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Interactions of Cationic Palladium(II)- and Platinum(II)-η^3-Allyl Complexes with Fluoride: Is Asymmetric Allylic Fluorination a Viable Reaction?

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The complex cations $[M(\eta^3\text{-}R_2All)(PPFPz\{3\text{-}t\text{Bu}\})]^+$ (M = Pd^{II}, R_2All = 1,3-diphenylallyl, 1,3-dicyclohexylallyl, indenyl; M = Pt^{II}, R_2All = 1,3-diphenylallyl; PPFPz-{3-*t*Bu} = 3-*tert*-butyl-1-{1-[2-diphenylphosphanyl-ferrocenyl]ethyl}-1*H*-pyrazole) have been prepared as salts with PF_6^- or SbF_6^-. They have been characterized by NMR spectroscopy in solution and by X-ray crystallography in the solid state. Their reactions with sources of nucleophilic and "naked" fluoride have been investigated by multinuclear NMR spectroscopy. The Pd^{II} complexes did not undergo any nucleophilic substitution with concomitant release of allyl fluorides. The dicyclohexylallyl fragment was released as a 1,3-diene by elimination, but with other allyl complexes nonspecific decomposition reactions predominated. The complex $[Pt(\eta^3\text{-}1,3\text{-}Ph_2C_3H_3)(PPFPz\{3\text{-}t\text{Bu}\})]PF_6$ underwent an anion exchange with Me_4NF to give $[Pt(1,3\text{-}Ph_2C_3H_3)(PPFPz\{3\text{-}t\text{Bu}\})]F$ which existed as a mixture of interconverting allyl isomers in solution at ambient temperature. For the bromide salt, $[Pt(\eta^3\text{-}1,3\text{-}Ph_2C_3H_3)(PPFPz\{3\text{-}t\text{Bu}\})]Br$, allyl isomerization was slow at ambient temperature. Precursors of Pt^0 reacted with bromo-1,3-diphenylprop-2-ene to give $[Pt_2(\mu\text{-}Br)_2(\eta^3\text{-}1,3\text{-}Ph_2All)_2]$ and precursors of Pd^0 underwent oxidative additions with bromo- and fluoro-1,3-diphenyl-2-propene to give 1,3-diphenylallyl complexes of Pd^{II}. Therefore, the nucleophilic attack of fluoride on the allyl fragment of Pd^{II} complexes is endergonic, and the high energy barrier of this step is difficult to overcome in a catalytic allylic fluorination reaction.

Introduction

The organometallic and coordination chemistry of fluoride and the C–F bond have recently received much attention. Initial work centered around transition-metal fluoro complexes,[1–3] the coordination ability of the notoriously inert C–F bond[4] and its cleavage by means of electron-rich transition-metal centers using either stoichiometric[5] or catalytic methods.[6] Furthermore, "fluoride effects" have been discovered in homogeneous catalysis, which points to an important role of fluoride as a steering ligand in transition-metal-catalyzed reactions.[7,8] By contrast, the metal-catalyzed generation of C–F bonds (i.e. catalytic fluorination of organic compounds) has long been limited to industrial applications of the Swarts reaction[9] and some examples of the Pd-catalyzed fluorocarbonylations.[10,11] Research on the generation of fluoroarenes by reductive eliminations from aryl-fluoropalladium(II) complexes is actively pursued but not yet realized.[12] The neglect of transition-metal mediated fluorination methodologies comes as a surprise when the importance of fluorinated organic compounds in the chemical, agricultural, and pharmaceutical industry is considered. Here, selectively fluorinated organic compounds are in high demand for diverse applications.[13] In response to this situation, we have initiated a research program directed towards transition-metal catalyzed selective fluorination reactions at sp^3 centers. This has already resulted in a fluoro-Ru^{II}-complex-mediated halogen exchange reaction[14] and a titanium-catalyzed asymmetric catalytic α fluorination of β-keto esters.[15] Similar asymmetric fluorinations have been discovered by us and others using Pd^{II},[16] Cu^{II},[17–19] Ni^{II},[18,20] and Ru^{II}[21] complexes as catalysts, all of them relying on electrophilic fluorination reagents. The present work involves a promising alternative strategy for asymmetric catalytic fluorination using fluoride nucleophiles. We were inspired by the observation that catalytic allylic substitution reactions enable the attachment of a variety of nucleophiles at allylic fragments with high enantioselectivity.[22] Consequently, we hoped to realize a palladium catalyzed allylic fluorination reaction starting from suitable allylic substrates and fluoride nucleophiles using chiral Pd^{II} complexes as catalysts.[23] Since cationic η^3-allyl complexes of palladium(II) are well-established intermediates in asymmetric allylic substitution reactions,[24] we also wanted to investigate the interaction of such species with fluoride anions in order to clarify: (a) if nucleophilic attack of fluoride takes place; or (b) what other interactions (coordination, ion-pairing etc.) play a role. Analogous experiments with platinum(II) complexes were also planned

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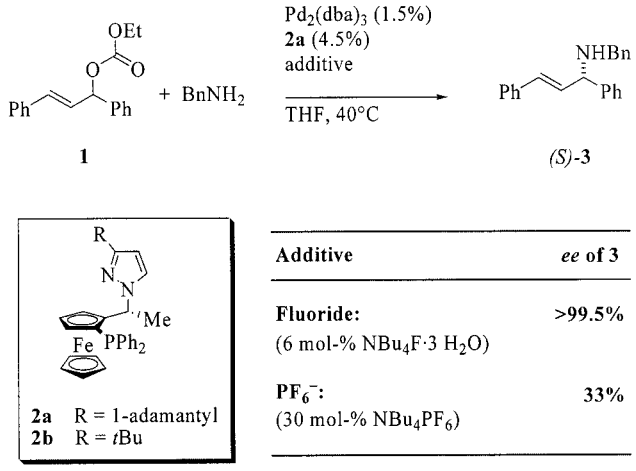
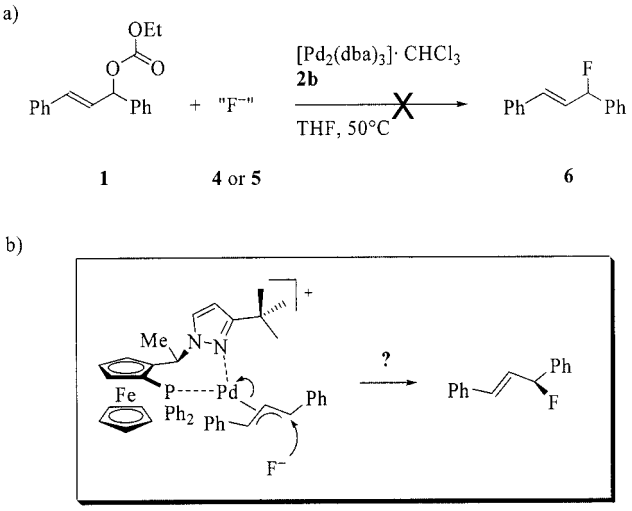
because the slower kinetics of Pt^{II} relative to Pd^{II} compounds should allow for the observation of short-lived intermediates with the added advantage of having ^{195}Pt NMR spectroscopy as a selective analytical tool.[25] Finally, we also hoped to clarify the issue of a "fluoride-effect" that we had observed earlier in the asymmetric amination of ethyl 1,3-diphenylallyl carbonate (**1**) catalyzed by Pd^{II} with ligand **2a** (Scheme 1). The reaction gives the amination product **3** in either very high or low enantioselectivity, depending on the counterion (F^- or PF_6^-) of the ammonium salt additive.[8]



Scheme 1. The palladium-catalyzed asymmetric allylic amination is subject to astonishing anion effects on enantioselectivity.[8] dba = dibenzylidene acetone, Bn = benzyl.

Results

The new phosphanyl-ferrocenyl pyrazole **2b**, (PPFPz-{3-*t*Bu}, 3-*tert*-butyl-1-{(*R*)-1-[2-(S_P)-diphenylphosphanyl-ferrocenyl]ethyl}-1*H*-pyrazole), (Scheme 1) was prepared from 3(5)-*tert*-butylpyrazole[26] and (*R*,*S*)-PPFA[27] (PPFA = *N*,*N*-dimethyl-1-[2-diphenylphosphanyl-ferrocenyl]ethylamine) in high yield as a single regioisomer according to our standard method.[28] A test run with **2b** as the ligand in the palladium-catalyzed allylic amination reaction,[29] shown in Scheme 1, using cocatalytic $NBu_4F{\cdot}3H_2O$ (3 equiv. relative to [Pd]),[8] gave the amination product (*S*)-**3** with an *ee* > 99.5%. Thus, **2a** and **2b** behaved identically in this reaction, but **2b** was the preferred ligand for mechanistic studies because of the simplicity of the ^1H NMR-signal of the *tert*-butyl group over the adamantyl group. Using similar reaction conditions, we next attempted to perform catalytic allylic fluorination reactions with carbonate **1** (Scheme 2, a). The catalyst was generated in situ from $Pd(dba)_2$ and **2b**. The sources of nucleophilic fluoride that were tested are TBAT {$NBu_4[SiF_2Ph_3]$ (**4**)},[30] a nucleophilic non-basic fluoride transfer reagent, and Me_4NF (**5**),[31] a "naked" fluoride[32] of high basicity. Anhydrous versions of these reagents are available and they also show considerable solubility in nonprotic organic solvents, which is an important characteristic because the nucleophilicity of fluoride is reduced by solvation in protic media or in the presence of trace water.[33] It should be noted that more traditional fluoride sources (such as KF, CsF, or NBu_4F) are either insoluble in nonprotic solvents or cannot be dried without decomposition.[34]



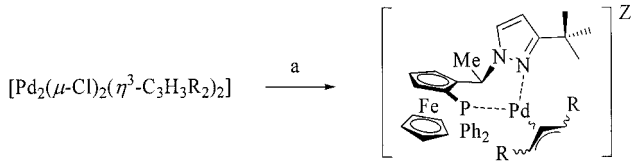
Scheme 2. Nucleophilic allylic fluorination of palladium complexes. (a) Attempted, but unsuccessful allylic fluorination with a Pd^0 catalyst. (b) The nucleophilic attack of fluoride on cationic allylpalladium(II) complexes is the key step in a postulated allylic fluorination reaction, as investigated in this work.

Analysis of reaction solutions from catalysis experiments using ^{19}F NMR spectroscopy did not show signals corresponding to 1,3-diphenylallyl fluoride (**6**),[14a,35] or any other organofluorine compound. Straightforward allylic fluorination in a catalytic manner is thus not feasible. We therefore proceeded to study the stoichiometric variant of this reaction, namely the attack of fluoride on isolated, fully-characterized cationic η^3-palladium(II) and -platinum(II) complexes (Scheme 2, b).

Synthesis and Structure of Allylpalladium(II) and -platinum(II) Complexes

Several cationic palladium(II) allyl complexes incorporating the ligand **2b**, (PPFPz-{3-*t*Bu}), were synthesized in the usual manner[36] by reaction with the dinuclear allylpalladium(II) chlorides (**7**) followed by halide abstraction with either $TlPF_6$, $AgSbF_6$, or $(Et_3O)BF_4$ (Scheme 3 and Scheme 5). In some cases, we applied a new halide abstraction technique that relies on the combination of epichlorohydrine (or any other reactive epoxide) with an acid and a nonnucleophilic counterion, such as HPF_6. This method relies on the ability of epoxides to scavenge halide anions by nucleophilic-ring opening.

The diphenylallyl complex **8a** occurs predominantly as the *exo-syn-syn* isomer[37] (>98% by ^{31}P NMR spectroscopy) in $CDCl_3$ solution, in agreement with observations on complexes with similar ligands.[29] The same isomer is also present in the solid state, as shown by X-ray crystallography (vide infra, Figure 7). η^3-1,3-Dicyclohex-

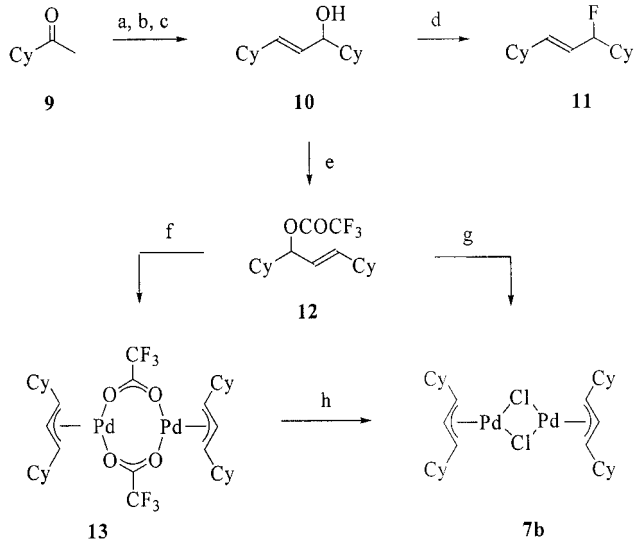


7a R = Ph
7b R = Cy
7c R_2 = 1,2-C_6H_4

8a R = Ph, Z = PF_6
8b R = Cy, Z = PF_6
8c R_2 = 1,2-C_6H_4, Z = SbF_6

Scheme 3. Synthesis of cationic allylpalladium(II) complexes. (a) **2b**, halide abstracting reagent (see Exp. Section). **8a**: 87%; **8b**: 96%; **8c**: 82%. Cy = cyclohexyl.

ylallyl complexes of palladium(II) are new. Our synthetic route (Scheme 4) started with an aldol addition of cyclohexyl methyl ketone (**9**) followed by elimination to the α,β-unsatuarated ketone and Luche reduction[38] to give dicyclohexylallyl alcohol (**10**). Fluorination with DAST [(diethylamino)sulfur(II) trifluoride][39] produced a reference sample of allyl fluoride **11**. According to a general procedure by Vitagliano et al.,[40] allyl trifluoroacetate (**12**) was treated with $Pd(dba)_2$ by oxidative addition to give the trifluoroacetate-bridged dimer **13**, and this complex underwent ligand exchange with LiCl to give the chloro-bridged dimer **7b**. Alternatively, and more conveniently, the last two steps could be performed in a single synthetic operation (**12**→**7b**).



Scheme 4. Synthesis of (1,3-dicyclohexylallyl)palladium(II) complexes. (a) 1. LDA, THF, –78 °C; 2. CyCHO; 3. MsCl. (b) DBU, Me_2CO; 70% (from **9**). (c) $NaBH_4$, $CeCl_3 \cdot 7H_2O$, MeOH, room temp.; 77%. (d) DAST, CH_2Cl_2, –78 °C; quant. (e) TFAA, Py, 0 °C; 93%. (f) $Pd(dba)_2$, THF/MeCN (3:1), 40 °C; 93%.·(g) $Pd(dba)_2$, LiCl, THF/MeCN (3:1); 97%. (h) LiCl. LDA = lithium diisopropylamide, DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene, TFAA = trifluoroacetic acid anhydride.

The bridged trifluoroacetate **13** showed interesting conformational isomerism in solution, similar to that reported for $[Pd_2(\mu\text{-}OAc)_2(\eta^3\text{-}R_2All)_2]$ complexes.[41] The VT ^1H NMR spectroscopic shifts (Table 1) were assigned to the C_S symmetric isomer **A**, which has two sets of allylic protons, and the C_{2v} symmetric isomer **B** (Figure 1). Interchange of **A** and **A′** was relatively slow up to a temperature of 273 K. Interchange of **A** with **B** was slow over the whole temperature range studied (253–298 K), but notable line broadening occurred at 298 K. The allyl units had the *syn-syn* configuration in both **A** and **B**, as deduced from the coupling [$^3J_{H,H}$ = 11 Hz] between the central and terminal allyl protons.

Table 1. ^1H NMR spectroscopic data for allyl hydrogen atoms within the conformational isomers of **13** at 253 K.

Conformer	Central H	*anti* H
A	5.39 ppm, t, J = 11.1	3.48 ppm, dd, J = 10.9, 5.1
	5.06 ppm, t, J = 11.1	3.71 ppm, dd, J = 10.9, 7.5
B	5.42 ppm, t, J = 11.1	3.43 ppm, dd, J = 11.0, 5.7

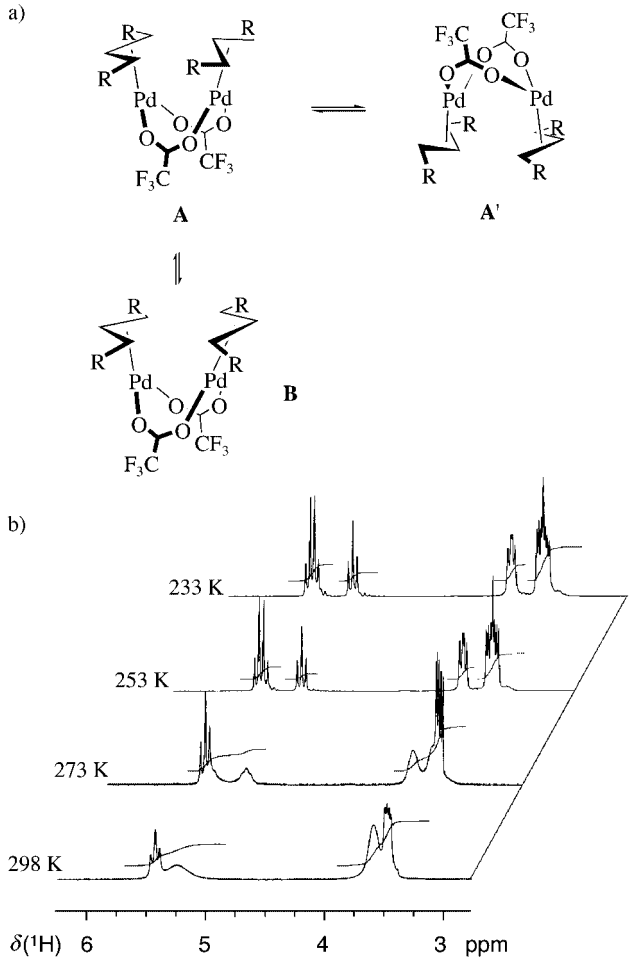


Figure 1. Conformational isomerism and VT ^1H NMR spectra of **13** ($CDCl_3$, 300 MHz). (a) Conformational isomerism and dynamic behavior of **13**. (b) VT-NMR: Signals of **A**/**A′** and **B** (compare in Table 1) are partially overlapping at all temperatures; the virtual quartet at 233 and 253 K is a superimposition of two triplets. At 298 K, the interconversion of **A** and **A′** approaches coalescence. Other processes such as conformational changes of the Cy substituents presumably add to the dynamics.

Incorporation of the (1,3-dicyclohexylallyl)palladium(II) fragment into a cationic complex with ligand **2b** (Scheme 3) yielded **8b**, initially as an 82:18 mixture of two allyl isomers. This ratio changed to about 1:1 (52:48) after recrystallization from hot methanol. On the basis of the ^{1}H NMR coupling data, the *syn-syn* configuration was assigned to the main isomer, and the *syn-anti* (*anti* Cy group *trans* to N) configuration to the minor isomer, but the one-dimensional analysis did not give conclusive information about the *endo* or *exo* orientation. An X-ray crystal structure of **8b** supported the NMR spectroscopic assignment in a surprising way: the complex had crystallized as a statistical 1:1 mixture of allyl isomers possessing the *exo-syn-syn* and *endo-anti-syn* (*anti trans* to N) configurations, respectively (Figure 2). Apparently, both isomeric dicyclohexylallyl fragments had flexibly adapted to the coordination environment of the metal-ligand framework (Figure 2, **A** and **B**), which was kept as a common unit during the refinement of the structure. The bonding data for the dicyclohexylallyl fragments are not very accurate because of the disorder and will not be discussed.

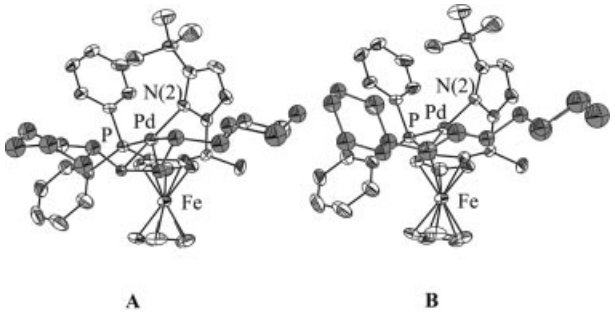
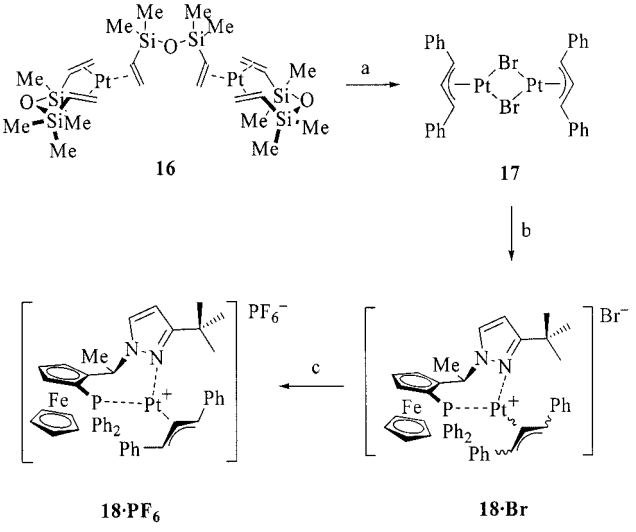


Figure 2. ORTEP representations (30% probability ellipsoids) of cationic fragments displaying configurational allyl isomerism in the solid-state structure of **8b**. PF_6 anions and hydrogen atoms are omitted for clarity, carbon atoms within the dicyclohexylallyl fragments are filled in as grey. **A**: *endo-syn-anti* isomer; **B**: *exo-syn-syn* isomer. Selected bond lengths [Å] and angles [°]: Pd–N(2) = 2.143(6), Pd–P 2.325(2); N(2)–Pd–P = 89.16(18). As a result of the disorder, values for the allyl fragments are not accurate.

The dark-red indenyl complex **8c** was prepared from $\{PdCl(Ind)\}_n$ (**7c**)[42] in the usual way (Scheme 3). Unlike most other cationic complexes described here, the indenyl compound was somewhat air-sensitive, with solutions of it slowly decomposing in air. A mixture of *exo* and *endo* isomers was present in solution, with *exo*-**8c** as the major species, as shown by H,H NOESY cross peaks of the central allyl hydrogen and the *tert*-butyl group. In the solid state only the *exo* isomer is present (Figure 3). The X-ray crystal structure also shows that the indenyl fragment is η^3-bonded, rather than η^5.

Unlike the much studied (1,3-diphenylallyl)palladium(II) complexes,[29,43,44] the corresponding platinum compounds are unknown, even though platinum-catalyzed allylic alkylation (including that of 1,3-diphenylallyl substrates) has been studied and the intermediacy of cationic η^3-allyl complexes have been invoked in analogy to Pd chemistry.[45,46] We have found that the addition of 1,3-diphenylallyl bromide (**15**)[47] to a Karstedt complex solution (**16**)[48,49] readily produces a yellow precipitate of the allylplatinum(II) bromide (**17**) (Scheme 5). $Pt_2(dba)_3$[50] also underwent this oxidative addition, but the resulting product was less pure due to metallic platinum residues in the precursor complex. Reaction of **17** with **2b** gave the complex **18·Br**, which was converted to **18·PF$_6$** using the new HPF_6/epichlorohydrine reagent (Scheme 5).



Scheme 5. Synthesis of (1,3-diphenylallyl)platinum(II) complexes. (a) PhCH=CHCH(Br)Ph (**15**), *t*BuOMe, 0 °C; 77%. (b) **2b**, THF; 97%. (c) 1. epichlorohydrine, HPF_6, Me_2CO; 2. crystallization from CH_2Cl_2/MeOH; 73% (from **17**).

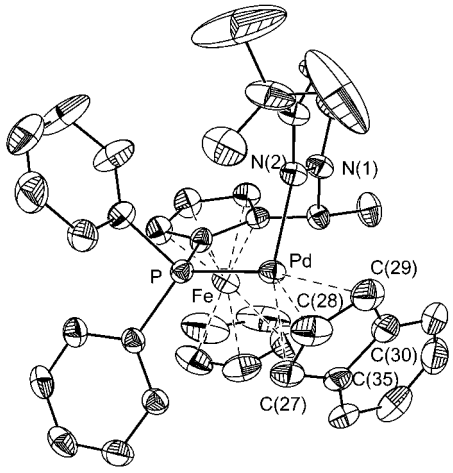
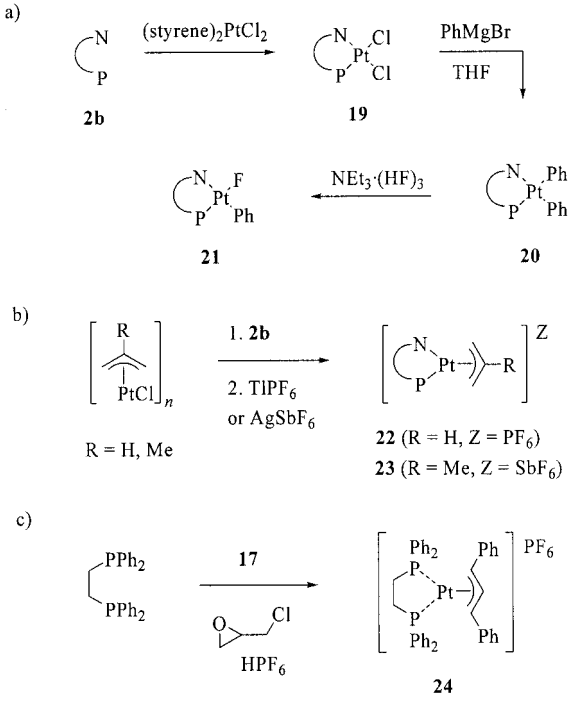


Figure 3. ORTEP plot (30% probability ellipsoids) of **8c·CH_2Cl_2**. Hydrogen atoms, CH_2Cl_2, and SbF_6 anion are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd–P = 2.303(2), Pd–N(2) = 2.122(6), Pd–C(27) = 2.191(8), Pd–C(28) = 2.225(9), Pd–C(29) = 2.260(10), Pd–C(30) = 2.570(9), Pd–C(35) = 2.576(8), C(27)–C(28) = 1.397(14), C(27)–C(35) = 1.460(13), C(28)–C(29) = 1.424(17), C(29)–C(30) = 1.421(17), C(30)–C(35) = 1.431(12); N(2)–Pd–P(1) = 92.32(18), C(27)–C(28)–C(29) = 106.4(10).

Comparative spectroscopic data for the platinum compounds was collected from a range of reference complexes

whose synthesis is displayed in Scheme 6. Pregosin's bis(styrene)platinum(II) chloride[51] served as the most suitable precursor for dichloro complex **19** under mild conditions. The diphenyl complex **20** resulted from reaction of **19** with excess Grignard reagent. Interestingly, the substance crystallized with one equivalent of phenol, which originated from a partially oxidized PhMgBr solution. The X-ray crystal structure of **20·PhOH** is shown in Figure 4. The phenolic OH group is presumably involved in a weak hydrogen bond with the electron-rich Pt^{II} center.[52] The phenol is arranged with the OH group pointing towards the Pt center and the O–Pt distance is 4.21 Å. By comparison, O–Pd distances of 3.2–3.7 Å have been observed for related interactions between Pd^0 and aliphatic alcohols.[53]



Scheme 6. Syntheses of platinum(II) complexes incorporating ligand **2b** and/or an allyl ligand.

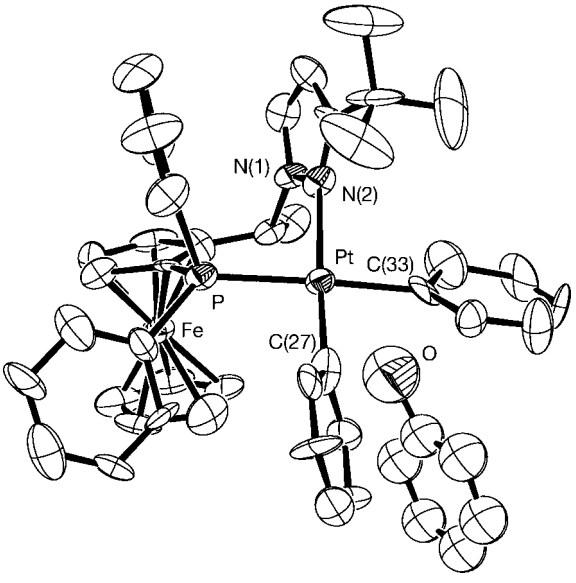


Figure 4. ORTEP plot (50% probability ellipsoids) of **20·PhOH**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pt–P = 2.33(2), Pt–N(2) = 2.18(5), Pt–C(27) = 1.97(5), Pt–C(33) = 2.08(3); P–Pt–N(2) = 88.7(16), C(27)–Pt–C(33) = 86.8(19), P–Pt–C(27) = 93.1(12), P–Pt–C(33) = 175.4(5), N(2)–Pt–C(33) = 91.8(13), N(2)–Pt–C(27) = 174.6(9).

The fluoro complex **21** was obtained in situ in an NMR tube by protonolysis of the diphenylplatinum complex **20** with NEt_3·$(HF)_3$. Only one bond was cleaved even though an excess of reagent was added. The presence of a Pt–F bond in this complex is evident from the coupling patterns in the ^{19}F NMR spectrum (doublet with platinum satellites) and the ^{31}P NMR spectrum (doublet with platinum satellites) (Figure 5). Any complex containing a covalent Pt–F bond in our study would have similar NMR characteristics, whereas ionic Pt^+/F^- interactions would not be expected to result in such ^{19}F NMR signals or coupling characteristics.

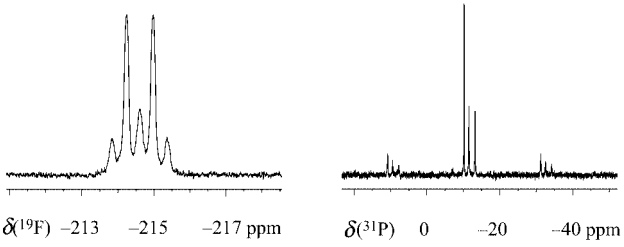


Figure 5. NMR spectra of fluoro complex **21**. (a) ^{19}F NMR (282.4 MHz, $CDCl_3$), the signal at δ = –214.6 ppm ($^2J_{P,F}$ = 207, $^1J_{Pt,F}$ = 210 Hz) is due to the platinum bound fluoro ligand. (b) ^{31}P NMR (121.5 MHz, $CDCl_3$), the signal at δ = –11.8 ppm (d, $J_{P,F}$ = 207, $J_{Pt,P}$ = 5104 Hz) is due to the fluoro complex, while the signal at δ = –9.6 ppm (s, $J_{Pt,P}$ = 5107 Hz) belongs to an unidentified side product.

The allyl complex **22** and the methallyl derivative **23** were obtained by the usual method (Scheme 6, b). They formed equilibrium mixtures of *exo* and *endo* isomers in solution, with the larger methallyl group inducing a slightly higher amount of the *exo* isomer (Table 2).

Solution Structure of (1,3-Diphenylallyl)platinum(II) Complexes

The η^3-allyl complex **18·PF$_6$** occurs predominantly as the *exo-syn-syn* isomer in either [D_8]THF or $CDCl_3$ solution in the same manner as its Pd-counterpart **8a** (Figure 6).

In contrast, the bromide **18·Br** exists as a mixture of four main isomers in $CDCl_3$ solution (Table 2) and the isomeric ratio remained unchanged on refluxing a solution of the complex in toluene. The allyl isomers of **18·Br** could be of the cationic η^3-type (eight possible diastereomers) or the neutral η^1-type with coordinated bromide (four possible diastereomers), or mixtures thereof. The $J_{Pt,P}$ coupling constants of the **18·Br** isomers were in the range of 4700 to 5100 Hz (Table 2), which is close to the value for the η^3-allyl complex **18·PF$_6$**, but rather high compared to the value of [$PtBr_2$(**2a**)].[55] The low frequency ^{195}Pt NMR chemical shifts of **18·Br** also point towards a cationic η^3-configuration. However, the most important notion is that the nature

Table 2. NMR data and isomer equilibrium composition of the platinum complexes. ^{31}P NMR spectroscopy at 101.3 or 121.5 MHz, ^{195}Pt NMR spectroscopy at 64.3 or 86 MHz. All data at room temp. in $CDCl_3$, besides **18·PF$_6$** ([D$_8$]THF), **18·F** ([D$_8$]toluene at 213 K).

Complex	Isomer	Abundance	^{31}P NMR [δ/ppm]	^{195}Pt NMR [δ/ppm]	$J_{Pt,P}$ [Hz]
18·PF$_6$	*exo*	>98%	10.4	–4453	5029
18·Br	**A**	12%	7.5	–4565	5056
	B	20%	9.2	–4790	4697
	C	44%	12.6	–4897	5130
	D	23%	13.5	–4903	4760
18·F	**A**	7%	1.1	n.d.	3903
	B	9%	1.8	n.d.	3890
	C	17%	3.1	n.d.	4098
	D	63%	7.5	n.d.	3925
	E	5%	10.7	n.d.	3818
[Pt(η^3-C$_3$H$_5$)(2b)]PF$_6$ (**22**)	*exo*	78%	12.5	n.d.	4413
	endo	22%	12.6	n.d.	n.d.
[Pt(η^3-C$_4$H$_7$)(2b)]PF$_6$ (**23**)	*exo*	81%	11.5	n.d.	4291
	endo	19%	11.9	n.d.	4010
[Pt(Ph$_2$All)(dppe)]PF$_6$ (**24**)		100%	44.7	–5521	3847
[PtCl$_2$(2b)] (**19**)		–	–16.1	–3700	3783
[PtBr$_2$(2a)][a]		–	–14.6	n.d.	3713
[PtPh$_2$(2b)] (**20**)		–	5.3	n.d.	1688
[Pt(Ph)F(2b)] (**21**)[b]		–	–11.8	n.d.	5104

[a] Ref.[55] [b] F is *trans* to P, deduced from the large values of $^1J_{Pt,P}$ or $^2J_{P,F}$.[54]

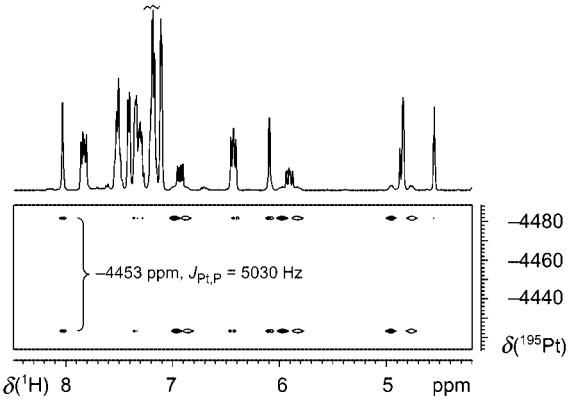


Figure 6. ^{195}Pt,^{1}H HMQC of **18·PF$_6$** in [D$_8$]THF. The crosspeaks lie below the positions of the ^{195}Pt satellites in the ^{1}H NMR spectrum and are split vertically into a doublet ($J_{Pt,P}$ = 5030 Hz). Intense crosspeaks are observed for allylic protons (δ = 4.9, 5.9, and 6.9 ppm), whereas weaker coupling is observed with two sets of *ortho*-hydrogen atoms of phenyl groups (δ = 6.4, 7.4 ppm) and with the pyrazole hydrogen 4-H at 8.0 ppm.

of the anion directly and strongly influences the equilibrium composition of the allyl isomer mixture.

Solid-State Structures of (1,3-Diphenylallyl)platinum(II) Complexes

Crystals of **18·PF$_6$** were easily obtained and the result of the X-ray structural analysis is shown in Figure 7 (a) along with a structure comparison generated by overlaying the structure of the palladium analog **8a** (Figure 7, b). These complexes are almost perfectly isostructural within differences in bond lengths of less than 2%. The interplane angle between the allyl plane and the coordination plane (defined by P, Pt, N) in these structures is 64.8°, and the rotation of the allyl vector normal plane [approximated by the plane C(27)–Pt/Pd–C(29)] out of the coordination plane is 14°. This numerical value serves as a measure of the asymmetry induced on the allyl fragment by the chiral ligand.[29] The ^{31}P NMR chemical shifts of **8a** and **18·PF$_6$** also match closely (Table 2). These results justify, once more, the approach of using kinetically more inert platinum complexes as analogs for the corresponding palladium species in mechanistic research. In fact, **18·PF$_6$** is also a catalyst for the allylic alkylation of ethyl 1,3-diphenylallyl carbonate (**1**) with dimethyl malonate, giving the product of allylic alkylation in 74% *ee* in a slow reaction,[56,65] whereas analogous Pd complexes (with ligand **2a**) react much faster to give the alkylation product in 91% *ee*.[55] Asymmetric allylic alkylation of 1,3-diphenylallyl substrates using Pt complexes has been studied in detail by Williams and coworkers.[46]

Another example of a cationic (1,3-diphenylallyl)platinum(II) complex is the DIPHOS derivative **24**, which was also structurally characterized as the *syn-syn* isomer in both the CD_2Cl_2 solution and in the solid state (Figure 7, c). The bite angle P–Pt–P in this complex is 86.4° instead of the 94.5° for **18·PF$_6$**. The interplane angle defined by C(1)–C(2)–C(3)/P(1)–Pt–P(2) is 67° in this complex and the rotation of the allyl fragment vector normal plane (approximated by C(1)–Pt–C(3)), out of the idealized perpendicularity to the coordination plane [defined by P(1)–Pt–P(2)], is only 1°, a very low value despite the local chiral C_2 symmetry that the DIPHOS ligand adopts in its solid-state conformation.

Reactions of Cationic Allyl Complexes with Fluoride

In the first series of experiments, one of the complexes **8a**, **8b**, or **8c** and one of the fluoride sources TBAT (**4**), Me$_4$NF (**5**), or Schwesinger's phosphazenium fluoride P$_2$F (**25**)[57] were mixed in deuterated solvents ($CDCl_3$ or [D$_3$]-

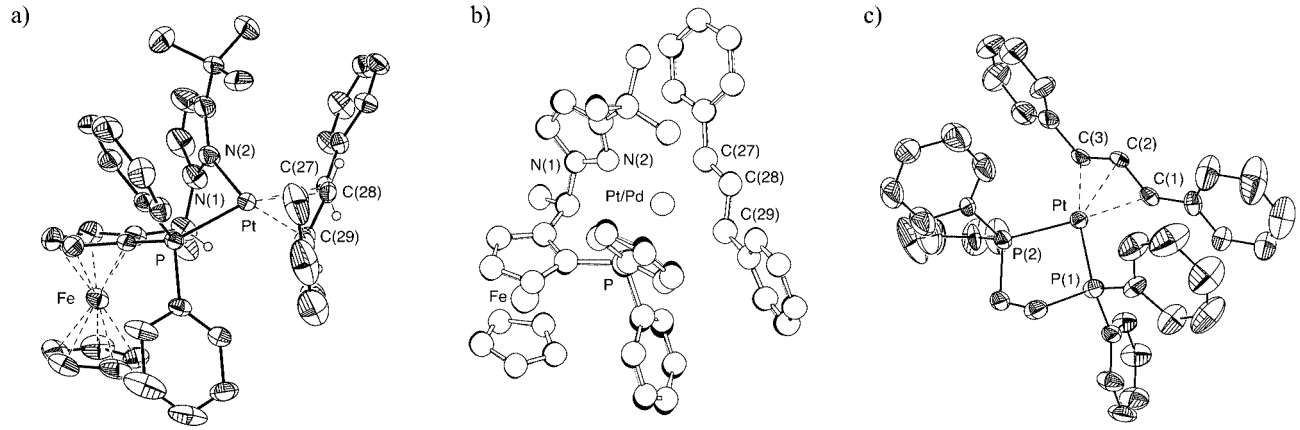
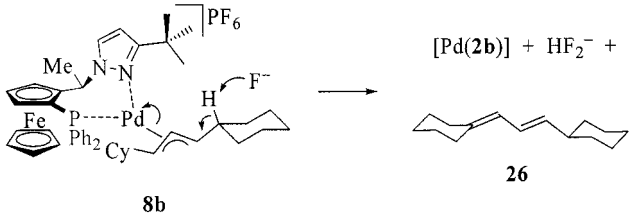


Figure 7. X-ray crystal structures of the cationic 1,3-diphenylallyl complexes **18·PF$_6$**, **8a**, and **24**. (a) ORTEP plot (30% probability ellipsoids) of platinum complex **18·PF$_6$**. The anion and most hydrogens are omitted for clarity. Selected data (bond lengths [Å]; bond angles [°]): Pt–P = 2.265(2), Pt–N(2) = 2.121(5), Pt–C(27) = 2.283(6) =, Pt–C(28) = 2.195(6), Pt–C(29) = 2.113(6); N(2)–Pt–P = 94.5(2). (b) Alignment of ball and stick representations of the complex cations of **8a** (grey filled atoms, below) and **18·PF$_6$** (white filled atoms, on top). The structures of the complexes match closely. Selected data for **8a**: Pd–P = 2.3123(8), Pd–N(2) = 2.159(3), Pd–C(27) = 2.283(3), Pd–C(28) = 2.193(3), Pd–C(29) = 2.137(3); N(2)–Pd–P = 94.49(8). The atom numbering has been adapted here to match that from the structure of **18·PF$_6$**, but is different in the CSD CIF file. (c) ORTEP plot (30% probability ellipsoids) of platinum complex **24**, anion and hydrogen atoms are omitted for clarity. Selected data: Pt–C(1) = 2.233(8), Pt–C(2) = 2.168(7), Pt–C(3) = 2.233(8), Pt–P(1) = 2.258(2), Pt–P(2) = 2.270(2); P(1)–Pt–P(2) = 86.37(8).

MeCN for **4**, [D$_3$]MeCN for **5**, C_6D_6 for **25**) and the samples were then monitored using ^{1}H, ^{19}F, and ^{31}P NMR spectroscopy over a suitable range of time. If no change was observed at room temperature the samples were warmed to 50 °C. The appearance of peaks arising from allyl fluorides was carefully checked by ^{19}F NMR spectroscopy (**6**: $\delta\{^{19}F\}$ = –165.4 ppm;[14a] **11**: –175.2 ppm; indenyl fluoride: –201.24 ppm[58]), but these signals were not detected. In experiments with Me_4NF (**5**) and 1,3-diphenylallyl complex **8a**, the main fluorinated species observed was DF_2^-, resulting from deprotonation of [D$_3$]MeCN by naked fluoride.[31] A specific reaction pattern was only observed with complex **8b** and the naked fluorides Me_4NF (**5**, in [D$_3$]-MeCN) and P_2F (**25**, in C_6D_6), where diene **26**[59] was released in an elimination reaction (Scheme 7). Other reactant combinations resulted in no reaction at all or unspecific decomposition with precipitation of palladium metal on heating.[60]



Scheme 7. Fluoride-mediated elimination of diene **26** from dicyclohexylallyl complex **8b**.

We then turned our attention to the reaction of cationic allylplatinum complex **18·PF$_6$** with naked fluoride Me_4NF (**5**). A suspension of the reactants in toluene was stirred at ambient temperature, which resulted in a slow but clean anion exchange reaction to give a yellow solution of **18·F** and a colorless precipitate of Me_4NPF_6. Evaporation of the filtered solution gave **18·F** as an amorphous yellow powder, which was soluble in most organic solvents. The ^{19}F NMR spectrum of **18·F** in $CDCl_3$ consisted of a broad signal at δ = –139.8 ppm ($\Delta_{1/2}$ = 15 Hz), a value which is close to that given by Grushin[61] (δ = –141 ppm, $\Delta_{1/2}$ = 9 Hz) for an in situ generated naked fluoride in $CDCl_3$. In [D$_8$]toluene solution the ^{19}F NMR peak for fluoride disappeared in background noise that was generated from fluorinated polymers within the NMR probe head. The ^{31}P NMR spectrum

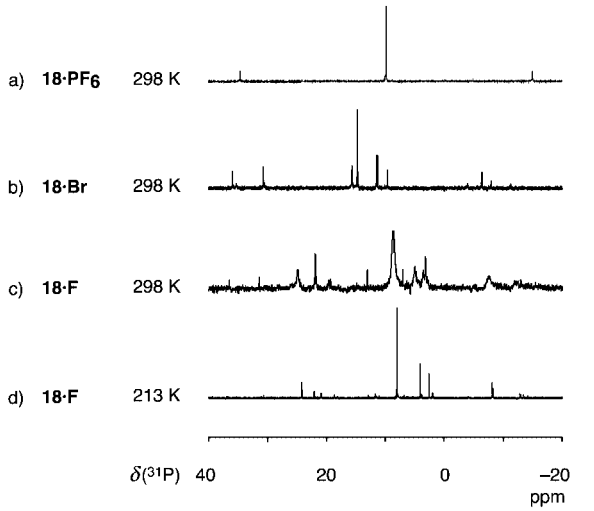
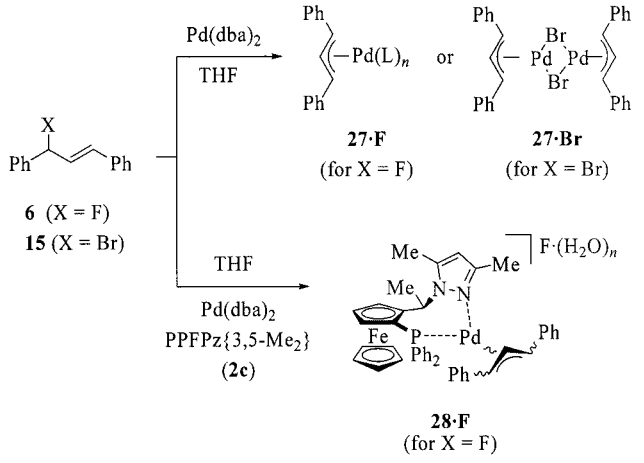


Figure 8. ^{31}P NMR spectra of **18·PF$_6$**, **18·Br**, and **18·F**. (a) 101.3 MHz, [D$_8$]THF. **18·PF$_6$** is exclusively present as the *exo-syn-syn* isomer. Note the ^{195}Pt satellites ($J_{Pt,P}$ = 5029 Hz). (b) 121.5 MHz, $CDCl_3$. **18·Br** forms a mixture of four allyl isomers. (c) 121.5 MHz, [D$_8$]toluene. **18·F** forms a mixture of allyl isomers whose lines are broadened due to exchange. (d) As in (c), but at 213 K (–60 °C). The interconversion of allyl isomers of **18·F** is "frozen" at low temperature, resulting in a spectrum similar to that of **18·Br** at room temperature. Splitting due to $J_{P,F}$ is absent.

consists of one main broad peak and smaller additional signals (Figure 8, c). On cooling to 213 K, the spectrum becomes clearer and a set of at least five lines (each with platinum satellites), corresponding to allyl isomers, appear (see d in Figure 8 and Table 2). Again, no peak was detected by ^{19}F NMR spectroscopy, but this should be seen in connection with experimental difficulties (mentioned above) and the low concentration of the sample. The absence of $^{31}P/^{19}F$ couplings (which are so clearly visible for **21**) shows that no inert covalent Pt–F bond is present in **18·F**. When combined these pieces of evidence suggest that **18·F** consists of a mixture of isomeric allyl cations $[Pt(\mathbf{2b})(\eta^3\text{-}Ph_2All)]^+$ in solution, which form lipophilic contact ion pairs with fluoride. The fluoride anions themselves are involved in a fast exchange between the ion pairs. At room temperature there is notable interconversion of configurationally isomeric allyl cations within **18·F** (broad lines in the ^{31}P NMR spectrum, Figure 8, c), but slow interconversion among the allyl isomers of **18·Br** (separate, sharp lines in the ^{31}P NMR spectrum, Figure 8, b). This important finding directly relates the nature of the counterion of a cationic allyl complex to the kinetics of its allyl isomerization.

Oxidative Addition of Pd^0 with Ph_2AllF (6) and Ph_2AllBr (15)

The failure to observe any allylic substitution products resulting from attack of fluoride on cationic allyl complexes indicates that this reaction is thermodynamically unfavorable.[62] To test this assumption, we investigated whether the reverse reaction, namely the oxidative addition of allyl fluorides to Pd^0, would proceed instead. The addition of a solution of **6**[14a] to either $Pd(dba)_2$ or mixtures of $Pd(dba)_2$ and phosphanyl pyrazole (**2c**) (Scheme 8) did, in fact, result in oxidative addition and the formation of η^3-allylpalladium(II) compounds **27·F** or **28·F**, respectively. Identification of these compounds was based on the characteristic ^1H NMR and ^{31}P NMR spectra of the cationic units since a well-defined complex did not crystallize from solutions of **27·F**. The properties and spectroscopic data of **28·F** match closely those of the hydrated fluoride salts of cationic palladium complexes investigated earlier in our laboratory.[8] The analogous oxidative addition of 1,3-diphenylallyl bromide (**15**) with $Pd(dba)_2$ gave the η^3-allyl bromide **27·Br** (Scheme 8).



Scheme 8. The oxidative addition of 1,3-diphenylallyl fluoride and bromide to Pd^0 complexes is a spontaneous reaction that leads to products containing the cationic allylpalladium(II) fragment. L = F or solvent molecules.

The ^1H NMR spectroscopic data of **27·F** and **27·Br** in DMSO are very similar to those of the known chloro analog **27·Cl**.[44b]

Discussion

Fluoride Effects in Asymmetric Allylation Reactions

We have identified two modes in the reaction of "naked" or nucleophilic fluorides with cationic allyl complexes of palladium(II) and platinum(II): Allyl complexes bearing hydrogens α to the allyl group can either undergo base-mediated elimination (see Scheme 7) or a simple anion exchange can take place, which gives cationic allyl complexes as contact ion pairs with fluoride as the counterion. NMR spectroscopic studies of the platinum complexes **18·PF$_6$**, **18·Br**, and **18·F** revealed that the counterion in these ion pairs dramatically influences: (a) the allyl isomer composition at equilibrium; and (b) the kinetics of exchange between these isomers. In the presence of fluoride, allyl isomers interconvert at room temperature (cf. Figure 8, c) whereas this process is slow for the bromide salt (Figure 8, b) and probably even slower for the hexafluorophosphate (Figure 8, a). This evidence, obtained from a platinum model system, supports our earlier proposal of an anion effect in the catalytic asymmetric amination reaction (cf. Scheme 1):[8] Addition of fluoride accelerates the isomerization of allyl isomers and therefore effectively deletes the "memory of chirality"[63] stored within the configuration of the allyl isomers. However, addition of PF_6^- has an inverse effect by slowing down isomerization. This assumption has now been justified by experimental results.

The Viability of an (Asymmetric) Catalytic Allylic Fluorination

The reaction of cationic allyl complexes of palladium(II) and platinum(II) with naked or nucleophilic fluorides does not produce allyl fluorides. On the contrary, the oxidative addition of allyl fluoride **6** to Pd^0 proceeds with ease. This finding is in agreement with calculations by Hagelin et al. who have found that the attack of fluoride on the allylpalladium(II) cation is energetically favorable in the gas phase, but becomes unfavorable in the polar condensed phase because of the solvation of the fluoride anion.[64] Despite this thermodynamically unfavorable step, an overall catalytic allylic fluorination reaction should still be exergonic, as long as energetically high lying (reactive) sources of fluoride are used. Nevertheless, the presence of an energetically low-lying, nonreactive intermediate (such as **18·F**) in the reaction

pathway presents a severe obstacle for catalysis for kinetic reasons. If possible, alternative pathways will be followed (cf. release of **26** from **8b**, Scheme 7) and Pd^0 will eventually precipitate. These factors appear to cause the failure of the desired palladium-catalyzed asymmetric allylic fluorination reaction when it is carried out in analogy to known asymmetric allylic substitutions.

Conclusion

We have reported the synthesis of new cationic allyl complexes of palladium(II) and platinum(II), among them the previously unknown (1,3-diphenylallyl)platinum(II) complexes. The reactivity of these complexes towards naked and nucleophilic sources of fluoride has been investigated. Stoichiometric allylic fluorination was shown to be thermodynamically unfeasible, and catalytic reactions are probably also unfeasible due to a kinetic barrier in the reaction pathway. It was shown that the counterions of cationic allylplatinum(II) complexes determine both the exchange kinetics between allyl isomers and the isomer composition at equilibrium. This finding has been used to rationalize a "fluoride anion effect" observed earlier in palladium-catalyzed asymmetric allylic amination reactions.

Experimental Section

General Remarks: Syntheses of, and with, sensitive products were performed using Schlenk and glovebox techniques. Naked fluorides were handled exclusively in a glovebox. NMR spectroscopy: ^{1}H NMR shifts relative to internal TMS, ^{13}C NMR shifts relative to TMS, but referenced by solvent signals, notably $\delta(CDCl_3)$ = 77.0 ppm. ^{19}F NMR shifts relative to external $CFCl_3$, ^{31}P NMR shifts relative to external H_3PO_4 (85%), ^{195}Pt NMR shifts relative to external $Na_2[PtCl_6]$ (aq). General techniques for NMR structure elucidation were the same as in ref.[29] For additional ^{13}C NMR and IR data, see ref.[65]

Abbreviations and Substances: All = allyl (C_3H_5), Ph_2All = 1,3-diphenylallyl etc., CC = column chromatography on SiO_2, HV = high vacuum (<0.01 mbar), Ms = methylsulfonyl, Pz = pyrazole, *t*BuOMe = *tert*-butyl methyl ether. The following substances were prepared according to literature procedures: (*R*,S_P)-PPFA[27] (recrystallized twice from EtOH to ensure high enantiomeric purity), anhydrous Me_4NF (**4**),[31] TBAT [tetrabutylammonium difluorotriphenylsilicate(II)] (**5**),[30] 3-*tert*-butylpyrazole,[26] $[Pt_2(dba)_3]$,[50] $[Pd_2(dba)_3]\cdot CHCl_3$ or $Pd(dba)_2$,[66] $[\{PdCl(Ph_2All)\}_2]$ (**7a**),[44b] $[\{PdCl(Ind)\}_n]$ (**7c**),[42] 1,3-diphenylallyl bromide (**15**),[47] Karstedt catalyst (**16**).[49b] Schwesinger's phosphazenium fluoride P_2F (**25**)[57] was obtained from Fluka.

3-*tert*-Butyl-1-{(*R*)-1-[(S_P)-2-(diphenylphosphanyl)ferrocenyl]ethyl}-1*H*-pyrazole (PPFPz{3-*t*Bu}, 2b): Degassed HOAc (5 mL), (*R*,*S*)-PPFA (2.047 g, 4.628 mmol) and 3-*tert*-butylpyrazole (862 mg, 6.94 mmol) were stirred for 1 d at 70 °C. After workup with water and extraction with CH_2Cl_2, CC (*t*BuOMe/pentane, 1:20, and 3% NEt_3) gave 2.022 g (84%) as orange crystals. $[\alpha]_D$ = –281.7 (*c* = 0.88, MeOH). M.p. 130 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.06 (s, 9 H, *t*Bu), 1.83 (d, *J* = 6.9 Hz, 3 H, *Me*CH), 3.87 (m, 1 H-Cp), 3.99 (s, 5 H, Cp′), 4.34 (t, *J* = 2.5 Hz, 1 H-Cp), 4.64 (br. s, 1 H-Cp), 5.52 (d, *J* = 2.3 Hz, 4-H, Pz), 5.77 (qd, *J* = 6.9 Hz, 3.2 Hz, 1 H, *H*CMe), 6.67–6.75 (m, 2 H, aryl), 6.82 (d, *J* = 2.3 Hz, 5-H, Pz), 6.92–7.02 (m, 3 H, aryl), 7.28–7.33 (m, 3 H, aryl), 7.49–7.56 (m, 2 H, aryl) ppm. ^{31}P NMR (101.3 MHz, $CDCl_3$): δ = –24.5 (s) ppm. MS (EI): *m*/*z* (%) = 520 (100) [M^+], 455 (25), 396 (20), 331 (59). $C_{31}H_{33}FeN_2P$ (520.44): calcd. C 71.54, H 6.39, N 5.38; found C 71.60, H 6.47, N 5.33.

Bis(μ-chloro)-bis(η³-1,3-dicyclohexylallyl)dipalladium(II) (7b): A suspension of $Pd(dba)_2$ (658.7 mg, 1.146 mmol), **12** (403 mg, 1.266 mmol), and LiCl (1.203 mmol 1.05 equiv.) in THF (15 mL) and MeCN (5 mL) was stirred for 15 min at 30 °C. The greenish reaction mixture was evaporated to dryness, taken up in CH_2Cl_2 and filtered through SiO_2. Evaporation yielded 385.5 mg (97%) of a light yellow powder. M.p. 174 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.02–1.36 (m, 20 H-Cy), 1.53–1.87 (m, 20 H-Cy), 2.02–2.07 (m, 4 H-Cy), 3.62 (dd, *J* = 11.2 Hz, 5.2 Hz, 4 H, 1-H/1′-H, 3-H/3′-H), 5.14 (t, *J* = 11.2 Hz, 2 H, 2-H/2′-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 26.1 (CH_2), 26.2 (CH_2), 31.7 (CH_2), 32.8 (CH_2), 39.5 (CH), 88.2 (CH), 103.43 (CH) ppm. MS (FAB): *m*/*z* (%) = 659 (100) [M – Cl]$^+$. $C_{30}H_{50}Cl_2Pd_2$ (694.47): calcd. C 51.89, H 7.26; found C 51.77, H 7.09.

Indenylpalladium(II) Chloride (7c): In our hands, only the method reported by Lin and Boudjouk gave a pure product.[42] Others have made similar observations.[42b] We note that the use of 94% EtOH in the synthesis is important because residual water favors the reaction.

[Pd(η³-Ph_2All)(2b)]PF_6 (8a): $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}Ph_2All)_2]$ (226.8 mg, 0.338 mmol) was added to **2b** (352.2 mg, 0.677 mmol) in acetone (40 mL) and the mixture was stirred until dissolution occurred (3 min). $TlPF_6$ (236.4 mg, 0.677 mmol) was added and the resulting suspension stirred for 1 h. Filtration through Celite, evaporation to dryness, and precipitation from CH_2Cl_2/pentane gave 570.4 mg (87%) of an orange powder. $[\alpha]_D$ = –278 (*c* = 0.50, $CHCl_3$). M.p. dec. from 190 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.48 (s, 9 H, *t*Bu), 2.35 (d, *J* = 6.9 Hz, 3 H, *Me*CH), 3.90 (s, 5 H, Cp′), 3.97–4.01 (m, 1 H-Cp), 4.41 (t, *J* = 2.6 Hz, 1 H-Cp), 4.54–4.58 (m, 1 H-Cp), 5.25 (d, *J* = 10.0 Hz, allyl H, *anti*, *trans* N), 5.91 (d, *J* = 2.7 Hz, 4-H, Pz), 6.21 (dd, *J* = 14.1 Hz, 9.9 Hz, allyl H, *central*), 6.08–6.16 (m, 2 H, aryl), 7.01–7.32 (m, 15 H, 13 H, aryl + allyl H, *anti*, *trans* P + C*H*Me), 7.45–7.55 (m, 3 H, aryl), 7.58 (d, *J* = 2.7 Hz, 5-H, Pz), 7.70–7.89 (m, 2 H, aryl) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 18.4 (CH_3), 29.6 (CH_3), 31.8 (C), 58.4 (d, $J_{P,C}$ = 5 Hz, CH, *C*HMe), 66.0 (d, $J_{P,C}$ = 3 Hz, CH, Cp), 66.1 (d, $J_{P,C}$ = 1 Hz, allyl CH, *trans* N), 70.6 (d, $J_{P,C}$ = 6 Hz, Cp-CH), 71.3 (CH, Cp′), 73.0 (CH, Cp), 74.9 [d, $J_{P,C}$ = 42 Hz, C(1)-Cp], 93.8 [d, $J_{P,C}$ = 20, C(2)-Cp], 107.1 [CH, C(4) Pz], 107.1 (d, $J_{P,C}$ = 19 Hz, allyl CH, *trans* P), 112.4 (d, $J_{P,C}$ = 4 Hz, allyl CH, *central*), 127.3 (d, $J_{P,C}$ = 2 Hz, CH), 127.9 (d, $J_{P,C}$ = 3, CH), 128.1 (d, $J_{P,C}$ = 9 Hz, CH), 128.3–129.4 (several CH), 130.7 (d, $J_{P,C}$ = 48 Hz, C), 130.9 (d, $J_{P,C}$ = 2 Hz, CH), 131.4 (d, $J_{P,C}$ = 11 Hz, CH), 133.1 (d, $J_{P,C}$ = 44 Hz, C), 134.3 (d, $J_{P,C}$ = 14 Hz, CH), 135.4 (d, $J_{P,C}$ = 5 Hz, C), 138.9 (d, $J_{P,C}$ = 3 Hz, C), 162.7 [C, C(3) Pz] ppm. ^{31}P NMR (101.3 MHz, $CDCl_3$): δ = –142 (sept, J_{PF} = 695 Hz, PF_6^-), 10.5 (s) ppm. IR (KBr): $\tilde{\nu}$ = 842 (s), 696 (m), 558 (m) cm^{-1}. MS (FAB): *m*/*z* (%) = 1783 (3) [2 M – PF_6]$^+$, 819 (100) [M – PF_6]$^+$, 625 (12) [M – PF_6 – Ph_2All]$^+$. $C_{46}H_{46}F_6FeN_2P_2Pd$ (965.07): calcd. C 57.25, H 4.80, N 2.90; found C 57.08, H 4.95, N 2.94.

[Pd(η³-Cy_2All)(2b)]PF_6 (8b): 7b (179.5 mg, 0.258 mmol) was added to a solution of **2b** (269.1 mg, 0.517 mmol) in acetone (35 mL) and the mixture was stirred until dissolution was complete (15 min). After addition of $TlPF_6$ (180.6 mg, 0.517 mmol) and stirring for 1.5 h, the suspension was filtered through Celite and the filtrate evaporated to dryness. Precipitation from CH_2Cl_2/pentane gave

484 mg (96%) of a yellow powder. M.p. 221° (dec.). ^{1}H NMR (250 MHz, $CDCl_3$). Major isomer: δ = 0.43–0.52 (m, 1 H-Cy), 0.82 (s, 9 H, *t*Bu), 0.76–1.85 (m, 21 H-Cy), 2.17 (d, J = 7.0 Hz, 3 H, CH*Me*), 3.94–3.98 (m, 1 H-Cp), 3.96 (s, 5 H, Cp′), 4.30 (dd, J = 10.4 Hz, 2.3 Hz, allyl H, *anti*, *trans* N), 4.46 (t, J = 2.6 Hz, 1 H-Cp), 4.65–4.69 (m, 1 H-Cp), 5.27 (dd, J = 13.4 Hz, 10.0 Hz, allyl H, *central*), 5.56 (dt, J = 13.3 Hz, 8.3 Hz, allyl H, *trans* P), 6.14 (d, J = 2.6 Hz, 4-H, Pz), 6.51–6.62 (m, 2 H, aryl), 6.67 (q, J = 7.0 Hz, C*H*Me), 7.14 –7.33 (m, 3 H, aryl), 7.58–7.66 (m, 3 H, aryl), 7.59 (d, J = 2.7 Hz, 5-H, Pz), 7.76–7.85 (m, 2 H, aryl); minor isomer): δ = 0.76–1.80 (m, 22 H-Cy), 0.91 (s, 9 H, *t*Bu), 2.04 (d, J = 7.0 Hz, 3 H, CH*Me*), 3.75–3.79 (m, 1 H-Cp), 3.90 (s, 5 H, Cp′), 4.42 (t, J = 2.6 Hz, 1 H-Cp), 4.58 (ddd, J = 13.7 Hz, 11.1 Hz, 5.5 Hz, allyl H, *anti*, *trans* P), 4.76–4.80 (m, 1 H-Cp), 5.44 (t, $J \approx$ 8.5 Hz, allyl H, *trans* N) 5.94 (dd, J = 13.5 Hz, 7.8 Hz, allyl H, *central*), 6.21 (d, J = 2.7 Hz, 4-H, Pz), 6.34 (q, J = 7.0 Hz, C*H*Me), 6.45–6.60 (m, 2 H, aryl), 7.14–7.33 (m, 3 H, aryl), 7.58–7.66 (m, 3 H, aryl), 7.68 (d, J = 2.7 Hz, 5-H, Pz), 7.76–7.85 (m, 2 H, aryl) ppm. ^{31}P NMR (101.3 MHz, $CDCl_3$): δ = –144.3 Hz (sept, $J_{P,F}$ = 698, PF_6^-), 10.9 (s, major isomer), 11.9 (s, minor isomer) ppm. MS (FAB): *m*/*z* (%) = 1809.5 (2) $[2\ M - PF_6]^+$, 831.4 (100) $[M - PF_6]^+$, 710 (6) $[M - PF_6 - Cy_2All]^+$, 627 (74). $C_{46}H_{58}F_6FeN_2P_2Pd$ (977.18): calcd. C 56.54, H 5.98, N 2.87; found C 56.48, H 5.91, N 2.82.

[Pd(η^3-Ind)(2b)]SbF$_6$ (8c): A mixture of **2b** (320 mg, 0.62 mmol) and **7c** (155 mg, 0.30 mmol) was stirred in THF (5 mL) until dissolution was complete (20 min). $AgSbF_6$ (206 mg, 0.60 mmol) was added to the dark red solution, and the resulting suspension was stirred for 1 h. After filtration through Celite and evaporation, the residue was precipitated from CH_2Cl_2/*t*BuOMe to give a dark red powder, which was redissolved in CH_2Cl_2 and set aside for slow diffusion against hexane at –20 °C. Within 2 d dark red crystals (also used for X-ray) of a CH_2Cl_2 solvate were formed. The yield of solvent-free compound after drying is 483 mg (82%). It is stable as a solid, but slow decomposition occurs in solution and in air. ^{1}H NMR (400 MHz, [D$_3$]MeCN, *exo* isomer): δ = 0.80 (s, 9 H, *t*Bu), 1.74 (d, J = 7.1 Hz, 3 H, CH*Me*), 3.85 (s, 5 H, Cp′), 4.08–4.10 (m, 5-H, Cp), 4.54 (t, J = 2.7 Hz, 4-H, Cp), 4.74–4.77 (m, 3-H, Cp), 5.52 (qd, J = 7.1 Hz, 1.2 Hz, 1 H, C*H*Me), 6.28 (d, J = 2.7 Hz, 4-H, Pz), 6.44–6.50 (m, 2 $H_{ortho,axial}$), 6.60 (t, J = 2.5 Hz, 3-H, Ind), 6.76 (dddd, J = 9.2 Hz, 3.5 Hz, 2.0 Hz, 0.8 Hz, 1-H, Ind), 6.82 (ddd, J = 3.5 Hz, 3.0 Hz, 0.6 Hz, 2-H, Ind), 7.14–7.19 (*m*, 2 $H_{meta,axial}$), 7.26, (obscured, 6-H, Ind), 7.28 (obscured, 7-H, Ind), 7.30 (obscured, 1 $H_{para,axial}$), 7.35, (obscured, 5-H, Ind), 7.68–7.75 (m, 2 $H_{meta,equ}$ + 1 $H_{para,equ}$), 7.70, (obscured, 4-H, Ind), 7.71 [d, J = 2.7 Hz, 5-H, Pz (obscured)]. 7.88–7.96 (m, 2 $H_{ortho,equ}$) ppm; assignments from HH COSY and long-range ^{1}H,^{13}C HMQC. ^{1}H NMR (300 MHz, $CDCl_3$, minor isomer, selected peaks): δ = 0.49 (s, 9 H, *t*Bu), 2.13 (d, J = 7.0 Hz, 3 H, MeCH), 4.00 (m, 1 H-Cp), 4.04 (s, 5 H, Cp′), 5.84 (t, J = 2.4 Hz, 1 H-Cp), 6.09 (d, J = 2.8 Hz, 1 H-Pz), 6.97 (m, CHMe), 7.59 (d, J = 2.8 Hz, 1 H-Pz) ppm. Isomer ratio in $CDCl_3$ *exo*/*endo* = 11:1, in [D$_3$]MeCN = 16:1. ^{1}H{^{31}P} NMR (250 MHz, [D$_3$]MeCN, ^{31}P-decoupling at δ = 12.2 ppm, selected peaks): δ = 4.08 (dd, J = 2.7 Hz, 1.3 Hz, 5-H, Cp), 4.54 (dt, J = 2.7 Hz, 0.6 Hz, 4-H, Cp), 4.75 (ddd, J = 2.7 Hz, 1.3 Hz, 0.5 Hz, 3-H, Cp), 6.27 (dd, J = 2.8 Hz, 0.6 Hz, 5-H, Pz), 6.44–6.49 (m, 2 H, H, aryl *ortho*), 6.60 (ddd, J = 3.1 Hz, 2.0 Hz, 0.5 Hz, 3-H, Ind), 6.75 (ddd, J = 3.5 Hz, 2.0 Hz, 0.8 Hz, 1-H, Ind), 6.82 (dd, J = 3.5 Hz, 3.1 Hz, 2-H, Ind) ppm. ^{13}C NMR (100 MHz, [D$_3$]MeCN): selected signals, δ = 77.3 [d, $J_{P,C}$ = 4 Hz, C(3) Ind], 99.0 (d, $J_{P,C}$ = 21 Hz, C(1) Ind), 115.9 [d, $J_{P,C}$ = 6 Hz, C(2) Ind] ppm, C(1) defined as *trans* to P. ^{19}F NMR (282.4 MHz, [D$_3$]MeCN): δ = –124.3 (6 lines, $J_{121Sb,19F}$ = 1935 Hz, and 8 lines, $J_{123Sb,19F}$ = 1060 Hz) ppm. ^{31}P NMR (121.5 MHz, [D$_3$]MeCN): δ = 12.2 (s, *exo* isomer), 12.4 (s, *endo* isomer) ppm. ^{121}Sb NMR ([Ξ] = 71.8223640 MHz, [D$_3$]-MeCN): 93.1 (sept, $J_{Sb,F}$ = 1936 Hz) ppm. MS (FAB): *m*/*z* (%) = 741.3 (100) $[M - SbF_6]^+$, 626.2 (33) $[M - Ind - SbF_6]^+$. $C_{40}H_{40}F_6N_2PFePdSb$ (977.74): calcd. C 49.14, H 4.12, N 2.87; found C 48.84, H 4.17, N 2.80.

(*E*)-1,3-Dicyclohexylprop-2-en-1-ol (10): (a) (*E*)-1,3-Dicyclohexylpropenone: Acetylcyclohexane (**9**) (6.9 mL, 50 mmol) was slowly dropped into a stirred solution of LDA (31 mL, 2 M in hexanes, 62 mmol) in THF (80 mL) at –78 °C. After 1 h, CyCHO (6.9 mL, 57.1 mmol) was slowly added and the reaction mixture stirred for 4 h at –78 °C. MsCl (9.7 mL, 125 mmol) was added dropwise. After 1 h the reaction mixture was warmed to room temp., quenched with sat. $NaHCO_3$ solution (50 mL) and extracted with *t*BuOMe. The organic phases were dried (Na_2SO_4) and the solvents evaporated. DBU (12.4 mL, 83.3 mmol) was added dropwise at 0 °C to the residue in acetone (100 mL). After 1 h stirring, workup (NH_4Cl sat/*t*BuOMe) gave an oil which was purified by CC (*t*BuOMe/hexanes, 1:20) to give 7.707 g (70%) of a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.08–1.82 (m, 20 H-Cy), 2.08–2.19 (m, 1 H-Cy), 2.50–2.60 (m, 1 H-Cy), 6.10 (dd, J = 15.9 Hz, 1.4 Hz, 2-H), 6.80 (dd, J = 15.9 Hz, 6.8 Hz, 3-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 25.7 (CH_2), 25.7 (CH_2), 25.9 (CH_2), 25.9 (CH_2), 28.7 (CH_2), 31.8 (CH_2), 40.6 (CH), 48.6 (CH), 126.0 [CH, C(3)], 151.9 [CH, C(2)], 203.9 [C(1)] ppm. MS (CI): *m*/*z* (%) = 221 (100) $[M + H]^+$, 165 (3), 137 (61) $[C_9H_{13}O]^+$, 83 (11), $[C_6H_{11}]^+$, 55 (15). IR ($CHCl_3$): $\tilde{\nu}$ = 1684 (m, C=O), 1655 (m), 1620 (m, C=C) cm^{-1}. $C_{15}H_{24}O$ (220.35): calcd. C 81.76, H 10.98; found C 82.02, H 11.03.

(b) (*E*)-1,3-Dicyclohexyl-2-propen-1-ol (10): $NaBH_4$ (167 mg, 4.41 mmol) was added to a solution of 1,3-dicyclohexylpropenone (973 mg, 4.41 mmol) and $CeCl_3 \cdot 7H_2O$ (1646 mg, 4.41 mmol) in MeOH (12 mL) at room temp. The mixture was stirred for 10 min and worked up with aq. HCl (2.5 M, 3 mL), H_2O and *t*BuOMe. Purification by CC (*t*BuOMe/hexanes, 1:10) gave 758 mg (77%) of a colorless liquid. ^{1}H NMR ($CDCl_3$): δ = 0.85–1.42 (m, 11 H-Cy), 1.45 (d, J = 3.0 Hz, OH), 1.63–1.74 (m, 9 H-Cy), 2.01–1.81 (m, 2 H-Cy), 3.75 (ddd, J = 6.9 Hz, 6.9 Hz, 3.1 Hz, 3-H), 5.39 (ddd, J = 15.5 Hz, 7.2 Hz, 0.9 Hz, 2-H), 5.56 (dd, J = 15.5 Hz, 6.5 Hz, 1-H) ppm. Known compound, CAS number 79605-63-3.

(*E*)-1,3-Dicyclohexylallyl Fluoride (11): DAST (101.8 mg, 0.63 mmol) was added at –78 °C to a solution of **10** (126.6 mg, 0.569 mmol) in CH_2Cl_2 (11 mL) while stirring. The temperature was raised to 0 °C and the mixture stirred for another 10 min. Quenching with aq. $NaHCO_3$ (10 mL), followed by extraction with three portions of *t*BuOMe (20 mL) gave, after drying ($MgSO_4$) and evaporation, 130 mg (quant.) of a yellowish oil. Kugelrohr distillation (90 °C/0.01 mbar) gave a colorless oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.9–2.1 (m, 22 H-Cy), 4.49 (dt, J = 48.6 Hz, 7.2 Hz, 1-H), 5.44 (dddd, J = 15.6 Hz, 9.8 Hz, 7.6 Hz, 1.3 Hz, 2-H), 5.67 (ddd, J = 15.6 Hz, 6.4 Hz, 4.6 Hz, 3-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 25.7 (CH_2), 25.9 (CH_2), 25.9 (CH_2), 26.1 (CH_2), 26.4 (CH_2), 28.1 (d, $J_{F,C}$ = 5, CH_2), 28.2 (d, $J_{F,C}$ = 5 Hz, CH_2), 32.5 (d, $J_{F,C}$ = 2 Hz, CH_2), 32.7 (d, $J_{F,C}$ = 2 Hz, CH_2), 40.3 (CH), 42.5 (d, $J_{F,C}$ = 22 Hz, CH), 98.5 [d, $J_{F,C}$ = 164 Hz, CH, C(1)], 124.5 [d, $J_{F,C}$ = 20 Hz, CH, C(2)], 141.8 [d, $J_{F,C}$ = 12 Hz, CH, C(3)] ppm. ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = –175.2 (dddt, $J_{F,H} \approx$ 48.5 Hz, 13.9 Hz, 9.8 Hz, 5 Hz) ppm.

(*E*)-1,3-Dicyclohexylallyl Trifluoroacetate (12): TFAA (0.634 mL, 4.56 mmol) was slowly added to **10** (506.8 mg, 2.28 mmol) in pyridine (8.6 mL) at 0 °C and the reaction mixture stirred for 1 h. Workup with *t*BuOMe and washing of the organic phase (aq. HCl, aq. sat. $NaHCO_3$, H_2O) gave, after drying (Na_2SO_4) and evaporation, 680 mg (93%) of a colorless liquid. An analytical sample was

purified by Kugelrohr distillation (90 °C/0.005 mbar). The substance decomposed within a few days at room temp. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.92–1.31 (m, 10 H-Cy). 1.60–1.77 (m, 10 H-Cy), 1.92–2.04 (m, 2 H-Cy), 5.10 (dd, J = 8.1 Hz, 7.2 Hz, 1-H), 5.34 (ddd, J = 15.5 Hz, 8.4 Hz, 1.3 Hz, 2-H), 7.75 (dd, J = 15.5 Hz, 6.6 Hz, 3-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 25.6 (CH_2), 25.7 (CH_2), 25.8 (CH_2), 26.0 (CH_2), 26.2 (CH_2), 28.4 (CH_2), 32.4 (CH_2), 40.3 (CH), 41.3 (CH), 84.7 (CH), 122.1 (CH), 143.8 (CH) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 1777 (s), 1450 (s), 1272 (s) cm^{-1}. $C_{17}H_{25}F_3O_2$ (318.38): calcd. C 64.13, H 7.91; found C 63.94, H 8.07.

Bis(μ-trifluoroacetato)-bis(η³-1,3-dicyclohexylallyl)dipalladium(II) (13): A suspension of $Pd(dba)_2$ (756 mg, 1.32 mmol) and **12** (461 mg, 1.45 mmol) in THF (12 mL) and MeCN (3 mL) was stirred for 1 h at room temp. , followed by 10 min at 40 °C. The resulting solution was evaporated to dryness and repeatedly extracted with MeCN/H_2O (70:30). The extract was evaporated to a yellow powder, which was purified by precipitation from Et_2O/pentane to give 520 mg (93%) of yellow crystals. M.p. 82 °C (dec.). ^{1}H NMR (250 MHz, C_6D_6 + 10% [D_3]MeCN): δ = 1.00–1.98 (m, 44 H-Cy), 3.43 (dd, J = 11.6 Hz, 4.9 Hz, 4 H, 1-H, 1′-H, 3-H, 3′-H), 5.10 (t, J = 11.6 Hz, 2 H, 2-H, 2′-H) ppm. VT NMR: see Scheme 5 and Table 1. ^{13}C NMR (75.5 MHz, $CDCl_3$/[D_3]MeCN 3:1): δ = 25.5 (CH_2), 25.6 (CH_2), 25.6 (CH_2), 31.6 (CH_2), 32.0 (CH_2), 39.1 (CH), 88.2 (br., CH), 106.5 (br., CH) ppm. MS (FAB): *m/z* (%) = 1084 (9), 737 (47) [M – $OCOCF_3$]$^+$, 311 (100) [Pd(Cy_2All)]$^+$. $C_{34}H_{50}F_6O_4Pd$ (849.60): calcd. C 48.99, H 6.05; found C 48.09, H 5.92.

Di-μ-bromo-bis(η³-1,3-diphenylallyl)diplatinum(II) (17): (a) A Karstedt complex solution (corresponding to 4 mmol of Pt) was added dropwise to a solution of **15** (1.37 g, 5.0 mmol) in *t*BuOMe (30 mL) at 0 °C while stirring. A vanilla-yellow powder precipitated. After stirring for 2 h at 0 °C, filtration and washing with MeOH, a fine, bright yellow powder (1.440 g, 77%) was obtained that was hardly soluble in any solvents, except for DMSO and pyridine. (b) A suspension of $Pt_2(dba)_3$ (109 mg, 0.1 mmol) and **15** (58 mg, 0.21 mmol) in acetone (2 mL) and THF (2 mL) was stirred for 1 d at room temp. The reaction mixture was evaporated to dryness and the solid was suspended in MeOH (2 mL) and filtered. Washing with MeOH and acetone gave 66 mg (70%) of a greyish yellow powder. The discoloration was caused by finely divided Pt^0 already present in $Pt_2(dba)_3$. M.p. 159 °C (dec.). ^{1}H NMR (250 MHz, [D_6]-DMSO): δ = 4.46 (d, J = 11.0 Hz, $J_{Pt,H} \approx$ 56 Hz, 4 H, 1-H, 3-H), 6.05 (t, J = 11.0 Hz, $J_{Pt,H} \approx$ 76 Hz, 2 H, 2-H), 7.10–7.70 (m, 20 H, aryl) ppm. ^{13}C NMR (62.9 MHz, [D_6]DMSO): δ = 74.6 (br.), 104.7, 130.7, 131.3, 131.8, 141.4 ppm. IR (KBr): $\tilde{\nu}$ = 755 (s), 698 (s) cm^{-1}. $C_{30}H_{26}Br_2Pt_2$ (936.50): calcd. C 38.48, H 2.80; found C 38.54, H 2.89.

[Pt(η³-Ph_2All)(2b)]PF_6 (18·PF_6): Ligand **2b** (515 mg, 0.99 mmol) and **17** (463 mg, 0.494 mmol) were stirred in acetone (10 mL) until they had completely dissolved. Epichlorohydrine (1.0 mL, 12.8 mmol) and HPF_6 (1 M, 1.1 mL, 1.1 mmol, freshly prepared from 75% aq. HPF_6 and EtOH) were added, and the mixture stirred for 20 min and then evaporated to dryness. The residue was thoroughly dried under HV, washed with *t*BuOMe and then dissolved in CH_2Cl_2 (5 mL) and the solution filtered through a cotton plug into MeOH (10 mL). On standing in the fridge (4 °C), dark orange crystals formed (763 mg, 73%). ^{1}H NMR (400 MHz, [D_8]-THF): δ = 0.51 (s, 9 H, *t*Bu), 2.37 (d, J = 6.9 Hz, 3 H, *Me*CH), 3.94 (s, 5 H, Cp′), 4.05–4.08 (m, 1 H-Cp), 4.51 (t, J = 2.3 Hz, 1 H-Cp), 4.79–4.80 (m, 1 Cp-H), 4.81 (d, J = 9.2 Hz, $J_{Pt,H}$ = 77 Hz, allyl H, *anti*, *trans* N), 5.86 (ddd, J = 13.9 Hz, 9.1 Hz, 2.1 Hz, $J_{Pt,H}$ = 56, allyl H, *central*), 6.05 (d, J = 2.9 Hz, $J_{Pt,H} \approx$ 11 Hz, 4-H, Pz), 6.35–6.43 (m, 2 H, aryl), 6.89 (dd, J = 13.8 Hz, 7.0 Hz, $J_{Pt,H}$ = 49 Hz, allyl H, *anti*, *trans* P), 7.04–7.08 (m, 3 H, aryl), 7.10–7.18 (5 H, aryl), 7.22–7.32 (m, 3 H, aryl), 7.25 (q, J = 6.9 Hz, C*H*Me), 7.34–7.39 (m, 2 H, aryl), 7.42–7.50 (m, 3 H, aryl), 7.75–7.82 (m, 2 H, aryl), 7.98 (d, J = 2.9 Hz, 5-H, Pz) ppm. ^{13}C NMR (62.9 MHz, [D_8]THF): δ = 18.2 (CH_3), 30.8 (s, $J_{Pt,C}$ = 7 Hz, CH_3), 33.1 (C), 51.4 (s, $J_{Pt,C}$ = 318 Hz, allyl CH, *trans* N), 59.5 (d, $J_{P,C}$ = 3 Hz, *C*HMe), 67.9 [d, $J_{P,C}$ = 7 Hz, CH, C(3) Cp], 71.9 [d, $J_{P,C}$ = 7 Hz, CH, C(4) Cp], 72.3 (CH, Cp′), 74.4 [d, $J_{P,C}$ = 3 Hz, $J_{Pt,C}$ = 40 Hz, CH, C(5′) Cp], 75.4 (d, $J_{P,C}$ = 58 Hz, C), 94.8 (d, $J_{P,C}$ = 17 Hz, C), 100.7 (d, $J_{P,C}$ = 19 Hz, CH, All *trans* P), 108.9 [s, $J_{Pt,C}$ = 34 Hz, CH, C(4) Pz], 109.8 (s, $J_{Pt,C}$ = 33 Hz, allyl CH, *central*), 127.2 (CH), 128.8 (CH), 129.1 (d, $J_{P,C}$ = 10 Hz, CH) 129.1 (d, $J_{P,C}$ = 2 Hz, CH), 129.3 (CH), 129.4 (d, $J_{P,C}$ = 1 Hz, CH), 129.5 (d, $J_{P,C}$ = 1 Hz, CH), 129.6 (d, $J_{P,C}$ = 1 Hz, CH), 130.9 (CH), 130.9 [CH, C(5) Pz], 131.1 (d, $J_{P,C}$ = 65 Hz, C), 131.8 (d, $J_{P,C}$ = 3 Hz, CH), 132.9 (d, $J_{P,C}$ = 10 Hz, CH, *ortho*-PPh axial), 134.2 (d, $J_{P,C}$ = 57 Hz, C), 135.4 (d, $J_{P,C}$ = 13 Hz, CH, *ortho*-PPh equatorial), 136.8 (d, $J_{P,C}$ = 4 Hz, C), 142.0 (d, $J_{P,C}$ = 1 Hz, C), 163.2 [C, C(3) Pz] ppm. ^{31}P NMR (161.9 MHz, [D_8]THF): δ = –142.7 (sept, J_{PF} = 714 Hz, PF_6^-), 10.4 (s, $J_{Pt,P}$ = 5029 Hz), 9.2 (s, minor isomer, <2%). ^{195}Pt NMR (86.0 MHz, HMQC, [D_8]THF): δ = –4453 (d, $J_{Pt,P}$ = 5030 Hz) ppm. $C_{46}H_{46}F_6FeN_2P_2Pt$ (1053.75): calcd. C 52.43, H 4.40, N 2.66; found C 52.38, H 4.44, N 2.63.

[Pt(η³-Ph_2All)(2b)]Br (18·Br): A combination of **2b** (30 mg, 58 mmol) and **17** (27 mg, 29 mmol) in THF (2 mL), followed by filtration and evaporation gave a yellow residue. Crystallization from CH_2Cl_2/pentane at 5 °C (over layering) produced fine yellow needles (43.5 mg, 76%). Additional material was crystallized from the mother liquors (12 mg, total 97%). M.p. 141–147 °C. ^{31}P NMR (101.3 MHz, $CDCl_3$) and ^{195}Pt NMR (HMQC, 64.3 MHz, $CDCl_3$): see Table 2. MS (FAB): *m/z* (%) = 908.4 (73) [M – Br]$^+$, 715.3 (100) [M – Br – Ph_2All]$^+$. $C_{46}H_{46}BrFeN_2PPt$ (988.69): calcd. C 55.88, H 4.69, N 2.83; found C 55.99, H 4.74, N 2.75.

[Pt(η³-Ph_2All)(2b)]F (18·F): (a) Me_4NF (17 mg, 0.18 mmol) was added to a solution of **18·PF_6** (128 mg, 0.12 mmol) in THF (1 mL) and the resulting suspension stirred at room temp. Samples of the supernatant solution were taken and C_6D_6 was added for locking purposes, and the NMR spectra recorded. After 1 d, some PF_6^- remained in the solution (^{19}F NMR, ^{31}P NMR), but after 2 d such signals had disappeared. The reaction mixture was filtered and the filtrate evaporated under HV. A yellow solid remained which was soluble in benzene. ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = –139.8 (br. s, $\Delta_{1/2}$ = 15 Hz, F^-) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 2.2 (s, $J_{Pt,P}$ = 3903 Hz), 3.5 (s, $J_{Pt,P}$ = 4094 Hz), 7.0 (br. s, $J_{Pt,P}$ = 3947 Hz) ppm.

(b) Reaction in toluene: **18·PF_6** (115 mg) and Me_4NF (15 mg) were stirred for 2 d in [D_8]toluene (3 mL). The sample was filtered into a J. Young NMR tube. ^{19}F NMR (282 MHz, [D_8]toluene, 298 K): δ = –116 (br. s) ppm. Note that the signal is within a region of heavy artifacts (due to fluoropolymers within the NMR probe head). ^{31}P NMR (121.5 MHz, [D_8]toluene, 298 K): δ = 2.4 (s, $J_{Pt,P}$ = 3908 Hz), 4.1 (br. s, $J_{Pt,P}$ = 4070 Hz), 7.8 (br. s, $J_{Pt,P}$ = 3938 Hz) ppm. VT ^{31}P NMR (121.5 MHz, [D_8]toluene, 213 K): see Table 2.

[$PtCl_2$(2b)] (19): Bis(styrene)platinum(II) chloride (0.475 g, 1.00 mmol) and **2b** (0.5377 g, 1.03 mmol) were stirred in CH_2Cl_2 (10 mL) for 1 d at 40 °C. Filtration through Celite, evaporation to 2 mL and addition of pentane gave an orange precipitate. This was dissolved in a little CH_2Cl_2 and over layered with EtOAc. Slow evaporation in the fume hood gave orange-red crystals containing

the solvent of crystallization. Yield as $[PtCl_2(\mathbf{2b})]\cdot 0.35\ CH_2Cl_2\cdot 0.25$ AcOEt: 0.716 g (87%). An analytical sample was dried to remove solvents of crystallization. M.p. 215 °C (dec.). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.18 (s, 9 H, *t*Bu), 2.12 (d, J = 7.2 Hz, 3 H, CH*Me*), 3.75–3.79 (m, 1 H-Cp), 4.16 (s, 5 H, Cp′), 4.41 (t, J = 2.5 Hz, 1 H-Cp), 4.74–4.79 (m, 1 H-Cp), 6.05 (d, J = 2.9 Hz, 4-H, Pz), 6.68–6.78 (m, 2 H, aryl), 7.14–7.23 (dt, J = 8 Hz, 3 Hz, 2 H, aryl), 7.29–7.36 (m, 1 H, aryl), 7.42–7.58 (m, 3 H, aryl), 7.52 (d, J = 2.9 Hz, 5-H, Pz), 8.08 (q, J = 7.2 Hz, C*H*Me), 8.11–8.20 (m, 2 H, aryl) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 17.3 (CH_3, CH*Me*), 31.3 (CH_3, *t*Bu), 33.3 (C, *t*Bu), 57.5 (CH, *C*HMe), 68.0 (d, $J_{P,C}$ = 8 Hz, CH, Cp), 70.7 (d, $J_{P,C}$ = 7 Hz, CH, Cp), 71.1 [d, $J_{P,C}$ = 67 Hz, C, C(1)-Cp], 71.3 (CH, Cp′), 73.8 (d, $J_{P,C}$ = 4 Hz, CH, Cp), 92.4 [d, $J_{P,C}$ = 15 Hz, C, C(2)-Cp], 107.8 [CH, C(4)-Pz], 127.4 (d, $J_{P,C}$ = 11 Hz, CH), 127.5 (d, $J_{P,C}$ = 68 Hz, C), 127.6 [CH, C(5)-Pz], 128.3 (d, $J_{P,C}$ = 10 Hz, CH), 130.1 (d, $J_{P,C}$ = 3 Hz, CH), 131.3 (d, $J_{P,C}$ = 3 Hz, CH), 131.6 (d, $J_{P,C}$ = 10 Hz, CH), 132.7 (d, $J_{P,C}$ = 61 Hz, C), 135.7 (d, $J_{P,C}$ = 10 Hz, CH), 162.7 [C, C(3)-Pz] ppm. ^{31}P NMR (125.5 MHz, $CDCl_3$): δ = –16.1 (s, $J_{Pt,P}$ = 3783 Hz) ppm. ^{195}Pt NMR (HMQC, 64.525 MHz, $CDCl_3$): δ = –3700 (d, $J_{Pt,P}$ = 3790 Hz) ppm. MS (FAB): *m*/*z* (%) = 1537 (50) [2 M – Cl]$^+$, 786 (27) M$^+$, 750 (92) [M – Cl]$^+$, 714 (100) [M – 2 Cl]$^+$, 630 (74). $C_{31}H_{33}Cl_2FeN_2PPt$ (786.42): calcd. C 47.35, H 4.23, N 3.56; found C 47.43, H 4.45, N 3.61.

[PtPh$_2$(2b)] (20): (a) Complex **19** (100 mg, 0.127 mmol) was added to a 10–20 fold excess of PhMgBr in THF (ca. 2 mL) and stirred for 1 d at 50 °C. Quenching with aq. NH_4Cl and extraction with *t*BuOMe, followed by drying of the organic phase ($MgSO_4$) and evaporation gave a yellow semisolid. This was crystallized from heptane/CH_2Cl_2 by slow evaporation at 4 °C to give orange-yellow crystals (81 mg, 73%).

(b) An aged solution of PhMgBr (2 mL, 2 M, 4 mmol) was added dropwise to **19** (0.21 mmol) in THF (7 mL). After stirring for 1 d at 50 °C the reaction was quenched with water and extracted with *t*BuOMe. Drying over $MgSO_4$ and evaporation gave an orange oil that was filtered through SiO_2 using *t*BuOMe/hexane (1:10). The yellow fractions were collected and the solvents evaporated. Heptane (3 mL) was added to the residue and enough CH_2Cl_2 to dissolve all solids. Diffusion against heptane at –20 °C gave 160 mg (79%) of orange crystals of the phenol adduct (**20·PhOH**, M_r = 963.82). The PhOH was apparently an impurity arising from the Grignard reagent used. Analytical data for the solvate-free compound: M.p. 185–189 °C (dec.). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.66 (s, 9 H, *t*Bu), 2.21 (d, J = 7.3 Hz, 3 H, *Me*CH), 3.66–3.71 (m, 1 H-Cp), 3.97 (s, 5 H, Cp′), 4.30 (t, J = 2.6 Hz, 1 H-Cp), 4.66–4.71 (m, 1 H-Cp), 5.95 (d, J = 2.7 Hz, 4-H,Pz), 6.49–6.59 (m, 2 H, aryl), 6.69–7.38 (m, 16 H, aryl), 7.49 (d, J = 2.7 Hz, 5-H, Pz), 7.52–7.91 (br. m, 2 H, aryl), 8.82 (q, J = 7.2 Hz, C*H*Me) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 18.4 (CH_3), 30.2 (CH_3), 31.9 (C), 56.8 (d, $J_{P,C}$ = 1 Hz, CH_3), 67.3 (d, $J_{P,C}$ = 6 Hz, CH), 70.3 (d, $J_{P,C}$ = 4 Hz, CH), 70.4 (CH, Cp′), 73.6 (CH), 74.9 (d, $J_{P,C}$ = 42 Hz, C, Cp), 93.5 (d, $J_{P,C}$ = 18 Hz, C, Cp), 106.0 (CH), 120.9 (d, $J_{P,C}$ = 1.5 Hz), 122.0 (d, $J_{P,C}$ = 1.0 Hz), 125.8 (CH), 126.2 (d, $J_{P,C}$ = 7 Hz, CH), 127.0 (d, $J_{P,C}$ = 9 Hz, CH), 127.5 (d, $J_{P,C}$ = 9 Hz, CH), 128.0 (d, $J_{P,C}$ = 2 Hz, CH), 128.5 (CH), 129.2 (d, $J_{P,C}$ = 56 Hz, C), 129.5 (d, $J_{P,C}$ = 2 Hz, CH), 131.3 (d, $J_{P,C}$ = 10 Hz, CH), 131.6 (d, $J_{P,C}$ = 44 Hz, C), 135.9 (d, $J_{P,C}$ = 10 Hz, CH), 137.7 ($J_{Pt,C}$ = 38 Hz), 138.7 (C), 138.9 (br.), 139.3 (C), 139.5 (br.), 143.0, 143.2, 144.6, 158.9, 160.8 ppm. Some of the signals were not detected due to line broadening, which arose from hindered rotation of the phenyl groups. ^{31}P NMR (101.3 MHz, $CDCl_3$): δ = 5.3 (s, $J_{Pt,P}$ = 1688 Hz) ppm. MS (FAB): *m*/*z* (%) = 1584.8 (14) [2 M – 2 Ph]$^+$, 868.4 (5) [M]$^+$, 791.3 (12) [M – Ph]$^+$, 715.3 (100) [M – 2 Ph]$^+$. $C_{43}H_{43}FeN_2PPt$ (869.73): calcd. C 59.38, H 4.98, N 3.22; found C 59.38, H 5.05, N 3.21.

[Pt(Ph)F(2b)] (21): In an NMR tube, **20** (10 mg) in $CDCl_3$ (0.5 mL) was mixed with 2 drops of $NEt_3\cdot(HF)_3$. NMR analysis revealed two species (ratio 1.4:1) with similar ^{1}H NMR spectra. The major species was the fluoro complex and the minor species remains unknown. No attempt was made to isolate the compounds. ^{1}H NMR (300 MHz, $CDCl_3$), selected signal: δ = 7.36 (s, 6 H, benzene) ppm. ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = –214.6 (d, $J_{P,F}$ = 207 Hz, $J_{Pt,F}$ = 210 Hz), –129.7 (br. s, Et_3NH^+/F^-, excess reagent), –165.0 (br. s, HF/HF_2^-) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = –9.6 (s, $J_{Pt,P}$ = 5107 Hz), –11.8 (d, J_{PF} = 207, $J_{Pt,P}$ = 5104 Hz) ppm.

[Pt(η^3-All)(2b)]SbF$_6$ (22): $[\{PtCl(C_3H_5)\}_4]$[67] (103 mg, 0.095 mmol) and **2b** (203 mg, 0.39 mmol) were stirred in acetone (3 mL) and CH_2Cl_2 (3 mL) until a homogeneous solution was obtained. $AgSbF_6$ (135 mg, 0.39 mmol) was added and the resulting suspension stirred for 30 min. After filtration through Celite and evaporation, the residue was purified by precipitation from acetone/hexane to give 284 mg (71%) of orange crystals containing 0.5 equiv. acetone. ^{31}P NMR (81.0 MHz, $CDCl_3$): δ = 12.5 (s, $J_{Pt,P}$ = 4413 Hz, *exo* isomer), 12.6 (s, *endo* isomer) ppm. MS (FAB): *m*/*z* (%) = 1276.8 (16) [2 M – PF_6]$^+$, 756.4 (100) [M – PF_6]$^+$, 715.4 (25), [M – PF_6 – C_3H_5]$^+$. $C_{34}H_{38}F_6FeN_2PPtSb\cdot 0.5\,C_3H_6O$ (1021.36): calcd. C 41.75, H 4.05, N 2.74; found C 41.83, H 4.00, N 2.83.

[Pt(η^3-2-MeAll)(2b)]PF$_6$ (23): Ligand **2b** (193 mg, 0.37 mmol) and $[Pt_2(\mu\text{-}Cl)_2(2\text{-}MeAll)_2]$[68] (98.6 mg, 0.17 mmol) were stirred at room temp. for 2 h in CH_2Cl_2 (3 mL). $AgPF_6$ (94 mg, 0.37 mmol) in MeOH (3 mL) was added and the resulting suspension was stirred for 30 min, then filtered through Celite. The solution was evaporated to dryness and the residue crystallized from CH_2Cl_2/*t*BuOMe (slow diffusion) to give 254 mg (81%) of orange crystals. ^{31}P NMR (81.0 MHz, $CDCl_3$): δ = –143.5 (sept, J_{PF} = 713 Hz, PF_6^-), 11.5 (s, $J_{Pt,P}$ = 4291 Hz, major isomer); 11.9 (s, $J_{Pt,P}$ = 4010 Hz, minor isomer) ppm. MS (FAB): *m*/*z* (%) = 770.4 (100) [M – PF_6]$^+$. $C_{35}H_{40}F_6FeN_2P_2Pt$ (915.57): calcd. C 45.91, H 4.40, N 3.06; found C 45.97, H 4.61, N 3.03.

[Pt(η^3-Ph$_2$All)(dppe)]PF$_6$ (24): A mixture of **17** (51.5 mg, 0.055 mmol) and 1,2-bis(diphenylphosphanyl)ethane (43.8 mg, 0.11 mmol) in acetone (1 mL) and CH_2Cl_2 (1 mL) was stirred until completely dissolved. Epichlorohydrine (0.1 mL, 1.28 mmol) and HPF_6 solution [0.1 mL, 0.114 mmol; freshly prepared from 0.6 mL HPF_6 (75%) and EtOH up to 5.0 mL total volume] were then added dropwise. After 30 min stirring, the reaction mixture was evaporated to dryness and the residue dried under HV. The yellow solid was dissolved in CH_2Cl_2 (2 mL), the solution filtered through Celite, and the filtrate reduced to a volume of 1 mL. Addition of butanone (1 mL) followed by slow evaporation in the fume hood gave yellow, rhombic crystals (67 mg, 65%), suitable for X-ray analysis. ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 2.28–2.62 (m, $J_{Pt,H}$ = 34 Hz, 4 H, CH_2CH_2), 4.80 (m, AA′ of AA′BXX′, J_{AB} = $J_{A'B}$ = 12.8 Hz, J_{AX} + $J_{AX'}$ = 22.1 Hz, $J_{Pt,H}$ = 45.3 Hz, 2 allyl H, *anti*), 6.14 (t, B of AA′BXX′, J = 12.8 Hz, $J_{Pt,H}$ = 45 Hz, 1 allyl H, *central*), 7.80–6.80 (m, 30 H, aryl) ppm. ^{13}C NMR (62.9 MHz, CD_2Cl_2): δ = 31.0 (AMM′, ψ-dd, J = 41 Hz, 9 Hz, $J_{Pt,C}$ = 56 Hz, CH_2), 83.5 [AMM′, ψ-d, J = 27 Hz, $J_{Pt,C}$ = 55 Hz, CH, All-C(1,3)], 110.9 [A of AM_2, t, $J_{P,C}$ = 4 Hz, $J_{Pt,C} \approx$ 17 Hz, CH, All–C(2)], 126.8 (AMM′, ψ-dd, J = 57 Hz, 0.8 Hz, $J_{Pt,C}$ = 49 Hz, C, PPh-*ipso*-C), 128.4 (AMM′, ψ-quint, J = 2 Hz, CH), 128.7 (AMM′, ψ-dd, J = 56 Hz, 0.6 Hz, $J_{Pt,C}$ = 38 Hz, C, PPh-*ipso*-C), 129.3 (AMM′, ψ-t, J = 1.5 Hz, CH), 130.3 (AMM′, ψ-t, J = 1.3 Hz, CH), 131.1–131.6 (m, 2 CH), 133.7 (AMM′, CH), 133.8 (AMM′, $J_{Pt,C}$ = 24 Hz, CH), 134.5 (AMM′, CH), 134.9 (AMM′, $J_{Pt,C}$ =

25 Hz, CH), 137.7 (AMM′, C) ppm. Spin system nomenclature: A corresponds to the carbon atom in question, M and M′ correspond to the ^{31}P nuclei. ^{31}P NMR (101.3 MHz, CD_2Cl_2): δ = –143.7 (sept, $J_{P,F}$ = 711 Hz, PF_6^-), 44.7 (s, $J_{Pt,Pt}$ = 3847 Hz) ppm. ^{195}Pt NMR (HMQC, 64.2 MHz, CD_2Cl_2): δ = –5521 (t, $J_{Pt,P} \approx$ 3830 Hz) ppm. MS (FAB): *m*/*z* (%) = 1717 (9) $[2\ M - PF_6]^+$, 786 (100) $[M - PF_6]^+$, 592 (10) $[M - PF_6 - Ph_2All]^+$. $C_{41}H_{37}F_6P_3Pt$ (931.72): calcd. C 52.85, H 4.00; found C 52.83, H 4.14.

(*E*)-1-Cyclohexyl-3-cyclohexylidenepropene (26): (a) The substance was formed, in NMR experiments, from **8b** and an excess of either Me_4NF (in $[D_3]$MeCN) or Schwesinger's P_2F[57] (in C_6D_6). (b) A reference sample was obtained as follows: MsCl (56.0 mg, 0.488 mmol) was added dropwise at –78 °C to a solution of **10** (98.8 mg, 0.444 mmol) and *i*Pr_2NEt (0.091 mL, 0.533 mmol) in THF (5 mL). After stirring for 45 min and another addition of *i*Pr_2NEt (0.18 mL, 1.06 mmol) and MsCl (120 mg, 1 mmol) the reaction mixture was warmed to room temp. and stirred for 2 h. Workup with H_2O/*t*BuOMe gave, after drying ($MgSO_4$) and evaporation to dryness, a residue that was filtered through SiO_2 (*t*BuOMe) to yield 38.7 mg (42%) of a colorless oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.75–2.30 (m, 21 H-Cy), 5.54 (dd, *J* = 15.2 Hz, 7.0 Hz, 1-H), 5.73 (dd, *J* = 10.9 Hz, 0.7 Hz, 3-H), 6.25 (ddd, *J* = 15.2 Hz, 10.8 Hz, 1.2 Hz, 2-H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 26.1 (CH_2), 26.2 (CH_2), 26.8 (CH_2), 27.6 (CH_2), 28.4 (CH_2), 29.2 (CH_2), 33.1 (CH_2), 37.2 (CH_2), 41.0 (CH), 122.1 (CH), 123.2 (CH), 138.3 (CH), 141.2 (C) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2930 (s), 2853 (m), 1616 (w), 1448 (m), 1344 (w), 968 (m) cm^{-1}. MS (EI): *m*/*z* = 204 $[M]^+$.

Oxidative Addition of Ph_2AllF (6) to Pd(dba)$_2$ (→27·F): Pd(dba)$_2$ (170 mg, 0.29 mmol) and Ph_2AllF (**6**)[14a] (76 mg, 0.36 mmol, solution in 7 mL hexane) were stirred in THF (10 mL). Within 15 min, the color changed from violet to yellow, and a yellow solid precipitated. After filtration, the solid was dried under HV. The product could not be further purified and was only analyzed spectroscopically for the presence of the (1,3-diphenylallyl)palladium(II) fragment. ^{1}H NMR ($[D_6]$DMSO): δ = 5.29 [d, *J* = 12.0 Hz, 4 H, C(2),C(3)], 6.98 [t, *J* = 11.8 Hz, 2 H, C(2)], 7.39 (br. m, 12 H, aryl), 7.78 (br. m, 8 H, aryl) ppm. ^{19}F NMR: no signal detected.

Di-μ-bromobis(η^3-1,3-diphenylallyl)dipalladium(II) (27·Br): Pd(dba)$_2$ (40 mg, 0.070 mmol) and **15** (22.8 mg, 0.083 mmol) were stirred in THF (20 mL) at room temp. The color of the violet suspension became brighter within 20 min and a yellow precipitate was deposited. The solid was isolated by filtration and dried under HV. No further purification was attempted due to the small scale of the reaction. ^{1}H NMR ($[D_6]$DMSO): δ = 5.19 (d, *J* = 11.7 Hz, 4 H, allyl H, *anti*), 6.80 (t, *J* = 11.7 Hz, 2 H, allyl H, *central*), 7.30–7.27 (m, 12 H, aryl), 7.66–7.69 (m, 8 H, aryl) ppm. $C_{30}H_{26}Br_2Pd_2$ (759.18): calcd. C 47.46, H 3.45; found C 46.87, H 3.48.

Oxidative Addition of Ph_2AllF (6) to Pd(dba)$_2$ in the Presence of PPFPz{3,5-Me$_2$} {→[Pd(η^3-Ph_2All)(PPFPz{3,5-Me$_2$})]F·(H_2O)$_n$ (28·F)}: PPFPz{3,5-Me_2} (**2c**)[28] (54.2 mg, 0.11 mmol) and Pd(dba)$_2$ (57.5 mg, 0.10 mmol) were stirred in THF (10 mL) at 40 °C for 30 min to give an orange-brown solution. Ph_2AllF (**6**)[14a] (2 mL, 75 mM in *N*,*N*-dimethylformamide, 0.15 mmol), was added and the reaction mixture, which quickly turned yellow, was stirred for 1 h at room temp. Solvents were removed under HV and the residue purified by precipitation (in air) from CH_2Cl_2/pentane. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.71 (s, 3 H, Me-Pz), 1.67 (s, ca. 4 H, H_2O), 2.29 (d, *J* = 7.4 Hz, 3 H, CH*Me*), 2.31 (s, 3 H, Me–Pz), 3.75 (s, 1 H-Cp), 4.18 (s, 5 H, Cp′); 4.35–4.37 (m, 1 H-Cp), 4.65 (s, 1 H-Cp), 5.30 (s, 1 H-Pz), 6.12–6.19 (m, 3 H, 1 allyl H,, 2 H, aryl), 6.43–6.52 (m, 1 allyl H,), 6.98–8.03 (m, 19 H, 1 allyl H,, 18 H, aryl) ppm,

Table 3. Crystallographic data for **8a**, **8b**, and **8c·CH_2Cl_2**.

	8a	**8b**	**8c·CH_2Cl_2**
CCDC number	279485	279484	279489
Formula	$C_{46}H_{46}F_6FeN_2P_2Pd$	$C_{46}H_{58}F_6FeN_2P_2Pd$	$C_{41}H_{42}Cl_2F_6FeN_2P$ Pd Sb
M_r	965.07	977.13	1062.64
Crystal system	orthorhombic	orthorhombic	triclinic
Space group	$P2_12_12_1$	$P2_12_12_1$	P_{1r}
a [Å]	10.677(2)	10.3481(16)	10.281(7)
b [Å]	19.505(3)	17.276(3)	15.338(10)
c [Å]	20.809(3)	25.231(4)	13.684(9)
α [°]	90	90	90.0100(10)
β [°]	90	90	92.1260(10)
V [Å^3]	4333.5(11)	4510.7(12)	2156(2)
Z	4	4	2
Density calcd. [Mg·m^{-3}]	1.479	1.439	1.637
μ [mm^{-1}]	0.884	0.850	1.584
F(000)	1968	2016	1056
Crystal size [mm^3]	0.94 × 0.34 × 0.16	0.50 × 0.44 × 0.28	0.80 × 0.54 × 0.26
θ range (°)	1.43–28.31	1.43–24.78	1.33–29.69
Index ranges	$-14 \le h \le 14$	$-12 \le h \le 11$	$-14 \le h \le 12$
	$-25 \le k \le 26$	$-20 \le k \le 20$	$-18 \le k \le 21$
	$-17 \le l \le 27$	$-29 \le l \le 19$	$-18 \le l \le 16$
Reflections collected/used	36689/10782	25274/7719	15564/12425
	[R_{int} = 0.0672]	[R_{int} = 0.1009]	[R_{int} = 0.0365]
Data/restraints/parameters	10782/0/523	7719/42/509	12425/3/994
Goodness-of-fit on F^2	0.964	0.949	1.062
R indices	R_1 = 0.0349	R_1 = 0.0589	R_1 = 0.0457
[$I > 2\sigma(I)$]	wR_2 = 0.0767	wR_2 = 0.1324	wR_2 = 0.1232
(all data)	R_1 = 0.0538	R_1 = 0.0983	R_1 = 0.0514
	wR_2 = 0.0837	wR_2 = 0.1489	wR_2 = 0.1338
Abs. struct. parameter	–0.04(2)	–0.05(4)	–0.02(2)
Largest diff. peak/hole [e·Å^{-3}]	0.490/–0.572	1.643/–0.750	0.829/–0.857

Table 4. Crystallographic data for **18·PF$_6$**, **20·PhOH**, and **24**.

	18·PF$_6$	**20·PhOH**	**24**
CCDC number	279486	279488	279487
Formula	$C_{46}H_{46}F_6FeN_2P_2Pt$	$C_{49}H_{49}FeN_2OPPt$	$C_{41}H_{37}F_6P_3Pt$
M_r	1053.73	963.85	931.71
Crystal system	orthorhombic	monoclinic	orthorhombic
Space group	$P2_12_12_1$	$P2_1$	*Pbca*
a [Å]	10.709(2)	11.591(14)	18.525(7)
b [Å]	19.566(3)	10.998(9)	18.644(9)
c [Å]	20.832(3)	16.464(3)	22.108(9)
α [°]	90	90	90
β [°]	90	94.72(9)	90
V [Å^3]	4376.3(3)	2092(4)	7636(6)
Z	4	2	8
Density calcd. [Mg·m^{-3}]	1.599	1.530	1.621
μ [mm^{-1}]	3.658	3.764	3.859
F(000)	2096	968	3680
Crystal size [mm^3]	0.95 × 0.3 × 0.3	0.5 × 0.3 × 0.2	0.2 × 0.17 × 0.13
θ range (°)	1.43–29.96	1.76–20.04	1.80–20.15
Index ranges	$-14 \le h \le 14$	$-11 \le h \le 11$	$0 \le h \le 17$
	$-18 \le k \le 27$	$-10 \le k \le 10$	$0 \le k \le 17$
	$-28 \le l \le 28$	$-15 \le l \le 15$	$0 \le l \le 21$
Reflections collected/used	32667/11386	3931/1989	3553/3553
	[R_{int} = 0.0683]	–	[R_{int} = 0.0000]
Data/restraints/parameters	11386/0/524	1989/0/461	3553/0/461
Goodness-of-fit on F^2	0.945	1.825	0.903
R indices	R_1 = 0.0405	R_1 = 0.036	R_1 = 0.0304
[$I > 2\sigma(I)$]	wR_2 = 0.0759	wR_2 = 0.033	wR_2 = 0.0752
(all data)	R_1 = 0.0925	R_1 = 0.037	R_1 = 0.0455
	wR_2 = 0.0897	wR_2 = 0.033	wR_2 = 0.0788
Abs. struct. parameter	–0.031(6)	–	–
Largest diff. peak/hole [e·Å^{-3}]	1.164/–1.020	0.754/–1.179	0.561/–0.637

peaks broadened. ^{19}F NMR (282.4 MHz, $CDCl_3$): no signal detected. ^{31}P NMR ($CDCl_3$): δ = 12.1 (br. s) ppm. $C_{44}H_{42}FFeN_2PPd + 3H_2O$ (865.10): calcd. C 61.09, H 5.59, N 3.24; found C 61.02, H 5.09, N 2.77.

X-ray Crystallography: Data were collected at 293 K with a Siemens SMART CCD diffractometer (graphite-monochromated Mo-K_α radiation, λ = 0.71073 Å, ω-scan technique), except for **20·PhOH** and **24**, for which the data was collected with a Syntex P21 4-circle diffractometer. The structures were solved by direct methods using SHELXS-97.[69] A full matrix least-squares refinement on F^2 was performed with SHELXL-97.[70] Allyl fragments in **8b** and the phenol solvate in **20·PhOH** were refined isotropically, all other non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions and assigned using an isotropic displacement parameter of 0.08 Å^2. SADABS[71] was used to perform area-detector scaling and absorption corrections. No absorption correction was applied for **20·PhOH** and **24**.

CCDC-279484 to -279489 (cf. Table 3 and Table 4) contain the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] M. N. Doherty, N. W. Hoffmann, *Chem. Rev.* **1991**, *91*, 553.
[2] E. F. Murphy, H. W. Roesky, *Chem. Rev.* **1997**, *97*, 3425.
[3] S. Thrasher, S. H. Strauss, *Inorganic Fluorine Chemistry towards the 21st Century*, American Chemical Society, Washington, DC, **1994**.
[4] H. Plenio, *Chem. Rev.* **1997**, *97*, 3363.
[5] J. L. Kiplinger, T. G. Richmond, C. E. Osterberg, *Chem. Rev.* **1994**, *94*, 373.
[6] a) J. Burdeniuc, B. Jedlicka, R. H. Crabtree, *Chem. Ber./Recueil* **1997**, *130*, 145; b) M. Aizenberg, D. Milstein, *Science* **1994**, *265*, 359.
[7] a) K. Fagnou, M. Lautens, *Angew. Chem.* **2002**, *114*, 26; *Angew. Chem. Int. Ed.* **2002**, *41*, 26; b) B. L. Pagenkopf, E. M. Carreira, *Chem. Eur. J.* **1999**, *5*, 3437.
[8] U. Burckhardt, M. Baumann, A. Togni, *Tetrahedron: Asymmetry* **1997**, *8*, 155.
[9] a) A. L. Henne, T. H. Newby, *J. Am. Chem. Soc.* **1948**, *70*, 130; b) A. L. Henne, A. M. Whaley, J. K. Stevenson, *J. Am. Chem. Soc.* **1941**, *63*, 3478; c) A. L. Henne, *Org. React.* **1944**, *2*, 49.
[10] Fluorocarbonylations: a) T. Okano, N. Harada, J. Kiji, *Chem. Lett.* **1994**, 1057; b) T. Okano, N. Harada, J. Kiji, *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1741; c) T. Sakakura, M. Chaisupakitsin, T. Hayashi, M. Tanaka, *J. Organomet. Chem.* **1987**, *334*, 205.
[11] Additional examples of transition-metal catalyzed or mediated fluorinations: a) R. D. Chambers, J. Hutchinson, *J. Fluorine Chem.* **1998**, *92*, 45; b) S. Bruns, G. Haufe, *J. Fluorine Chem.* **2000**, *104*, 247.
[12] V. V. Grushin, *Chem. Eur. J.* **2002**, *8*, 1006.
[13] a) M. Shimizu, T. Hiyama, *Angew. Chem.* **2005**, *117*, 218; *Angew. Chem. Int. Ed.* **2005**, *44*, 214; b) P. Kirsch, *Modern Fluoroorganic Chemistry*, Wiley-VCH, Weinheim, **2004**; c) T. Hi-

yama, *Organofluorine Compounds*, Springer, Berlin, **2000**; d) V. A. Soloshonok, *Enantiocontrolled Synthesis of Fluoro-Organic Compounds*, Wiley, Chichester, **1999**; e) M. Hudlicky, A. E. Pavlath, *Chemistry of Organic Fluorine Comounds II*, American Chemical Society, Washington, DC, **1995**; f) J. T. Welch, *Selective Fluorination in Organic and Bioinorganic Chemistry*, American Chemical Society, Washington, DC, **1991**.

[14] a) P. Barthazy, L. Hintermann, R. M. Stoop, M. Wörle, A. Mezzetti, A. Togni, *Helv. Chim. Acta* **1999**, *82*, 2448; b) P. Barthazy, A. Togni, A. Mezzetti, *Organometallics* **2001**, *20*, 3472.

[15] L. Hintermann, A. Togni, *Angew. Chem.* **2000**, *112*, 4530; *Angew. Chem. Int. Ed.* **2000**, *39*, 4359.

[16] Y. Hamashima, K. Yagi, H. Takano, L. Tamás, M. Sodeoka, *J. Am. Chem. Soc.* **2002**, *124*, 14530.

[17] J. Ma, D. Cahard, *Tetrahedron: Asymmetry* **2004**, *15*, 1007.

[18] N. Shibata, T. Ishimaru, T. Nagai, J. Kohno, T. Toru, *Synlett* **2004**, 1703.

[19] M. Sanna, PhD Dissertation, ETH Nr. 15191, Zürich, **2003**.

[20] N. Shibata, J. Kohno, K. Takai, T. Ishimaru, S. Nakamura, T. Toru, S. Kanemasa, *Angew. Chem.* **2005**, *117*, 4276; *Angew. Chem. Int. Ed.* **2005**, *44*, 4204.

[21] H. Ibrahim, A. Togni, *Chem. Commun.* **2004**, 1147.

[22] B. M. Trost, M. L. Crawley, *Chem. Rev.* **2003**, *103*, 2921.

[23] Preliminary communication: A. Togni, A. Mezzetti, P. Barthazy, C. Becker, I. Devillers, R. Frantz, L. Hintermann, M. Perseghini, M. Sanna, *Chimia* **2001**, *55*, 801.

[24] G. Helmchen, A. Pfaltz, *Acc. Chem. Res.* **2000**, *33*, 336.

[25] Example: H. C. Clark, M. J. Hampden-Smith, H. Ruegger, *Organometallics* **1988**, *7*, 2087.

[26] J. Elguero, E. Gonzalez, R. Jacquier, *Bull. Soc. Chim. Fr.* **1968**, 707.

[27] a) T. Hayashi, T. Mise, M. Fukushima, M. Kagotani, N. Nagashima, Y. Hamada, A. Matsumoto, S. Kawakami, M. Konishi, K. Yamamoto, M. Kumada, *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1138; b) Improved procedure for preparing PPFA: S. Gischig, A. Togni, *Organometallics* **2004**, *23*, 2479.

[28] a) A. Schnyder, L. Hintermann, A. Togni, *Angew. Chem.* **1995**, *107*, 996; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 931; b) U. Burckhardt, L. Hintermann, A. Schnyder, A. Togni, *Organometallics* **1995**, *14*, 5415.

[29] A. Togni, U. Burckhardt, V. Gramlich, P. S. Pregosin, R. Salzmann, *J. Am. Chem. Soc.* **1996**, *118*, 1031.

[30] A. S. Pilcher, H. L. Ammon, P. DeShong, *J. Am. Chem. Soc.* **1995**, *117*, 5166.

[31] K. O. Christe, W. W. Wilson, R. D. Wilson, R. F. Bau, J. A. Feng, *J. Am. Chem. Soc.* **1990**, *112*, 7619.

[32] K. Seppelt, *Angew. Chem.* **1992**, *104*, 299; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 292.

[33] D. Landini, A. Maia, A. Rampoldi, *J. Org. Chem.* **1989**, *54*, 328.

[34] a) R. K. Sharma, J. L. Fry, *J. Org. Chem.* **1983**, *48*, 2112; b) However, preparation of truly dry TBAF has just been claimed: H. Sun, S. G. DiMagno, *J. Am. Chem. Soc.* **2005**, *127*, 2050.

[35] Compound **6** is characterized by $\delta(^{19}F) = -165.4$ ppm.[14a]

[36] a) J. A. Davies, in: *Comprehensive Organometallic Chemistry II* (Ed.: R. J. Puddephatt), Elsevier *Science* Oxford, **1995**, Vol. 9, p. 291; b) P. M. Maitlis, P. Espinet, M. J. H. Russell, in: *Comprehensive Organometallic Chemistry* (Ed.: G. Wilkinson), Pergamon, Oxford, **1982**, vol. 6, p. 385.

[37] *exo*: the arrow head defined by the three allyl carbons points away from the lower Cp ring of the ferrocene unit; *endo*: the allyl vector points towards the lower Cp ring. The nomenclature is used as in ref.[29]

[38] A. L. Gemal, J. Luche, *J. Am. Chem. Soc.* **1981**, *103*, 5454.

[39] W. J. Middleton, *J. Org. Chem.* **1975**, *40*, 574.

[40] A. Vitagliano, B. Åkermark, S. Hansson, *Organometallics* **1991**, *10*, 2592.

[41] a) R. G. Brown, R. V. Chaudhari, J. M. Davidson, *J. Chem. Soc., Dalton Trans.* **1977**, 176; b) J. Powell, *J. Am. Chem. Soc.* **1969**, *91*, 4311.

[42] a) S. Lin, P. Boudjouk, *J. Chin. Chem. Soc. (Taipei)* **1989**, *36*, 35; b) C. Sui-Seng, G. D. Enright, D. Zargarian, *Organometallics* **2004**, *23*, 1236.

[43] Recent examples: a) C. Amatore, A. A. Bahsoun, A. Jutand, L. Mensah, G. Meyer, L. Ricard, *Organometallics* **2005**, *24*, 1569; b) G. Malaise, S. Ramdeehul, J. A. Osborn, L. Barloy, N. Kyritsakas, R. Graff, *Eur. J. Inorg. Chem.* **2004**, 3987; c) P. B. Armstrong, L. M. Bennett, R. N. Ryan, J. L. Fields, J. P. Jasinski, R. J. Staples, R. C. Bunt, *Tetrahedron Lett.* **2005**, *46*, 1441.

[44] a) P. S. Pregosin, R. Salzmann, *Coord. Chem. Rev.* **1996**, *155*, 35; b) P. von Matt, G. C. Lloyd-Jones, A. B. E. Minidis, A. Pfaltz, L. Macko, M. Neuburger, M. Zehnder, H. Rüegger, P. S. Pregosin, *Helv. Chim. Acta* **1995**, *78*, 265; c) P. Barbaro, P. S. Pregosin, R. Salzmann, A. Albinatti, R. Kunz, *Organometallics* **1995**, *14*, 5160.

[45] a) J. M. Brown, J. E. MacIntyre, *J. Chem. Soc., Perkin Trans. 2* **1985**, 961; b) H. Kurosawa, *J. Chem. Soc., Dalton Trans.* **1979**, 939.

[46] Asymmetric catalytic allylation with platinum: a) A. J. Blacker, M. L. Clarke, M. S. Loft, M. F. Mahon, M. E. Humphries, J. M. J. Williams, *Chem. Eur. J.* **2000**, *6*, 353; b) A. J. Blacker, M. L. Clark, J. M. J. Williams, M. S. Loft, *Chem. Commun.* **1999**, 913.

[47] R. Lespieau, R. L. Wakeman, *Bull. Soc. Chim. Fr.* **1932**, *51*, 384.

[48] The Karstedt catalyst solution is used industrially and is commercially available.

[49] a) M. F. Lappert, F. P. A. Scott, *J. Organomet. Chem.* **1995**, *492*, C11; b) P. B. Hitchcock, M. F. Lappert, N. J. W. Warhurst, *Angew. Chem.* **1991**, *103*, 439; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 438; c) B. D. Karstedt, U. S. Patent 3775452, **1973**.

[50] L. N. Lewis, T. A. Krafft, J. C. Huffman, *Inorg. Chem.* **1992**, *31*, 3555.

[51] A. Albinati, W. R. Caseri, P. S. Pregosin, *Organometallics* **1987**, *6*, 788.

[52] L. Brammer, D. Zhao, F. T. Ladipo, J. Braddock-Wilking, *Acta Crystallogr. Sect. B* **1995**, *51*, 632.

[53] K. Hallman, A. Frölander, T. Wondimagegn, M. Svensson, C. Moberg, *PNAS* **2004**, *101*, 5400.

[54] a) P–Pt–F *trans* complexes: A. Yahav, I. Goldberg, A. Vigalok, *J. Am. Chem. Soc.* **2003**, *125*, 13634; b) P–Pt–F *cis* complexes: A. Yahav, I. Goldberg, A. Vigalok, *Inorg. Chem.* **2005**, *44*, 1547.

[55] U. Burckhardt, PhD Dissertation, ETH Nr. 12167, Zürich, **1997**.

[56] L. Hintermann, A. Togni, result presented at the *XVIIIth International Conference on Organometallic Chemistry*, Munich, **1998**.

[57] R. Schwesinger, R. Link, G. Thiele, H. Rotter, D. Honert, H. H. Limbach, F. Männle, *Angew. Chem.* **1991**, *103*, 1376; *Angew. Chem. Int. Ed.* **1991**, *30*, 1372.

[58] W. E. Barnette, *J. Am. Chem. Soc.* **1984**, *106*, 452.

[59] Diene **26** was identified by comparison with a reference sample, see Exp. Section.

[60] The decomposition of phosphane complexes of Pd^{II} induced by fluoride is known: P. A. McLaughlin, J. G. Verkade, *Organometallics* **1998**, *17*, 5937.

[61] V. V. Grushin, *Angew. Chem.* **1998**, *110*, 1042; *Angew. Chem. Int. Ed.* **1998**, *37*, 994.

[62] We exclude a high kinetic barrier in allylic substitutions by using a small and reactive nucleophile-like "naked" fluoride.

[63] G. C. Lloyd-Jones, S. C. Stephen, M. Murray, C. P. Butts, S. Vyskocil, P. Kocovsky, *Chem. Eur. J.* **2000**, *6*, 4348.

[64] H. Hagelin, B. Åkermark, P. Norrby, *Chem. Eur. J.* **1999**, *5*, 902.

[65] L. Hintermann, PhD Dissertation, ETH Nr. 13892, Zürich, **2000**.

[66] M. F. Rettig, P. M. Maitlis, *Inorg. Synth.* **1990**, *28*, 110.
[67] J. Lukas, *Inorg. Synth.* **1974**, *15*, 75.
[68] D. J. Mabbott, B. E. Mann, P. M. Maitlis, *J. Chem. Soc., Dalton Trans.* **1977**, 294.
[69] G. M. Sheldrick, *SHELXS-97 Program for the Solution of Crystal Structures*, University of Göttingen, **1990**.
[70] G. M. Sheldrick, *SHELXL-97 Program for the Refinement of Crystal Structures*, University of Göttingen, **1997**.
[71] G. M. Sheldrick, *SADABS Program for Empirical Absorption Correction of Area Detector Data*, University of Göttingen, **1996**.

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