Synthesis, Structure, and Reactivity of Arylfluoro Platinum(II) Complexes

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Complexes of the type *trans*-[PtPhFL$_2$], where L = PPh_3 (**4**), PMe_2Ph (**5**), were synthesized. Complex **4** was characterized by X-ray crystallography. The equilibrium constant for the substitution of the fluoride trans to phenyl in **4** by Cl^- and I^- was determined, and the stability sequence follows the normal trend seen in "soft" metal centers: i.e., the Pt has a preference for the halide in the order I > Cl > F; the difference is, however, fairly small. The substitution kinetics follow the usual two-term rate law, and the rate constants for the solvolytic (k_1) and the direct (k_2) reaction pathways were determined to be $k_1 = (9.7 \pm 2.4) \times 10^{-5}$ s^{-1}, $k_2 = (11.7 \pm 0.3) \times 10^{-2}$ M^{-1} s^{-1} and $k_1 = (7.1 \pm 4.9) \times 10^{-5}$ s^{-1}, $k_2 = (23.0 \pm 1.3) \times 10^{-2}$ M^{-1} s^{-1} for Cl^- and I^-, respectively. Activation parameters for the solvolytic and direct pathways with Cl^- as incoming ligand are typical for associative processes and were determined to be $\Delta H^‡ = 77.8 \pm 5.5$ kJ mol^{-1}, $\Delta S^‡ = -56 \pm 18$ J K^{-1}mol^{-1} and $\Delta H^‡ = 67.6 \pm 1.8$ kJ mol^{-1}, $\Delta S^‡ = -37 \pm 6$ J K^{-1}mol^{-1}, respectively. Complexes **4** and **5** react with Me_3SnPh, and within 2−15 min there is a complete conversion to products. **4** gives a single product, *trans*-[PtPhMe(PPh_3)$_2$], which was characterized by X-ray crystallography. **5** gives two products: *trans*-[PtPhMe(PMe_2Ph)$_2$] and *trans*-[$PtPh_2$(PMe_2Ph)$_2$]. Steric effects on the reactivity speak in favor of an associative mechanism. The surprisingly high reactivity for the transmetalations, compared to the substitution reactions, can be explained in terms of an associative mechanism, where a strong, bridging Sn−F interaction stabilizes the transition state. Furthermore, only trans products are formed; i.e., we have an exclusive F-for-R (R = Me, Ph) substitution at these platinum fluoro complexes. Treatment of **4** with phenylacetylene in benzene at room temperature gives the alkynyl complex *trans*-[PtPh(CCPh)(PPh_3)$_2$] (**8**).

Introduction

Very few examples of late-transition-metal complexes with covalent metal−fluorine bonds have been reported in the literature.[1] There is, however, a growing interest in the study of these types of complexes due to their high reactivity,[2] relevance to metal-mediated C−F bond activation,[3] and potential use in catalysis.[4] Their rare abundance, compared to the analogous chloro, bromo, and iodo complexes, stems mainly from two reasons. First, according to the hard−soft acid−base principle,[5] the bond between the "soft" low-valent late-transition-metal center and the "hard" fluoro ligand is supposed to be weak. Second, the difficulties in introducing the fluoro ligand have contributed to troublesome and sometimes low-yielding synthetic strategies.

Organometallic fluoro complexes are of special interest in catalysis, because likely the metal−fluoro intermediate could play a crucial role in the cleavage and formation of the strong C−F bond. Fluorocarbons are reluctant to coordinate to metal centers and are in general chemically inert, due to the strong C−F bond and the high electronegativity of fluorine. Hence, organometallic fluoro complexes are rare in the literature. It is also known that fluoride can activate organo-silicon compounds, producing a pentacoordinated silicate, which is another reason fluorides have received attention in catalysis. One application is the so-called Hiyama coupling,[6] where organosilanes are used as nucleophiles in palladium-catalyzed cross-coupling reactions. Fluorides have also been used in Stille cross-couplings to precipitate insoluble tin−fluoro compounds, thereby effectively removing the toxic tin byproduct.[7] In this context there is still a lack of understanding of the reactivity of late-transition-metal fluoro complexes.

Here we report the synthesis of complexes of the type *trans*-[PtPhF(PR_3)$_2$]; these are among the first organometallic Pt^{II}−F complexes to be reported and fully

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(1) (a) Doherty, N. M.; Hoffman, N. W. *Chem. Rev.* **1991**, *91*, 553. (b) Grushin, V. V. *Chem. Eur. J.* **2002**, *8*, 1006−1014.

(2) (a) Vicente, J.; Gil-Rubio, J.; Bautista, D. *Inorg. Chem.* **2001**, *40*, 2636. (b) Veltheer, J. E.; Burger, P.; Bergman, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 12478.

(3) (a) Kiplinger, J. L.; Richmond, T. G.; Osterberg, C. E. *Chem. Rev.* **1994**, *94*, 373. (b) Hofmann, P; Unfried, G. *Chem. Ber.* **1992**, *125*, 659.

(4) Mezzetti, A.; Becker, C. *Helv. Chim. Acta* **2002**, *85*, 2686.

(5) (a) Leden, I.; Chatt, J. *J. Chem. Soc.* **1955**, 2936. (b) Ahrland, S.; Chatt, J.; Davies, N. R. *Q. Rev., Chem. Soc.* **1958**, *12*, 265. (c) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533.

(6) (a) Hiyama, T.; Hatanaka, Y. *Pure Appl. Chem.* **1994**, *66*, 1471. (b) Mateo, C.; Fernández-Rivas, C.; Echavarren, A. M.; Cárdenas, D. J. *Organometallics* **1997**, *16*, 1997.

(7) Diederich, F., Stang, P. J., Eds. *Metal-Catalyzed Cross-Coupling Reactions;* Wiley-VCH: New York, 1998; Chapter 4.

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characterized.[8] The reactivity of these complexes toward organosilanes and organostannanes was investigated and will be discussed together with a thorough kinetic investigation of the nucleophilic substitution of the fluoro ligand in *trans*-[PtPhF(PPh_3)$_2$]. The crystal structures of this complex and *trans*-[PtPhMe(PPh_3)$_2$] are also reported.

Experimental Section

General Procedures and Materials. All experiments involving air-sensitive compounds were carried out using standard high-vacuum-line or Schlenk techniques or in a glovebox under nitrogen. Unless otherwise stated, all reagents and solvents were of the best quality available and used as received from Aldrich. Tetrabutylammonium chloride (Janssen Chimica) and iodide (Merck) were recrystallized,[9] dried in vacuo, and stored under nitrogen prior to use. *cis*-/*trans*-[$PtCl_2$(SMe_2)$_2$] (**1**) was prepared according to the method of Cox et al.,[10] and *trans*-[PtPhCl(SMe_2)$_2$] (**2**) was prepared according to the method of Otto,[11] using a modification of the procedure developed by Kukushkin et al.[12] *trans*-[PtPhCl(PPh_3)$_2$] (**3**) was conveniently prepared from **2** by the substitution of SMe_2 by PPh_3. This procedure has also been described by Otto and has been used in the synthesis of the corresponding *trans*-[$PtCl_2$(PPh_3)$_2$] complex.[13] Using the same procedure, the corresponding iodo complexes, *trans*-[PtPhI(L)$_2$] (L = PMe_2Ph, PPh_3), were prepared and their NMR data were in agreement with those in the literature.[14] Elemental analyses were performed by H. Kolbe Mikroanalytisches Laboratorium, Mülheim an der Ruhr, Germany. IR spectra were recorded as polyethylene pellets on a Bio-Rad FTS 6000 FT-IR spectrometer. Fast atom bombardment (FAB) mass spectroscopic data were obtained on a JEOL SX-102 spectrometer using 3-nitrobenzyl alcohol as matrix.

NMR Measurements. ^{1}H, ^{31}P, and ^{19}F NMR spectra were recorded on a Varian Unity 300 spectrometer working at 299.79 MHz (^{1}H). The ^{13}C and 2D spectra were recorded on a Bruker DRX 400 working at 100.6 MHz (^{13}C). Chemical shifts are given in ppm downfield from TMS using residual solvent peaks (^{1}H, ^{13}C NMR) or H_3PO_4 (^{31}P NMR, δ 0) and $CFCl_3$ (^{19}F NMR, δ 0) as external references. The temperature was measured using the temperature-dependent shift of the CH_2 and OH protons of ethylene glycol.

***trans*-[PtPhF(PPh_3)$_2$] (4).** A Schlenk flask was charged with 193 mg (0.232 mmol) of complex **3** and 76.7 mg (0.605 mmol) of AgF (Merck). The flask was evacuated and refilled with nitrogen, and approximately 30 mL of benzene was added. After the addition of approximately 10 drops of chlorobenzene, the flask was shaken and placed in a sonication bath in the absence of light. After 36 h the reaction mixture was filtered and the precipitate (residual silver) was washed three times with benzene and twice with dichloromethane. The combined organic phases were filtered through Celite, and the solvent was removed from the filtrate. The brownish crystals were washed with petroleum ether and recrystallized from dichloromethane and petroleum ether, giving 177 mg (0.217 mmol, 94%) of an off-white product. Anal. Calcd for $C_{42}H_{35}FP_2Pt$: C, 61.84; H, 4.32. Found: C, 61.71; H, 4.40. ^{1}H NMR ($CDCl_3$): δ 6.08 (t, 2H), 6.26 (t, 1H), 6.59 (d, 2H, $^3J_{Pt-H}$ = 50 Hz), 7.22−7.36 (m, 18H), 7.53−7.59 (m, 12H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 23.7 (d, $^1J_{Pt-P}$ = 3269 Hz, $^2J_{P-F}$ = 19 Hz). ^{19}F NMR ($CDCl_3$): δ −107.6 (t, $^1J_{Pt-F}$ = 399 Hz, $^2J_{P-F}$ = 16 Hz). IR (cm^{-1}) 416 (ν(Pt−F)).

***trans*-[PtPhF(PMe_2Ph)$_2$] (5).** The synthesis was performed in accordance with the procedure described for complex **4**. The starting compound was the corresponding iodo complex, *trans*-[PtPhI(PMe_2Ph)$_2$] (**6**). The product was isolated as a yellow oil, which resisted further purification. ^{1}H NMR (CD_2Cl_2 at 298 K): δ 1.44 (t, 12H, $^2J_{P-H}$ = 6.0 Hz, $^3J_{Pt-H}$ = 30 Hz), 6.64−6.73 (m, 3H, *o*-, *p*-H, Pt−Ph), 6.95−7.05 (m, 2H, $^3J_{Pt-H}$ = 60 Hz, *m*-H, Pt−Ph), 7.30−7.51 (m, 6H), 7.55−7.70 (m, 4H). ^{31}P{^{1}H} NMR (CD_2Cl_2/C_6H_6 at 277 K): δ 4.3 (d, $^1J_{Pt-P}$ = 2983 Hz, $^2J_{P-F}$ = 24 Hz). ^{19}F NMR (CD_2Cl_2 at 298 K): δ −161 (bs). MS (FAB$^+$): *m*/*z* 548 [PtPh(PMe_2Ph)$_2^+$], 686 [PtPh(PMe_2Ph)$_3^+$].

***trans*-[PtPhMe(PPh_3)$_2$] (7).** A 22.2 mg (27 μmol) portion of complex **5** was dissolved in 10 mL of dry dichloromethane in a Schlenk flask under nitrogen. Seven microliters of Me_3SnPh was added, and the solution was allowed to stand overnight before evaporation of the solvent gave the product. It was washed with *n*-hexane and dried under vacuum. Recrystallization from dichloromethane and *n*-pentane gave 11.8 mg (14.5 μmol, 53%) of the product. Anal. Calcd for $C_{43}H_{38}P_2Pt$: C, 63.62; H, 4.72. Found: C, 63.47; H, 4.64. ^{1}H NMR (CD_2Cl_2): δ −0.57 (t, 3H, $^2J_{Pt-H}$ = 48 Hz, $^3J_{P-H}$ = 6 Hz), 6.23−6.29 (m, 3H, *o*-, *p*-H, Pt−Ph), 6.7−6.9 (m, 2H, $^3J_{Pt-H}$ = 30 Hz, *m*-H, Pt−Ph), 7.1−7.6 (m, 30H). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 29.7 (s, $^1J_{Pt-P}$ = 3223 Hz).

***trans*-[PtPh(C≡CPh)(PPh_3)$_2$] (8)**. A 4.3 mg (5.3 μmol) portion of complex **4** was almost completely dissolved in benzene in a J. Young NMR tube. Approximately 25 μL (150 μmol) of degassed phenylacetylene was added, and the reaction mixture was left for 1 h at room temperature before the volatile substances were removed under reduced pressure. Washing with acetone and drying in vacuo gave a few milligrams of white crystals. Anal. Calcd for $C_{50}H_{40}P_2Pt$: C, 66.88; H, 4.49. Found: C, 66.3; H, 4.5. ^{1}H NMR (CD_2Cl_2): δ 6.17−6.31 (m, 4H, *m*-H, C≡C−*Ph*/Pt−*Ph*), 6.62−6.66 (m 2H, *p*-H, C≡C−*Ph*/Pt−*Ph*), 6.82−6.85 (m, 4H, *o*-H, C≡C−*Ph*/Pt-*Ph*), 7.22−7.34 (m, 18H, *o*-/*p*-H P−*Ph*), 7.54−7.56 (m, 12H, *m*-H, P−*Ph*). ^{31}P-{^{1}H} NMR (C_6D_6): δ 24.6 (s, $^1J_{Pt-P}$ = 2979 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 115.3 (t, 1C, $^2J_{P-C} \approx$ 20 Hz, Pt−*C*≡C), 116.1 (s, 1C, Pt−C≡*C*), 128.0 (vt, 12C, $^3J_{P-C}$ = 5 Hz, 12C, *o*-C, P−*Ph*), 130.1 (s, 6 C, *p*-C, P−*Ph*), 132.0 (vt, $^1J_{P-C}$ = 14 Hz, $^2J_{Pt-C}$ = 56 Hz, 6C, *i*-C, P−*Ph*), 135.2 (vt, $^2J_{P-C}$ = 6 Hz, 12C, *m*-C, P−*Ph*), 120.8, 124.4, 127.37, 127.44, 131.1, 139.9 (s, Pt−*Ph*/≡C−*Ph*), 129.8 (s, 1C, *i*-C, ≡C−*Ph*), 157.7 (s, $^1J_{Pt-C} \approx$ 15 Hz, 1C, *i*-C, Pt−*Ph*).

Reaction of 4 and 5 with Silanes and Stannanes. In a typical experiment, a J. Young NMR tube was loaded with the platinum fluoro complex and solvent. The reaction mixture was thermostated prior to addition of an excess of the silane or the tin compound, and the reaction was monitored using ^{1}H, ^{31}P, or ^{19}F NMR spectroscopy. In most cases the products were not separated and isolated but characterized in situ.

Structure Determination. Crystal data and details of the data collection are given in Table 1. The intensity data sets for **4** and **7** were collected at 293 K with a Bruker SMART CCD system using ω-scans and a rotating anode with Mo Kα radiation (λ = 0.710 73 Å).[15] The intensities were corrected

(8) (a) McAvoy, J.; Moss, K. C.; Sharp, D. W. A. *J. Chem. Soc. A* **1965**, 1376. (b) Howard, J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1973**, 1840. (c) Coulson, D. R. *J. Am. Chem. Soc.* **1976**, *98*, 3111. (d) Rusell, D. R.; Mazid, M. A.; Tucker, P. A. *J. Chem. Soc., Dalton Trans.* **1980**, 1737.

(9) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: Oxford, England, 1988.

(10) Cox, E. G.; Saenger, H.; Wardlaw, W. *J. Chem. Soc.* **1934**, 182.

(11) Otto, S. Structural and Reactivity Relationships in Platinum(II) and Rhodium(I) Complexes; Thesis, University of The Orange Free State, Bloemfontein, South Africa, 1999; Chapter 3.

(12) (a) Clark, H. C.; Dixon, K. R. *J. Am. Chem. Soc.* **1969**, *91*, 596. (b) Kukushkin, V. Y.; Lövqvist, K.; Norén, B.; Oskarsson, Å.; Elding, L. I. *Phosphorus, Sulfur Silicon Relat. Elem.* **1992**, *73*, 253. (c) Kapoor, P.; Kukushkin, V. Y.; Lövqvist, K.; Oskarsson, Å. *J. Organomet. Chem.* **1996**, *517*, 71.

(13) Johansson, M. H.; Otto, S. *Acta Crystallogr.* **2000**, *C56*, e12.

(14) (a) Eaborn, C.; Kandu, K.; Pidcock, A. *J. Chem. Soc., Dalton Trans.* **1981**, 933. (b) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *J. Organomet. Chem.* **1974**, *65*, 275. (c) Mintcheva, N.; Nishihara, Y.; Mori, A.; Osakada, K. *J. Organomet. Chem.* **2001**, *629*, 61.

(15) BrukerAXS, SMART, Area Detector Control Software; Bruker Analytical X-ray Systems, Madison, WI, 1995.

Table 1. Crystal Data and Details of Data Collection and Refinement

	4	**7**
chem formula	$C_{42}H_{35}FP_2Pt$	$C_{43}H_{38}P_2Pt$
M_r	815.75	811.79
cryst syst	orthorhombic	monoclinic
space group	*Pbca*	$P2_1/c$
a/Å	11.532(2)	15.4989(12)
b/Å	23.943(5)	12.0592(9)
c/Å	25.042(5)	20.2752(15)
β/deg	90	110.864(2)
V/Å^3	6914(2)	3541.0(5)
Z	8	4
D_{calcd}/g cm^{-3}	1.567	1.523
μ/mm^{-1}	4.186	4.682
θ range/deg	1.63−32.07	1.41−31.75
no. of rflns collected	63 546	34 866
no. of unique rflns	11 202 (R_{int} = 0.188)	10 998 (R_{int} = 0.0662)
no. of params	412	416
$R(F)^a$, $R_w(F^2)^b$ ($I > 2\sigma(I)$)	0.0517, 0.0637	0.0371, 0.0628
$R_w(F^2)$ (all data)	0.0767	0.0724
S^c	0.969	0.982

^{a} $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2}$. ^{c} $S = [\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$.

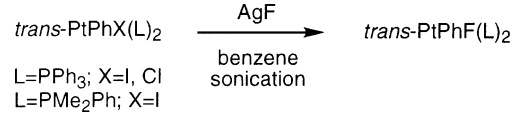
for Lorentz, polarization, and absorption effects using SADABS.[16] In both structures the first 50 frames were collected again at the end to check for decay; no decay was observed. All reflections were integrated using SAINT.[17] Both structures were solved by Patterson methods and refined by full-matrix least-squares calculations on F^2 using SHELXTL 5.1.[18] Non-H atoms were refined with anisotropic displacement parameters. Hydrogen atoms were constrained to parent sites, using a riding model. The crystals of **4** were weak scatterers, giving rise to a large fraction of weak reflections and thus a large R_{int} value.[19]

Kinetics. The kinetic experiments for the substitution reactions were performed on a Varian Cary 300 UV/vis spectrophotometer. The substitutions with chloride or iodide as nucleophile were studied in tetrahydrofuran by observing the change in absorbance at 250 and 315 nm, respectively. All reactions were studied under pseudo-first-order conditions with at least a 10-fold excess of the nucleophile ((0.8−11.9) × 10^{-3} mol dm^{-3}) with respect to the complex ((2−4) × 10^{-5} mol dm^{-3}). Stock solutions of the nucleophile were prepared daily, whereas the stock solutions of complexes **3** and **4** were stored for 5 days at the maximum. The kinetic traces were fitted to single exponentials using the software provided by Varian,[20] resulting in observed rate constants at different concentrations of incoming ligand. Variable-temperature experiments were performed between 288 and 318 K. Complete data are reported in the Supporting Information.

Results and Discussion

Synthesis and Characterization of Fluoro Complexes. Late-transition-metal fluoro complexes are scarce in comparison to complexes of the heavier halogens. Lately, however, a number of methods have been developed for the synthesis of Pd−F complexes. Applying one of these, the ultrasound promoted I/F exchange,[21] we obtained **4** from *trans*-[PtPhI(PPh$_3$)$_2$] (**9**) in good yield (cf. Scheme 1). Complex **4** was also obtained directly from the chloro complex **3** with AgF under sonication. This latter procedure afforded **4** in excellent yield, and the complex was characterized by NMR spectroscopy, elemental analysis, and X-ray crystallography (vide infra).

Scheme 1



Complex **5** was successfully synthesized from the corresponding iodo complex, **6**. It was isolated as a yellow oil, which resisted further purification and was characterized by NMR spectroscopy.

^{31}P NMR data in dichloromethane solvent confirm the trans configuration for complexes **4** and **5** with $^1J_{Pt-P}$ coupling constants of 3269 and 2983 Hz, respectively. These values are larger than those of the corresponding chloro complexes (3157 and 2868 Hz), indicating a low demand for the Pt 6s orbital by the polar Pt−F bond.[22] The presence of $^1J_{Pt-F}$ and $^2J_{F-P}$ coupling constants in the ^{31}P and ^{19}F NMR spectra confirm the presence of a Pt−F bond in both complexes also in solution. There is no indication of any solvolysis of **4** in dichloromethane, chloroform, or THF. Complex **5**, however, having a less sterically hindered environment, is subject to some dynamic behavior in dichloromethane solution. At room temperature the $^2J_{F-P}$ coupling is not resolved in the ^{31}P NMR spectrum, but when the temperature is lowered to ca. 4 °C, the peak sharpens and splits into the expected doublet. There is no sign of any solvolysis product in the spectrum, thus indicating that also for **5** the solvolytic equilibrium is shifted far to the fluoro complex. The stability to air and moisture is good for both complexes. In solution there is no sign of decomposition in the presence of air and moisture, and in the pure state the compounds can be kept at ambient temperature and under air for a very long time.

Single crystals of **4** suitable for X-ray diffraction were obtained by slow evaporation of a dichloromethane solution of the complex in a pentane bath. The X-ray determination confirms the molecular structure of **4** (cf. Figure 1). Selected bond distances and angles are given in Table 2. The complex has a distorted-square-planar coordination geometry with angles ranging from 85.9(1) to 92.9(2)°; the maximum deviation from a least-squares plane through PtP_2CF is 0.045 Å. Only a few examples of Pt^{II}−F bond distances are available in the literature.[8b,8d] These Pt−F bonds are trans to a tertiary phosphine and are significantly shorter (by almost 0.1 Å) than that observed in complex **4**, presumably due to the higher trans influence of the phenyl ligand. However, the difference between the Pt−F bond in *cis*-[PtF(CH(CF$_3$)$_2$)(PPh$_3$)$_2$] (2.03 Å) and that in **4** is larger than one would expect on the basis of similar trans

(16) G. M. Sheldrick, SADABS, Program for Absorption Correction; University of Göttingen, Göttingen, Germany, 1996.
(17) BrukerAXS, SAINT, Integration Software; Bruker Analytical X-ray Systems, Madison, WI, 1995.
(18) Sheldrick, G. M. SHELXTL5.1, Program for Structure Solution and Least-Squares Refinement; University of Göttingen, Göttingen, Germany, 1998.
(19) Wiess, M. S.; Hilgenfeld, R. *J. Appl. Crystallogr.* **1997**, *30*, 203.
(20) Varian Cary WinUV, Software manual; Varian Australia Pty Ltd, 1997.
(21) Pilon, M. C.; Grushin, V. V. *Organometallics* **1998**, *17*, 1774.
(22) The complex *trans*-[PtPhCl(PMe$_2$Ph)$_2$] has also been synthesized, and the NMR data were in agreement with those in the literature: Cross, R. J.; Wardle, R. *J. Chem. Soc. A* **1970**, 840.

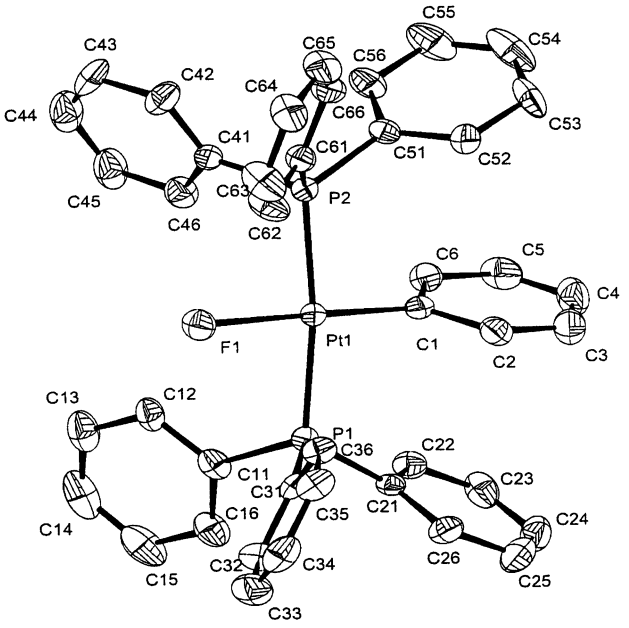


Figure 1. Diamond drawing with atomic numbering of the molecular structure of complex **4**. The ellipsoids denote 30% probability.

Table 2. Selected Crystallographic Distances (Å) and Angles (deg) with Estimated Standard Deviations

	4 (E = F)	**7** (E = C7)
	Distances	
Pt1−P1	2.2975(14)	2.2730(10)
Pt1−P2	2.2957(13)	2.2816(10)
Pt1−C1	1.978(5)	2.058(4)
Pt1-E	2.117(3)	2.226(4)
P1−C11	1.824(5)	1.840(4)
P1−C21	1.816(5)	1.819(4)
P1−C31	1.829(5)	1.816(4)
P2−C41	1.815(6)	1.815(4)
P2−C51	1.819(5)	1.826(4)
P2−C61	1.820(5)	1.821(4)
	Angles	
P1−Pt1−C1	92.92(15)	93.68(10)
P2−Pt1−C1	92.80(15)	90.22(10)
P1−Pt1−E	85.92(9)	86.45(10)
P2−Pt1−E	88.34(9)	90.04(10)

influence comparisons in Pt−Cl complexes.[23] One possibility is that the π-acceptor properties of the phosphine are more pronounced in the fluoro complex, since the fluoride is a better π-donor.[1,4] This push/pull interaction would result in a relative strengthening of the Pt−F bond in *cis*-[PtF(CH(CF$_3$)$_2$)(PPh$_3$)$_2$], giving it some π-character. The phenyl group in **4**, on the other hand, is almost perpendicular (71.5°) to the coordination plane; thus, any π-interaction in the Pt−C bond is probably weak. Needless to say, the limited data on Pt−F bonds preclude any far-reaching conclusions. Tables giving detailed crystallographic data, atomic positional parameters, and bond lengths and angles in the CIF format are given in the Supporting Information.

Substitution Reactions. Substitution reactions seemed like a reasonable starting point when trying to understand the reactivity of the Pt−F bond, especially in light of the extensive knowledge about substitution reactions in platinum(II) complexes. Complex **4** reacts with various anionic nucleophiles, substituting the fluoro ligand. Thus, treatment of **4** with 1 equiv of Cl$^-$ or I$^-$ in THF is complete in ca. 3 h, as indicated by ^{31}P NMR spectroscopy, and gives **3** and **9** as the sole products of reaction 1. No intermediates were identified.

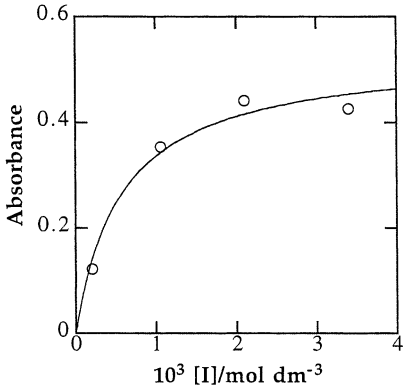


Figure 2. Equilibrium absorbance as a function of iodo concentration at [Cl$^-$] = 6.78 × 10^{-5} mol dm^{-3} and [**3**] = 1.76 × 10^{-5} mol dm^{-3}. T = 298 K.

$$\textit{trans}\text{-}[PtPhY(PPh_3)_2] + X^- \rightarrow \textit{trans}\text{-}[PtPhX(PPh_3)_2] + Y^- \quad (1)$$

To our knowledge, this is the first substitution reaction of a Pt(II) complex where F$^-$ is the leaving ligand, and we decided to pursue a more detailed investigation of this reaction.

According to NMR measurements in THF the equilibrium constant, K_e, for reaction 1 with Y = F$^-$ and X = Cl$^-$ is around 4, thus indicating that the position of the equilibrium is to the right even at low concentrations of nucleophile. In the case where Y = F$^-$, Cl$^-$ (the latter included for comparative purposes) and X = I$^-$, NMR measurements were of limited use because of problems of solubility of the nucleophile in the fairly high concentration range that was needed in the NMR experiments (compared to UV/vis measurements). Therefore, the equilibrium constant was determined by measuring the absorbance at different chloride and iodide concentrations for reaction 1 with Y = Cl$^-$ and X = I$^-$. Equation 2, where ϵ_M (the extintion coefficient of **9** at the path length used) and K_e are the adjustable parameters, was fitted to the data. In this equation A_0 is the absorbance before reaction and C_{Pt} is the total concentration of platinum: i.e., complexes **3** and **9** together. The fit (Figure 2) gave $K_e = 11.6 \pm 3.9$. The stability in the *trans*-[PtPhX(PPh$_3$)$_2$] series is thought to increase on going down the halogen group according to conventional wisdom, as expressed in, for example, the HSAB concept.[5] Lately, however, this has been shown to not always be true in nonpolar solvents and with noninnocent spectator ligands. Thus, the stability in methylene chloride of the corresponding palladium complexes,

$$A = \frac{A_0[Cl^-] + \epsilon_M K_e[I^-]C_{Pt}}{[Cl^-] + K_e[I^-]} \quad (2)$$

(23) The difference between a Pt−Cl bond trans to a tertiary phosphine and one trans to a phenyl group is approximately 0.05 Å. See: (a) Conzelmann, W.; Koola, J. D.; Kunze, U.; Strahle, J. *Inorg. Chim. Acta* **1984**, *89*, 147. (b) Johansson, M. H.; Malmström, T.; Wendt, O. F. *Inorg. Chim. Acta* **2001**, *316*, 149.

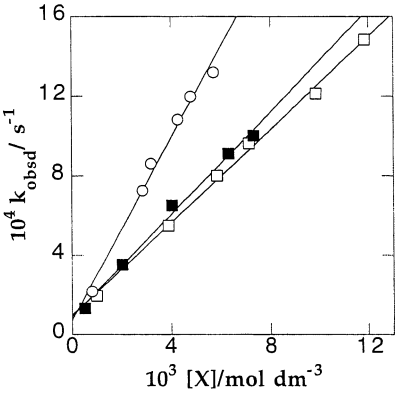


Figure 3. Observed pseudo-first-order rate constants for reaction 1 as a function of nucleophile concentration in THF at 298 K: (○) X = I and [**4**] = 3.8×10^{-5} mol dm^{-3}; (□) X = Cl and [**4**] = 2.1×10^{-5} mol dm^{-3}; (■) X = I and [**3**] = 1.8×10^{-5} mol dm^{-3}.

Table 3. Rate Constants for Reaction 1 at 25 °C in THF Solvent

	nucleophile			
	Cl^-		I^-	
complex	$10^5 k_1/s^{-1}$	$10^2 k_2/M^{-1}\ s^{-1}$	$10^5 k_1/s^{-1}$	$10^2 k_2/M^{-1}\ s^{-1}$
3			9.0 ± 2.7	12.9 ± 0.6
4	9.7 ± 2.4	11.7 ± 0.3	7.1 ± 4.9	23.0 ± 1.3

trans-[PdPhX(PPh_3)$_2$], was shown to be opposite: i.e., the stability decreased on going down group 17.[24] Likewise, *trans*-[Pt($SiPh_3$)I(PMe_2Ph)$_2$] was shown to be less stable than the corresponding chloro and bromo complexes in acetonitrile.[25] In the present case the conventional stability sequence is obviously followed so that the preference for the Pt center decreases in the order F < Cl < I. This reversed order as compared to that for palladium is probably due to the higher solvational power of THF (as compared to CH_2Cl_2, for example), which will give a stronger solvation of the smaller free halides, thus stabilizing the free halides in the order F > Cl > I. It should be noted that the order of stability between the various halide complexes is that expected for a "soft" metal center, but the difference is small.

The kinetics of reaction 1 was studied using high nucleophile concentration to ensure first-order conditions and to avoid reversibility. Plots of the observed first-order rate constant vs ligand concentration are linear with intercepts. The usual two-term rate law, eq 3, was fitted to the data (cf. Figure 3). Values of the

$$\text{rate} = (k_1 + k_2[X^-])[Pt] \qquad (3)$$

rate constants k_1 and k_2 are given in Table 3.

Enthalpies and entropies of activation were determined for chloride as incoming ligand by fitting the Eyring equation to the first- and second-order rate constants, k_1 and k_2, at different temperatures. These first- and second-order rate constants were obtained as slopes and intercepts from plots of the observed rate constants vs concentration of chloride at different temperatures. Values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are given in Table 4.

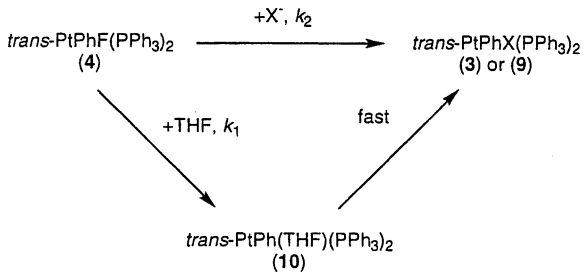
(24) Flemming, J. P.; Pilon, M. C.; Borbulevitch, O. Y.; Antipin, M. Y.; Grushin, V. V. *Inorg. Chim. Acta* **1998**, *280*, 87.
(25) Wendt, O. F.; Elding, L. I. *Inorg. Chem.* **1997**, *36*, 6028.

Table 4. Activation Parameters for the Solvolytic (k_1) and Direct (k_2) Pathways of Reaction 1 with Complex 4 and Chloride as Entering Ligand in THF Solvent[a]

	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}
k_1 path	77.8 ± 5.5	-56 ± 18
k_2 path	67.6 ± 1.8	-37 ± 6

[a] A weighted linear regression has been used to obtain the most accurate activation parameters. Each point has been given a weighting inversely proportional to the corresponding variance.

Scheme 2



Tables of all observed rate constants as a function of temperature and concentration are given in the Supporting Information.

Scheme 2 depicts the classical substitution mechanism involving a solvent species (**10**). The rate law derived from this scheme, using the steady-state approximation for the solvento species, results in a rate law of the form of eq 3. The alternative explanation for the intercept is a reversible reaction, but the equilibrium constants allowed us to compare the intercept with a calculated rate constant for the reverse reaction, indicating that the reversible reaction can be excluded under the experimental conditions used. On the basis of this evaluation and the activation parameters, the intercept and slope are interpreted as associative attacks on the metal center by the solvent and nucleophile, respectively.

The intrinsic reactivities of **3** and **4** (as displayed by k_1) are the same within experimental error. Thus, there is nothing to suggest that the Pt−F is more susceptible to solvolysis than other halides, as observed for example for the Ir−F bond.[2b] On the other hand, **4** displays a slightly higher nucleophilic discrimination than **3** as seen from the higher k_2 value. This could be explained by the smaller size of the fluoride or the higher electronegativity giving a more electrophilic metal center, but one should keep in mind that a factor of 2 higher reactivity on going from chloride to iodide as an incoming nucleophile speaks in favor of a very open transition state also for **4**; this is in keeping with the activation parameters, which show that the enthalpy is the dominating contribution to the activation barrier.

Transmetalation Reactions. The reaction of complex **4** or **5** with Me_3SnPh was studied in CD_2Cl_2 at room temperature by ^1H and ^{31}P NMR spectroscopy (cf. Scheme 3). Complex **4** reacts with Me_3SnPh, and within 15 min there is a complete conversion to a single product, complex **7**. It was fully characterized by NMR spectroscopy, elemental analysis, and X-ray crystallography. It displays a $^1J_{Pt-P}$ value of 3223 Hz, typical of a trans compound, and in the ^1H NMR spectrum there is a triplet with platinum satellites at −0.57 ppm

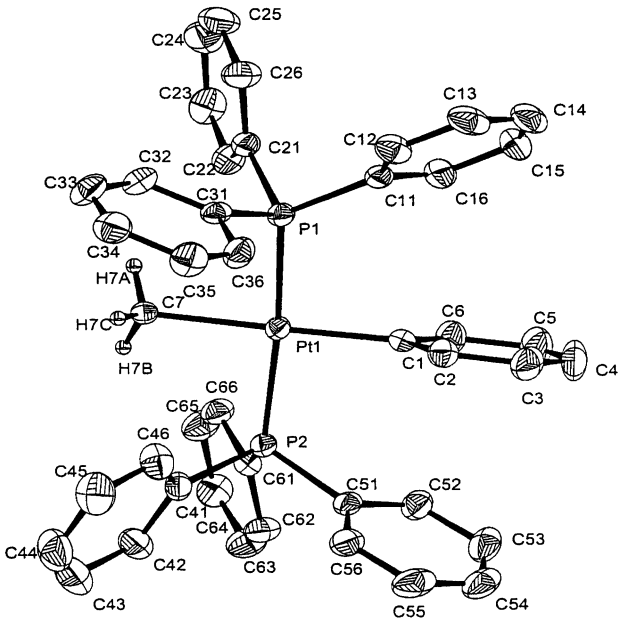
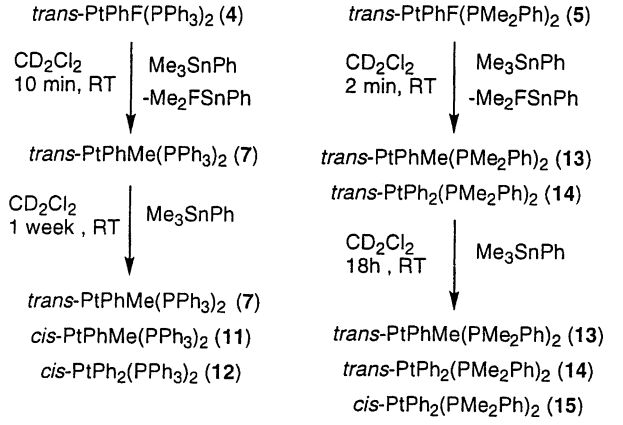


Figure 4. Diamond drawing with atomic numbering of the molecular structure of complex **7**. The ellipsoids denote 30% probability.

Scheme 3



corresponding to the platinum methyl group. Keeping the NMR sample at room temperature for 1 week changed the product distribution, as seen by ^{31}P NMR spectroscopy. The reaction mixture now contained not only **7** but also the analogous cis complex, **11**, in approximately the same amount. Also *cis*-[$PtPh_2(PPh_3)_2$] (**12**) was formed, though only to an extent of about 10%. **11** and **12** were characterized by ^{1}H and ^{31}P NMR spectroscopy.

Single crystals of **7** suitable for X-ray diffraction were obtained by slow evaporation of the solvent from a reaction mixture of **4** and Me_3SnPh in dichloromethane-d_2 at room temperature. The molecular structure is given in Figure 4, and selected bond distances and angles are given in Table 2. The complex has a distorted-square-planar coordination geometry with the two phosphines in a trans arrangement. The maximum deviation from a least-squares plane through PtP_2C_2 is 0.11 Å, and the plane of the phenyl group is oriented almost perpendicular to the coordination plane (80.9°). As expected from the higher trans influence of the methyl group as compared to that of the fluoride ion, the Pt−C(phenyl) distance is 2.058(4) Å in **7** as compared to 1.978(5) Å in **4**. The Pt−C(methyl) distance in **7** is substantially longer at 2.226(4) Å. Again, this is in line with what one would expect, and it corresponds to the difference in s character for the two bonds; the higher s character gives a stronger and, hence, shorter bond. This is also manifested in the ^{31}P NMR spectrum of **11**, where the $^1J_{Pt-P}$ coupling constant trans to the Pt−C(sp^3) bond is some 275 Hz higher than that trans to the Pt−C(sp^2) bond. Due to the high trans influence of hydrocarbyl ligands, a cis disposition is usually the most stable form, and there are not many Pt−methyl bond distances trans to other hydrocarbyl ligands reported in the literature. The Pt^{II}−C(methyl) distance in **7** is the second longest reported in the literature; the only one longer is one of the chemically equivalent Pt−C distances in (2,2-diethyl-1,3-bis(diphenylphosphino)propane)dimethylplatinum(II), reported to be 2.258(4) Å.[26]

Table 5. NMR Data for Compounds 11−15

	nucleus	chem shift/δ (multiplicity, coupling const/Hz, assignt)[a]
11	^{1}H	0.35 (dd, 3H, $^3J_{H-P}$ = 6.0, $^3J_{H-P}$ = 9.0), 6.05−6.71 (m, 5H), 6.97−7.60 (m, 30H)
	^{31}P{^{1}H}	26.4 (d, $^1J_{Pt-P}$ = 1725, $^2J_{P-P}$ = 10.9), 27.7 (d, $^1J_{Pt-P}$ = 2003, $^2J_{P-P}$ = 10.9)
12	^{1}H	6.30−6.50 (m, 10H), 7.00−7.62 (m, 30H)
	^{31}P{^{1}H}	20.8 (s, $^1J_{Pt-P}$ = 1762)
13[b]	^{1}H	−0.19 (t, 3H, $^2J_{Pt-H}$ = 50, $^3J_{P-H}$ = 6 Hz, Pt−Me), 1.22 (vt, 12H, $^2J_{P-H}$ = 3, $^3J_{Pt-H}$ = 42, P−Me), 6.72−6.77 (m, 2H, Pt−Ph)
	^{31}P{^{1}H}	−8.3 (s, $^1J_{Pt-P}$ = 2898)
14	^{31}P{^{1}H}	−5.5 (s, $^1J_{Pt-P}$ = 2916)
15	^{31}P{^{1}H}	−14.8 (s, $^1J_{Pt-P}$ = 1754)

[a] The solvent is CD_2Cl_2 unless stated otherwise. The assignment is only displayed for clarification when necessary. [b] Not all protons could be assigned due to interference with protons from the tin compound.

The reaction between **5** and Me_3SnPh is also very fast. Within 2 min all the starting material is consumed and two products have formed in approximately a 9:11 molar ratio: *trans*-[$PtPhMe(PMe_2Ph)_2$] (**13**) and *trans*-[$PtPh_2(PMe_2Ph)_2$] (**14**). They were characterized by NMR spectroscopy (cf. Table 5). After 18 h also *cis*-[$PtPh_2(PMe_2Ph)_2$] (**15**) was identified in the reaction mixture, in addition to complexes **13** and **14**. The formation of **15** correlates with the loss of **14**; i.e., what is observed is an isomerization of **14** to **15**. The cis to trans ratio of the diphenyl complexes after 18 h was about 5:7, whereas there was no sign of any isomerization of **13**. Over the course of several days this ratio increased, making the cis complex the dominant species. Complex **15** has been synthesized elsewhere,[27] giving the same NMR signature as observed here.

Qualitatively it is clear that **5** is more reactive than **4**, in agreement with what is observed for the simple substitution reaction. On the basis of the fact that PMe_2Ph is less sterically demanding than PPh_3, this speaks in favor of an associative mechanism also for the transmetalation. Furthermore, it is clear that only trans products are formed, regardless of substrate; i.e., we have an exclusive F-for-R (R = Me, Ph) substitution at

(26) Smith, D. C.; Haar, C. M.; Stevens, D. E.; Nolan, S. P.; Marshall, W. J.; Moloy, K. G. *Organometallics* **2000**, *19*, 1427.

(27) Wendt, O. F. Platinum(II) and Palladium(II) Complexes with Group 14 and 15 Donor Ligands. Synthesis, Structure and Substitution Mechanisms; Thesis, Lund University, Lund, Sweden, 1997.

these platinum fluoro complexes. The formation of cis products seems to be a consecutive process; i.e., the cis complex forms via isomerization of the trans products and not directly from the fluoro complexes. Also notable is the fact that **14** isomerizes but not **13**. This could be due to a difference in kinetics, but the likely explanation is that a trans arrangement of an sp^3- and sp^2-hybridized carbon is a more tolerable configuration than a trans arrangement of two sp^2 carbons. This is in line with the trans influence sequence observed in **7**.

Although the intimate mechanism for the transmetalation is unknown, the nonpolar nature of the Sn−C bond speaks in favor of some type of concerted mechanism. Typically in concerted reactions, the substrate bond with the highest s character has the highest reactivity; a classical example is the σ-bond metathesis of C−H bonds on a Sc metal center, where the reactivity follows the hybridization of the carbon atom.[28]

In light of this, one would expect the Sn−Ph bond to be the most reactive in the Me_3SnPh substrate, and this is almost always observed in, for example, palladium-catalyzed Stille couplings.[7] However, there are examples where the tin−alkyl bond is more reactive than a tin−aryl bond; in the work by Eaborn, Pidcock, and coworkers on the reactivity of platinum metal centers toward organotin reagents it was shown that, with sterically demanding substrates or ancillary ligands, Sn−Me bonds are favored over Sn−aryl bonds.[29] Our results also follow along these lines. When the first step of the reactions depicted in Scheme 2 is considered, it is clear that products **7** and **13** are formed via transmetalation over the Sn−Me bond. To form product **14**, the transmetalation also occurs over the Sn−Ph bond. The differences in the reaction patterns can be rationalized in terms of steric effects. Obviously, the steric demand of the PMe_2Ph ligand is less than that of the PPh_3 ligand, thus facilitating the transmetalation over both the Sn−Me bond and the Sn−Ph bond.

In the simple substitutions the reactivity of the fluoride is not substantially different from that of a chloride. In the transmetalation reaction the picture is quite different. We know from the literature and from experiments of our own that chlorobis(phosphine)-platinum(II) complexes are virtually unreactive toward organotin reagents.[29] The high, or in some cases very high, reactivity of the present fluoro complexes was therefore somewhat surprising, especially in light of the results from the substitution reactions. The transmetalations are clearly driven by something other than an extremely weak Pt−F bond; we suggest that this is the presence of a strong Sn−F bond in the products. The transmetalations are, however, not only thermodynamically favored but they are also faster than the substitutions by a factor of 10−100. To understand the high reactivity, it is necessary to invoke some stabilizing property of the associative transition state, most likely a fairly strong Sn−F interaction: i.e., the fluoride probably acts as a bridging ligand in the transmetalation transition state.

The expected tin byproducts of these reactions were not observed in solution using, for example, ^{19}F NMR spectroscopy. However, it is a well-known fact that organotin fluorides have a propensity to polymerize and the polymer of Ph_3SnF thus formed is highly insoluble in organic solvent, thus preventing its observation. In a very recent paper, Me_2SnPhF was characterized, and it turns out that this compound also is highly polymeric but also highly soluble in organic solvents.[30] The polymeric nature of Me_2SnPhF gives rise to a very broad ^{19}F NMR peak; this might be the explanation why we failed to observe this species in solution.

In light of the high reactivity of the fluoro complexes toward organostannanes we decided to also investigate their reactivity toward organosilanes. Thus, complexes **4** and **5** were reacted with trimethylvinylsilane or trimethylphenylsilane in THF or C_6D_6. No reaction was observed, and neither addition of CsF(s) nor the presence of water enabled the desired transmetalation reaction.

Reaction with Acetylenes. Treatment of **4** with degassed phenylacetylene in benzene at room temperature gave the alkynyl complex *trans*-[PtPh(C≡CPh)-$(PPh_3)_2$] (**8**). It was characterized by 1D and 2D NMR spectroscopy and elemental analysis. ^{13}C NMR data confirm the presence of a σ-bonded alkynyl unit, displaying a triplet at δ 115.25 ($^2J_{P-C} \approx 20$ Hz) and a singlet at δ 116.06, assigned to the α- and β-carbons, respectively. The ^{31}P NMR spectrum displays a singlet with Pt satellites ($^1J_{Pt-P} = 2979$ Hz), unambiguously showing **8** to be a trans complex. Platinum acetylide complexes are well-known in the literature,[31] but they are usually synthesized from the acetylene in the presence of base, although there is an example in the literature of a synthesis of an acetylene complex from phenylacetylene and a Pt alkoxide complex.[32] This suggests that the coordinated fluoride has considerable basicity (just as the alkoxide), and this is also supported by the weak, but significant, intramolecular H−F interaction (2.13 Å) between the fluoride and the aromatic hydrogens H12 and H62.[33]

A C−F reductive elimination from **4** was also attempted. A benzene solution of **4** in the presence of an excess of diphenylacetylene was heated to approximately 75 °C for 48 h, but no reaction was observed.

Conclusions

We have prepared two platinum fluoride complexes of the type *trans*-$PtPhF(PR_3)_2$ and tested their reactivity. Our investigations of simple substitution reactions show that the Pt−F bond behaves in a manner similar to that for other Pt−X bonds. In THF solution it is thermodynamically slightly less stable and kinetically about as labile as a Pt−Cl bond. In the transmetalation reaction with Me_3SnPh the reactivities of the Pt−F complexes are very high, especially in comparison to

(28) Thomson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203.

(29) Eaborn, C.; Odell, K. J.; Pidcock, A. *J. Chem. Soc., Dalton Trans.* **1979**, 758.

(30) Beckmann, J.; Horn, D.; Jurkschat, K.; Rosche, F.; Schürmann, M.; Zachwieja, U.; Dakternieks, D.; Duthie, A.; Lim, A. E. K. *Eur. J. Inorg. Chem.* **2003**, 164.

(31) Kowalski, M. H.; Arif, A. M.; Stang, P. J. *Organometallics* **1988**, *7*, 1227.

(32) Kim, Y.-J.; Osakada, K.; Yamamoto, A. *J. Organomet. Chem.* **1993**, *452*, 247.

(33) Osterberg, C. E.; King, M. A.; Arif, A. M.; Richmond, T. G. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 888.

those of the corresponding Pt−Cl complexes. Our explanation for this high reactivity is that the reaction takes place in an associative fashion and that the fluoride stabilizes the transition state through a strong Sn−F binding interaction.

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Supporting Information Available: Tables giving detailed crystallographic data, atomic positional parameters, and bond lengths and angles and all observed rate constants as a function of temperature and concentration; X-ray data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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