) m/z 397 $[M-H]^+$.

2.3. Crystal structure

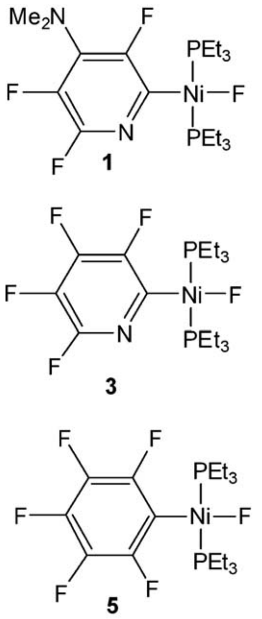
X-ray data were collected on a Bruker SMART Apex X-ray diffractometer equipped with an MoKα radiation source (λ 0.71073 Å) for $\theta > 1.39$ up to $\theta < 30.04°$. The crystals were cooled to 110 K using an Oxford Cryosystems Cryostream. Diffractometer control, data collection and initial unit cell determination was performed using "SMART" (v5.625 Bruker-AXS). Frame integration and unit cell refinement software was carried out with the "SAINT+" (v6.22, Bruker-AXS). Absorption corrections were applied by SADABS (v2.03, Sheldrick). The structures were solved by direct methods using SHELXS-97 and refined by full-matrix least-squares using SHELXL-97 [33,34]. One of the triethylphosphines was disordered and modelled in two positions in a 47:53 ratio although the position of one of the ethyl groups (C11 and C12) was the same for both forms. Some restraints were required to maintain a chemically sensible model for both the disordered triethylphosphine groups as follows.

Bond lengths Ni1–P3A and Ni1–P3B were restrained to be similar in magnitude. Bond lengths P3A–C9A, P3A–C11, P3A–C13A, P3B–C9B, P3B–C11 and P3B–C13B were restrained to be 1.83 Å. Bond lengths C9A–C10B, C13A–C14A, C9B–C10B, C13B–C14B were restrained to be 1.52 Å. The initial locations for H11A and H11B were determined by difference map, with the C–H bond lengths being subsequently restrained to be 0.99 Å. All the other hydrogen atoms were placed using a "riding model" and included in the refinement at calculated positions.

Empirical formula $C_{19}H_{36}F_4N_2NiP_2$, formula weight 489.15, T 110(2) K, λ 0.71073 Å, monoclinic, space group $C2/c$, a = 29.590(3), b = 9.5175(9) Å, c = 16.8866(17) Å, β = 98.355(3)°, V = 4705.2(8) Å^3, Z = 8, density ρ_{calc} 1.381 Mg/m^3, μ = 0.999 mm^{-1}, crystal size 0.39 × 0.32 × 0.10 mm^3, reflections collected 26278, independent reflections 6817 [R(int) = 0.0320], refinement method full-matrix least-squares on F^2, data/restraints/parameters 6817/13/317, goodness-of-fit on F^2 1.061, final R indices [$I > 2\sigma(I)$] $R1$ = 0.0331, $wR2$ = 0.0794, R indices (all data) $R1$ = 0.0404, $wR2$ = 0.0832, largest diff. peak and hole 0.553 and −0.223 e Å^{-3}.

3. Results and discussion

Our initial studies centered on nickel fluoride complexes made by C–F oxidative addition of hexafluorobenzene and of fluorinated



Scheme 1.

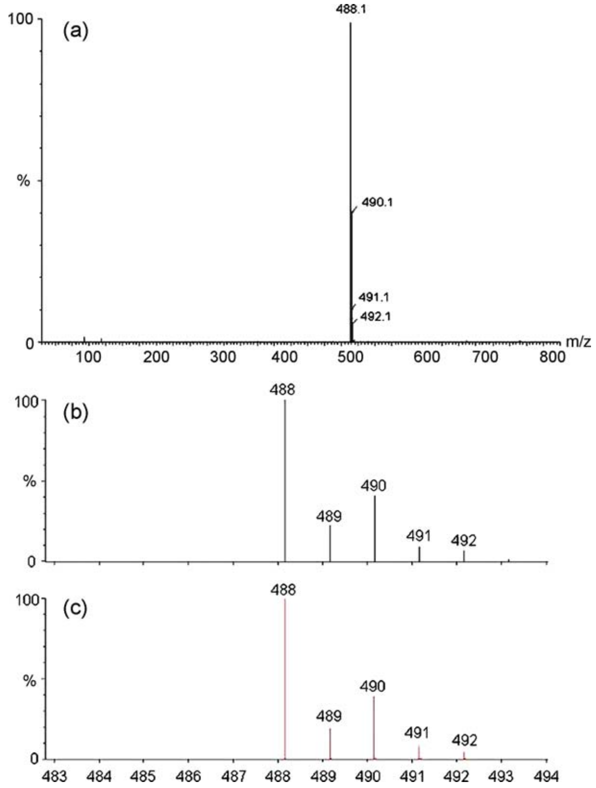


Fig. 1. LIFDI mass spectra of *trans*-NiF{2-C_5NF_3(4-NMe_2)}$(PEt_3)_2$ (**1**) in toluene: (a) full range spectrum; (b) calculated spectrum of molecular ion; and (c) observed spectrum of molecular ion showing isotopic pattern.

pyridines. We report investigations of two new complexes selected for their potential for ESI methods and three complexes that had been previously reported (Scheme 1). For ESI mass spectrometry, we used fluorinated pyridines with dimethylamino and methoxy groups at the 4-position in the expectation that they would be sufficiently basic for protonation or sodiation.

3.1. Trans-NiF{2-C_5NF_3(4-NMe_2)}$(PEt_3)_2$ (1)

Trans-NiF{2-C_5NF_3(4-NMe_2)}$(PEt_3)_2$ **1** was prepared from the reaction of 4-dimethylamino-2,3,5,6-tetrafluoropyridine with Ni(1,5-cyclooctadiene)$_2$ and PEt_3. The ^{31}P NMR spectrum shows a doublet at δ 12.7 (J_{PF} = 48.2 Hz), indicative of coupling with a single fluorine nucleus. The ^{19}F NMR spectrum shows a triplet at δ −367.8 (J_{PF} = 47.4 Hz), which provides evidence for the presence of metal fluoride (Fig. S1). The other three resonances at δ −91.28, −121.15 and −164.33 confirm the presence of the C_5F_3N group. Complex **1** was further studied by mass spectrometry using LIFDI and ESI techniques. LIFDI gave the $[M]^+$ as base peak at 488 (Fig. 1), while ESI gave decomposition.

The molecular structure of **1** was confirmed by X-ray diffraction (Fig. 2 and Table 1). The Ni–F distance of 1.8521(9) Å compares with 1.836(5) Å in *trans*-NiF$(C_6F_5)(PEt_3)_2$, 1.856(2) Å in *trans*-NiF$(C_5NHF_3)(PEt_3)_2$ Å [2], 1.916(3) Å in *trans*-NiF$(C_6HF_4)(PEt_3)_2$ [12], 1.8589(15) Å in *trans*-NiF(C_6F_5)(iPrNC$_5$H$_4$NMe)$_2$ [13] and 1.856(4) Å in NiF(4-$(CF_3)C_6F_4$)(*i*Pr$_2$Im)$_2$ [15]. The dimethylamino group is twisted out of the plane of the pyridine ring (torsional angles C4–C5–N2–C7 = −21.4(2)° and C6–C5–N2–C8 = −42.4(2)°); the angles at N2 add up to 357.5°. There are very few other structures with an NMe_2 group ortho to two fluorine substituents, but three that we found all show substantial twists out of the plane of the benzene ring [35].

3.2. Trans-NiF{2-C_5NF_3(4-OMe)}$(PEt_3)_2$ (2)

Trans-NiF{2-C_5NF_3(4-OMe)}$(PEt_3)_2$ (**2**) was prepared from the reaction of 2,3,5,6-tetrafluoro-4-methoxypyridine with Ni(1,5-cyclooctadiene)$_2$ and PEt_3. The ^{31}P NMR spectrum shows a doublet at δ 13.05 (J_{PF} = 48.1 Hz), indicative of coupling with a single fluorine nucleus. The ^{19}F NMR spectrum shows a triplet at δ −368.78 which provides evidence for the presence of metal fluoride, with coupling to both phosphorus nuclei (J_{PF} = 45.7 Hz). The other three resonances at δ −170.11, −128.33 and −88.71 confirm the presence of the C_5F_3N group.

Complex **2** was studied by mass spectrometry using LIFDI and ESI techniques. The isotopic pattern of transition metal is well resolved in mass spectrometry with excellent agreement between observed and calculated isotope pattern (Table 2). LIFDI gave the molecular ion peak $[M]^+$ at 475 as base peak (100%, Fig. S2), whereas the compound showed decomposition with ESI.

3.3. Trans-Ni$(PEt_3)_2$(2-C_5NF_4)F (3), trans-Ni$(PEt_3)_2$(2-C_5NF_3H)F (4) and trans-Ni$(PEt_3)_2$(C_6F_5)F (5)

Complexes **3**, **4** and **5** have been reported previously [2], but gave mass spectra with very weak molecular ions (0.5%) by EI methods. We have now re-investigated them by mass spectrometry using LIFDI techniques. LIFDI of **3**, **4** and **5** gave the molecular ion peaks $[M]^+$ as base peaks (100%) at 463, 445 and 480 (Fig. S3–S5), respectively. With ESI, the compounds showed decomposition.

3.4. $(Cp^*)_2TiF_2$ (6) and $(Cp^*)_2ZrF_2$ (7)

The formation of $(Cp^*)_2TiF_2$ was confirmed by NMR and mass spectrometry. [31] The ^{19}F NMR spectrum exhibits a sharp resonance (C_6D_6) at δ 74.69 which is assigned to the two metal fluoride nuclei [36]. Note that the ^{19}F resonance of these d^0 metal fluoride complexes appears in a completely different region from the corresponding resonance of the complexes with several d electrons. $(Cp^*)_2ZrF_2$ **7** shows a sharp resonance (C_6D_6) at δ 1.96 in the ^1H NMR spectrum, assigned to the Cp* hydrogens, while the ^{19}F NMR spectrum exhibits a sharp resonance (C_6D_6) at δ 28.72. These values are in close agreement with the literature values: the ^1H

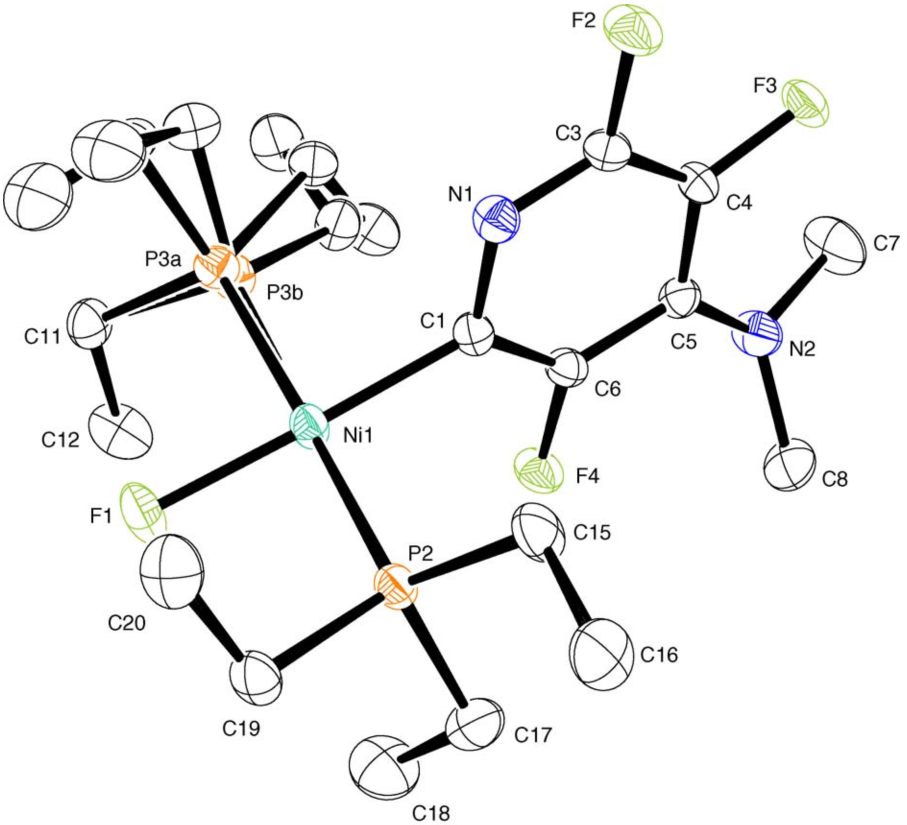


Fig. 2. Molecular structure of *trans*-NiF{2-C_5NF_3(4-NMe_2)}(PEt_3)$_2$ (**1**). Ellipsoids set at 50% probability, hydrogen atoms not shown. Note the disorder in the position of one PEt_3 group.

NMR spectrum (C_6D_{12}) shows a resonance at δ 1.96 and ^{19}F NMR spectrum (C_6D_{12}) at δ 34.1 [37].

Complexes **6** and **7** were also studied by mass spectrometry using LIFDI and ESI techniques. Excellent agreement between observed and calculated isotope patterns was observed for all the major peaks (Table 2). LIFDI gave the molecular ion peaks $[M]^+$ at 356 as base peak (100%, ^{48}Ti) for **6** (Fig. 3) and 398 (100%, ^{90}Zr) for **7** (Fig. S6). ESI-MS of **6** gave ion peaks at 337 $[M-F]^+$, 379 $[M+Na]^+$ and 395 $[M+K]^+$ with significant intensity (from CH_3CN solution) and 397$(M-H)^+$ (from $CHCl_3$ solution) for **7** ion peaks appeared at 421$[M+Na]^+$, 437 $[M+K]^+$ from CH_3CN.

Table 1
Principal bond lengths (Å) and angles (°) of **1**.

Ni–F(1)	1.8521(9)
Ni–P(2)	2.1920(4)
Ni–P(3B)	2.194(2)
Ni–P(3A)	2.201(2)
C(1)–Ni	1.8749(13)
F(1)–Ni–C(1)	178.11(5)
F(1)–Ni–P(2)	90.21(3)
F(1)–Ni–P(3A)	88.01(9)
F(1)–Ni–P(3B)	90.94(8)
C(1)–Ni–P(2)	91.62(4)
C(1)–Ni–P(3A)	90.11(10)
C(1)–Ni–P(3B)	87.23(9)

Table 2
Calculated and observed mass spectra observed by LIFDI for **2** and **6**.

Complex **2**			Complex **6**		
m/*z*	Calcd.	Obsvd.	*m*/*z*	Calcd.	Obsvd.
475.0	100.0	100	354.0	10.4	10.1
476.0	20.2	20.1	355.0	12.0	10.5
477.0	44.1	41.2	356.0	100.0	100
478.0	10.4	9	357.0	29.4	30
479.0	7.1	7	358.0	11.0	10.2
480.0	1.3	1.7	359.0	1.9	3
481.0	1.6	1.8	360.0	0.2	0
482.0	0.3	0.07	361.0	0.0	0
483.0	0.0	0			

3.5. *Ru(PPh_3)$_3$(CO)(H)F (**8**) and Rh(PPh_3)$_3$F (**9**)*

The formation of **8** and **9** was confirmed by comparison with literature NMR data [1,32]. The LIFDI spectrum of **8**

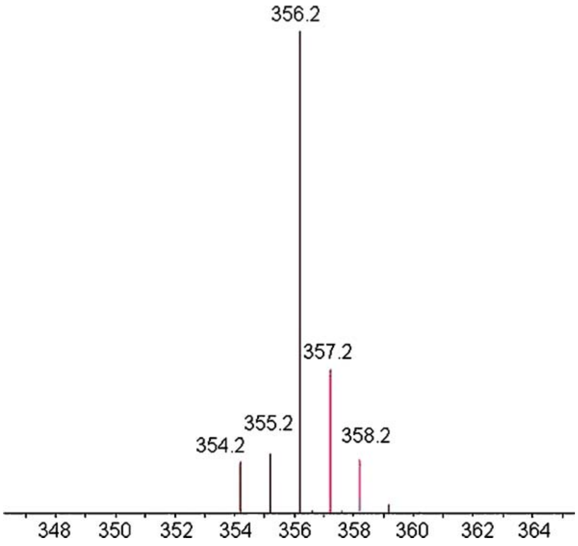


Fig. 3. Mass spectrum (LIFDI) of $(Cp^*)_2TiF_2$ (**6**) in toluene.

showed $[M-HF]^+$ ($m/z = 916$) as base peak, and the molecular ion with intensity 27% ($m/z = 936$) (Fig. S7). The LIFDI spectrum of **9** also showed $[M-HF]^+$ ($m/z = 888$) as base peak and the molecular ion with 10% intensity ($m/z = 908$). In contrast, the ESI spectrum of **9** showed $[M-F]^+$ as base peak and no molecular ion. Since the NMR spectrum of **9** showed resonances of the isomer, $Rh(PPh_3)_2(PPh_2F)Ph$ [1], as a minor species, we cannot exclude the isomer as the source of the molecular ion.

4. Conclusions

The LIFDI method has proved very successful for the mass spectrometric characterization of a range of metal fluoride complexes. The nickel complexes had been very difficult to identify mass spectrometrically by conventional ionization methods but gave the molecular ions as base peaks by LIFDI. We have also observed the molecular ions as base peaks in platinum complexes [23]. Nevertheless, there are other examples of higher molecular mass than the complexes reported here that were less successful. The ruthenium complex, $Ru(PPh_3)_3(CO)(H)F$ showed a molecular ion of 27%, while the fluorine analogue of Wilkinson's complex, $Rh(PPh_3)_3F$, showed a much weaker molecular ion. Both of these molecules showed loss of HF as the base peaks.

The reactivity of 2,3,5,6-tetrafluoro-4-dimethylaminopyridine and 2,3,5,6-tetrafluoro-4-methoxypyridine towards $Ni(PEt_3)_2$ proved to be exactly equivalent to that of pentafluoropyridine itself. Thus the product resulted from C–F bond activation at the 2-position of the fluoropyridine and there was no evidence that the OMe or NMe_2 groups played any role in the reaction. These groups were also not basic enough to facilitate observation of the product fluoride complexes by ESI mass spectrometry.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jfluchem.2010.05.008.

References

[1] S.A. Macgregor, D.C. Roe, W.J. Marshall, K.M. Bloch, V.I. Bakhmutov, V.V. Grushin, J. Am. Chem. Soc. 43 (2005) 15304.
[2] L. Cronin, L.C. Higgitt, R. Karch, R.N. Perutz, Organometallics 16 (1997) 4920.
[3] N.A. Jasim, R.N. Perutz, S.P. Foxon, P.H. Walton, J. Chem. Soc. Dalton Trans. (2001) 1676.
[4] N.D. Ball, J.W. Kampf, M. Sanford, Dalton Trans. 39 (2010) 632.
[5] V.J. Murphy, T. Hascall, J.Y. Chen, G. Parkin, J. Am. Chem. Soc. 118 (1996) 7428.
[6] T. Furuya, T. Ritter, J. Am. Chem. Soc. 130 (2008) 10060.
[7] A. Yahav, I. Goldberg, A. Vigalok, Inorg. Chem. 44 (2005) 1547.
[8] M.K. Whittlesey, R.N. Perutz, B. Greener, M.H. Moore, Chem. Commun. (1997) 187.
[9] T. Braun, R.N. Perutz, Chem. Commun. (2002) 2749.
[10] T. Schaub, M. Backes, U. Radius, Eur. J. Inorg. Chem. (2008) 2680.
[11] H. Amii, K. Uneyama, Chem. Rev. 109 (2009) 2119.
[12] S.A. Johnson, E.T. Taylor, S.J. Cruise, Organometallics 28 (2009) 3842.
[13] M.E. Doster, S.A. Johnson, Angew. Chem. Int. Ed. 48 (2009) 2185.
[14] S.A. Johnson, C.W. Huff, F. Mustafa, M. Saliba, J. Am. Chem. Soc. 130 (2008) 17278.
[15] T. Schaub, M. Backes, U. Radius, J. Am. Chem. Soc. 128 (2006) 15964.
[16] T. Schaub, P. Fischer, A. Steffen, T. Braun, U. Radius, A. Mix, J. Am. Chem. Soc. 130 (2008) 9304.
[17] T. Schaub, U. Radius, Chem. Eur. J. 11 (2005) 5024.
[18] U. Jäger-Fiedler, P. Arndt, W. Baumann, A. Spannenberg, V.V. Burlakov, U. Rosenthal, Eur. J. Inorg. Chem. (2005) 2842.
[19] A. Steffen, M.I. Sladek, T. Braun, B. Neumann, H.-G. Stammler, Organometallics 24 (2005) 4057.
[20] T. Braun, A. Steffen, V. Schorlemer, B. Neumann, H.-G. Stammler, Dalton Trans. (2005) 3331.
[21] T. Braun, V. Schorlemer, B. Neumann, H.G. Stammler, J. Fluorine Chem. 127 (2006) 367.
[22] W. Henderson, E. Cameron, Inorg. Chim. Acta (1999) 183.
[23] A. Nova, S. Erhardt, N.A. Jasim, R.N. Perutz, S.A. Macgregor, J.E. McGrady, A.C. Whitwood, J. Am. Chem. Soc. 130 (2008) 15499.
[24] W. Henderson, J.S. McIndoe, Mass Spectrometry of Inorganic, Coordination and Organometallic Compounds, Wiley, Chichester, 2005.
[25] L. Prokai, Field Desorption Mass Spectrometry, Marcel Dekker, New York, 1990.
[26] F.D. Smith, M.T. Schaub, R.P. Rodgers, C.L. Hendrickson, A.G. Marshall, Anal. Chem. 80 (2008) 7379.
[27] J.H. Gross, J. Am. Soc. Mass Spectrom. 18 (2007) 2254.
[28] J.H. Gross, N. Nieth, H.B. Linden, U. Blumbach, F.J. Richter, M.E. Tauchert, R. Tompers, P. Hofmann, Anal. Bioanal. Chem. 386 (2006) 52.
[29] http://fluorine.ch.man.ac.uk/research/mstool.php.
[30] R.E. Banks, J.E. Burgess, W.M. Cheng, R.N. Haszeldine, J. Chem. Soc. (1965) 575.
[31] P.G. Gassman, W.H. Campbell, D.W. Macomber, Organometallics 3 (1984) 385.
[32] S.P. Reade, D. Nama, M.F. Mahon, P.S. Pregosin, M.K. Whittlesey, Organometallics 26 (2007) 3484.
[33] G.M. Sheldrick, A Program for Crystal Structure Solution, SHELXS-97, ed., Göttingen University, Göttingen, Germany, 1997.
[34] G.M. Sheldrick, A Program for Crystal Structure Determination, SHELXL-97 ed., Göttingen University, Göttingen, Germany, 1997.
[35] (a) K.M. Kadish, C. Araullo-McAdams, B.C. Han, M.M. Franzen, J. Am. Chem. Soc. 112 (1990) 8364;
(b) D. Lahaye, K. Muthukumaran, C.-H. Hung, D. Gryko, J.S. Reboucas, I. Spasojevic, I. Batinic-Haberle, J.S. Lindsey, Bioorg. Med. Chem. 15 (2007) 7066;
(c) R. Nakagaki, S. Kohtani, Y. Nakamura, M. Okamura, S. Kitoh, K.-K. Kunimoto, Anal. Sci.: X-ray Struct. Anal. Online 19 (2003) x5.
[36] I.M. Piglosiewicz, S. Kraft, R. Beckhaus, D. Hasse, W. Saak, Eur. J. Inorg. Chem. (2005) 938.
[37] B.M. Kraft, W.D. Jones, J. Am. Chem. Soc. 124 (2002) 8681.