angles are 137.5 and 137.7°. The observed envelope conformations are clearly a result of the exceedingly long Al–P bonds (2.676 (3)/2.782 (2) Å), which have no precedent in the literature.[25] Their slight but significant inequality reflects the steric congestion around the aluminum center, the effect of which should be especially pronounced because of the inherent weakness of the Al–P bonds. These weak Al–P bonds also account for the extremely rapid fluxionality of **2**.

In conclusion, all spectroscopic and structural results for **2** are consistent with C_3P_2 pentacoordination at aluminum both in solution as in the solid state. The structural details not only reveal a tbp geometry but also indicate a rather weak Al–P bonding.

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Supplementary Material Available: Complete tables of atomic coordinates, displacement parameters, and bond distances and angles (19 pages). Ordering information is given on any current masthead page.

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Articles

Kinetics and Mechanism of Biaryl Reductive Elimination from Electron-Poor $[(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2]Pt(Ar)_2$ Complexes

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The syntheses and elimination properties of electron-deficient (fluoroaryl)- and (fluoroalkyl)phosphine complexes of platinum are described. Treatment of (cod)$PtCl_2$ with $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$ (dfppe) or $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$ (dfepe) at elevated temperatures gives the dichlorides (dfepe)$PtCl_2$ (**1**) and (dfppe)$PtCl_2$ (**2**) in high yield. The diaryls (dfppe)$Pt(Ph)_2$ (**3**) and (dfppe)Pt(p-tol)$_2$ (**4**) and the dialkyls (dfppe)$Pt(Me)_2$ (**5**) and (dfepe)$Pt(Me)_2$ (**6**) are prepared by metathesis of **1** or **2** with the appropriate Grignard reagent. Thermolysis of the diphenyl complex **3** cleanly yields biphenyl as the sole observed organic elimination product. No organic products derived from ancillary ligand degradation are observed. The fate of the released metal fragment is solvent-dependent, with the bis chelate (dfppe)$_2$Pt (**7**) being the major product in noncoordinating aromatic solvents. The crystal structure of **7** has been determined. Crossover labeling studies for **3** and the regiospecific formation of 4,4′-dimethylbiphenyl from the thermolysis of **4** confirm that these elimination reactions proceed via an intramolecular 1,1′-coupling process. Elimination kinetics for **3** and **4** are conveniently followed by ^1H NMR spectroscopy. Decomposition rates follow first-order behavior in all solvents examined and are independent of added phosphine concentration. The rate of biphenyl reductive elimination from **3** is found to be inversely proportional to solvent polarity, varying by almost a factor of 10 between benzene ($\epsilon = 2.28$, $k = [2.44\ (5)] \times 10^{-4}\ s^{-1}$) and DMSO ($\epsilon = 45.0$, $k = [2.50\ (2)] \times 10^{-5}\ s^{-1}$) media at 100 °C. Entropies of activation obtained in benzene ($\Delta S^{\ddagger} = -1.5 \pm 1$ eu) and DMSO ($\Delta S^{\ddagger} = -1.7 \pm 2$ eu) are essentially equivalent and suggest that there is no significant solvent coordination along the elimination reaction coordinate. The mechanistic interpretation of these results and comparisons with prior group 10 elimination studies are discussed.

Introduction

Transition-metal-mediated carbon–carbon bond formation is a pivotal step in many organometallic transformations.[1] Accordingly, the elementary process of reductive elimination from late-transition-metal dialkyl and diaryl complexes has been the focus of numerous mechanistic[2-8] and theoretical[8,9] investigations. Despite the

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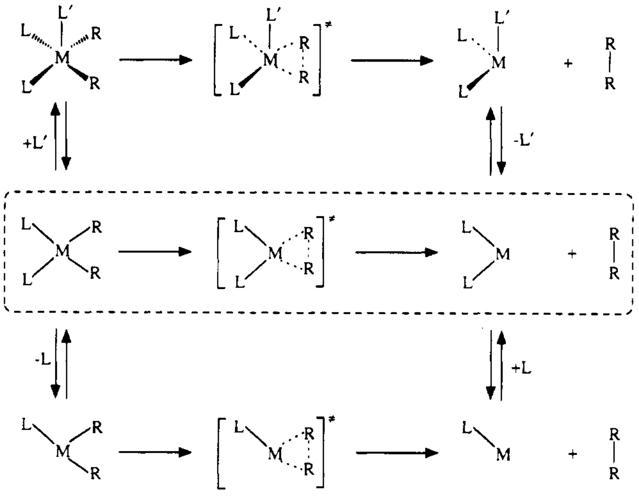
Scheme I



simplicity implied in the stoichiometry of this reaction, the intrinsically higher activation barrier for C–C bond reductive elimination relative to H–H or C–H bond elimination increases the possibility of alternative, potentially more complex competing mononuclear[10] or dinuclear[11] reaction pathways. It is perhaps for this reason that relatively few "direct" examples of dialkyl reductive elimination have been demonstrated unequivocally.

The mechanistic diversity encountered in dialkyl reductive-elimination reactions is particularly apparent in the d^8 metal series *cis*-$L_2M(R)_2$ (M = Ni, Pd, Pt; L = R_3P, py; R = Me, aryl) (Scheme I). In particular, contrasting ancillary ligand kinetic dependencies observed in a number of different systems indicate that reductive elimination may occur via three- (dissociative),[2,3] four-,[12] or five-coordinate (associative) reaction pathways.[3b,6,9b] The dependence of elimination rates on solvent polarity (or coordination ability) is similarly variable, and in at least one related system the nature of the solvent appears to govern the molecularity of the reaction.[8b] An additional complicating feature that has been noted is the reactivity of the unstable d^{10} metal elimination products toward intermolecular[13] and intramolecular C–H activation or ancillary ligand degradation.[2,7]

We have been exploring the application of degradation-resistant, sterically encumbering fluorinated alkylphosphine ligands to a variety of problems in coordination chemistry.[14] As part of our program of developing new robust hydrocarbon activation systems,[15] we have recently begun to examine the chemistry of d^8 $[(R_f)_2PCH_2CH_2P(R_f)_2]Pt(R)(R')$ (R_f = C_2F_5, C_6F_5; R, R′ = alkyl, aryl, H) compounds as precursors to highly reactive $[(R_f)_2PCH_2CH_2P(R_f)_2]Pt^0$ intermediates.[13,16] In accordance with both qualitative and theoretical expectations we find that when R = R′ = aryl, reductive elimination from platinum is quite facile in comparison to the case for more electron-rich donor phosphine analogues. In the case where R_f = pentafluorophenyl, the elimination is particularly clean and provides an ideal system for study of this basic process; herein we report the results of our kinetic and mechanistic investigations on $[(R_f)_2PCH_2CH_2P(R_f)_2]Pt(R)(R')$ elimination reactions.

Results and Discussion

Synthesis of $[(R_f)_2PCH_2CH_2P(R_f)_2]Pt(R)_2$ Complexes. Dialkyl- and diarylplatinum fluorophosphine complexes with $R_f = C_2F_5$ (dfepe) and $R_f = C_6F_5$ (dfppe) are readily prepared by alkylation of the corresponding dichlorides, $(\text{P}\frown\text{P})\text{PtCl}_2$ (eqs 1 and 2). In contrast to the

$$(\text{cod})\text{PtCl}_2 + \text{P}\frown\text{P} \xrightarrow[-\text{cod}]{\Delta} \underset{\mathbf{1,\,2}}{(\text{P}\frown\text{P})\text{PtCl}_2} \qquad (1)$$

$\text{P}\frown\text{P}$ = dfepe (**1**), dfppe (**2**)

$$(\text{P}\frown\text{P})\text{PtCl}_2 + 2\text{RMgBr} \xrightarrow[\text{Et}_2\text{O}]{} \underset{\mathbf{3\text{–}6}}{(\text{P}\frown\text{P})\text{Pt(R)}_2} \qquad (2)$$

$\text{P}\frown\text{P}$ = dfppe, R = Ph (**3**), *p*-tol (**4**), Me (**5**);
$\text{P}\frown\text{P}$ = dfepe, R = Me (**6**)

normally facile synthesis of donor phosphine complexes from $(\text{cod})\text{PtCl}_2$, the formation of $(\text{dfepe})\text{PtCl}_2$ (**1**) requires several days in refluxing xylenes to reach completion. The displacement of cod by the more basic dfppe ligand to form **2** occurs under relatively milder conditions (toluene reflux, 24 h). With the exception of $(\text{dfepe})\text{Pt(Ph)}_2$ (vide infra), treatment of the dichlorides **1** and **2** with Grignard reagents gave the corresponding alkylated derivatives in high yield. Attempts to alkylate using more reducing alkyllithium reagents were unsuccessful. Complexes **1**–**6** are readily characterized by ^{1}H and ^{31}P NMR spectroscopy. The sensitivity of platinum–ligand coupling constants to hybridization effects is well documented and has been used as a measure of relative trans influence.[17,18] For the dimethyl series $(\text{dppe})\text{PtMe}_2$ ($^1J_{\text{PtP}}$ = 1794 Hz, $^2J_{\text{PtH}}$ = 71 Hz),[18] $(\text{dfppe})\text{PtMe}_2$ ($^1J_{\text{PtP}}$ = 1608 Hz, $^2J_{\text{PtH}}$ = 75 Hz), and $(\text{dfepe})\text{PtMe}_2$ ($^1J_{\text{PtP}}$ = 1403 Hz, $^2J_{\text{PtH}}$ = 79), the pro-

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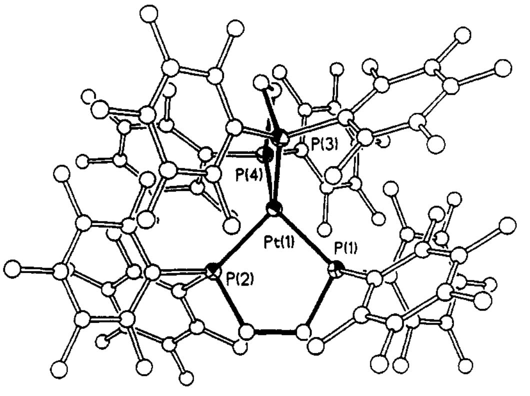

Figure 1. ORTEP view of $(dfppe)_2Pt$ (7) with atom-labeling scheme.

Table I. Summary of Crystallographic Data for $(dfppe)_2Pt$ (7)

cryst size (mm)	0.28 × 0.50 × 0.88	ρ_{calc} (g/cm^3)	1.931
		wavelength (Å)	0.71073
cryst syst	triclinic	μ (mm^{-1})	2.411
space group	$P\bar{1}$	2θ range (deg)	4–45
temp (°C)	22	scan type	$2\theta/\theta$
a (Å)	12.508 (2)	scan range (deg)	2.0
b (Å)	12.664 (2)	no. of rflns measd	9100
c (Å)	21.069 (4)	no. of unique rflns	8628
α (deg)	99.709 (14)	no. of rflns with $F > 4.0\sigma(F)$	7434
β (deg)	92.474 (14)		
γ (deg)	93.472 (13)	R_F (%)	3.89
V (Å^3)	3278.7 (10)	R_{wF} (%)	4.70
Z	2	goodness of fit	1.50

nounced decrease in $^1J_{PtP}$ together with the increase in platinum–methyl proton coupling is consistent with a lower trans influence for the fluorinated phosphine ligands.

Comparative Thermal Stabilities of *cis*-$L_2M(R)_2$ (M = Pd, Pt) Complexes. A number of reductive-elimination studies for palladium and platinum *cis*-$L_2M(R)_2$ compounds have been reported. For dimethylpalladium complexes *cis*-$(R_3P)_2Pd(Me)_2$, ethane elimination readily occurs between 45 and 80 °C, with a relative phosphine rate dependence of $k(Ph_3P) > k(Ph_2MeP) > k(Ph_2PCH_2CH_2PPh_2)$.[2,3] With the exception of cyclopropane elimination from platinacyclobutanes,[4a] dialkyl reductive elimination from platinum(II) has never been observed.[4,19] Diaryl elimination is much more facile and has been observed for several platinum *cis*-$L_2Pt(Ar)_2$ systems.[6,7] Palladium diaryls undergo rapid biaryl elimination at room temperature and have not been isolated.[20] Although reductive elimination predominates for platinum complexes when L = Ph_3P or Ph_2MeP, when L = bpy or py ancillary ligand metalation is a major competitive reaction pathway.[7,21] Reductive elimination from diphosphine complexes such as $(dppe)Pt(Ph)_2$ and $(dmpe)Pt(Ph)_2$ has not been reported.[22]

Elimination of biphenyl from $(dfppe)Pt(Ph)_2$ readily occurs at 80 °C. In contrast to previous thermolysis studies which report significant amounts of decomposition products derived from ancillary ligand degradation, potential side products such as benzene, C_6F_5H, and C_6F_5Ph have not been observed in the thermolysis of 3 by ^1H or ^{19}F NMR spectroscopy. The fate of the (dfppe)Pt fragment released from 3 after biphenyl elimination is solvent-dependent. In aromatic solvents, the bis chelate $(dfppe)_2Pt$ (7) is the only solution metal species seen by ^{31}P NMR spectroscopy. Thermolysis of 3 in toluene in the presence of 1 equiv of free dfppe cleanly produced 7 in 82% isolated yield (eq 3). The formulation of 7 as a tetrahedral

$$\underset{3}{(dfppe)Pt(Ph)_2} + dfppe \xrightarrow[\text{toluene}]{\Delta} \underset{7}{(dfppe)_2Pt} + C_{12}H_{10} \quad (3)$$

$(R_3P)_4Pt^0$ complex is consistent with the large $^1J_{PtP}$ coupling observed (4269 Hz) and has been confirmed by an X-ray structural determination. An ORTEP diagram of 7 is given in Figure 1; data collection parameters and selected bond distances and angles are given in Tables I and II, respectively. Despite widespread studies of Pt(0) systems, 7 is one of the few structurally characterized examples of a Pt(0) tetrakisphosphine complex.[23,24] The average Pt–P bond length for 7 (2.288 (2) Å) is substantially shorter than bond lengths found for the 4-coordinate Pt(0) donor phosphine complexes $(Ph_3P)_3Pt(CO)$ (average Pt–P = 2.350 (8) Å)[25] and $(EtPh_2P)_2Pt(CO)_2$ (average Pt–P = 2.360 (2) Å)[26] and is comparable to the value reported for $(dppp)_2Pt$ (Pt–P = 2.286 (1) Å).[24] The dihedral angle between the chelate planes for $(dfppe)_2Pt$ (76.5°) is less than the value of 87.2° reported for $(dppp)_2Pt$ and reflects an increased distortion away from an ideal tetrahedral geometry.

Although 7 is also the major (>75%) observed product in DMSO, a complex mixture of products is obtained in

Table II. Selected Bond Distances (Å) and Angles (deg) for $(dfppe)_2Pt$ (7)

Bond Distances			
Pt(1)–P(1)	2.293 (2)	P(2)–C(31)	1.872 (6)
Pt(1)–P(2)	2.290 (2)	P(2)–C(41)	1.869 (7)
Pt(1)–P(3)	2.284 (2)	P(3)–C(3)	1.836 (8)
Pt(1)–P(4)	2.286 (2)	P(3)–C(51)	1.865 (7)
P(1)–C(1)	1.849 (7)	P(3)–C(61)	1.868 (6)
P(1)–C(11)	1.858 (6)	P(4)–C(4)	1.855 (7)
P(1)–C(21)	1.860 (7)	P(4)–C(71)	1.855 (7)
P(2)–C(2)	1.852 (7)	P(4)–C(81)	1.868 (6)
Bond Angles			
P(1)–Pt–P(2)	89.6 (1)	P(2)–Pt–P(3)	126.0 (1)
P(1)–Pt–P(3)	112.7 (2)	P(2)–Pt–P(4)	112.9 (1)
P(1)–Pt–P(4)	130.7 (1)	P(3)–Pt–P(4)	89.4 (1)

Dihedral Angles[a]	
P(1)–Pt(1)–P(2) and P(3)–Pt(1)–P(4)	76.5
P(1)–Pt(1)–P(3) and P(2)–Pt(1)–P(4)	63.2
P(1)–Pt(1)–P(4) and P(2)–Pt(1)–P(3)	104.2

[a] Angles between the two planes shown.

Scheme II

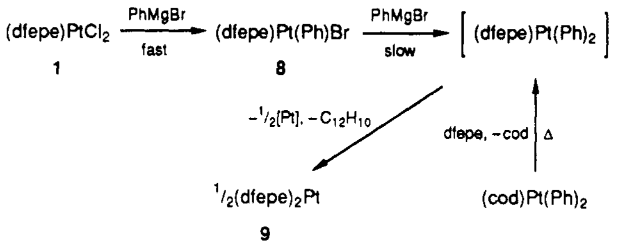

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Table III. Rate of Thermal Decomposition for (dfppe)Pt(Ph)$_2$ (3) and (dfppe)Pt(p-tol)$_2$ (4)

compd	temp (°C)	solvent, conditions	[Pt] (M)	k (10^6 s^{-1})
(dfppe)Pt(Ph)$_2$	100	benzene-d_6	0.023	244 (5)
	100	CD$_2$Cl$_2$	0.032	76.2 (5)
	100	CD$_2$Cl$_2$	0.062	78.0 (4)
	100	CD$_2$Cl$_2$, 2 equiv of dfppe	0.032	82.0 (8)
	100	acetone-d_6	0.032	36.4 (4)
	100	DMSO-d_6	0.032	25.0 (2)
	90	DMSO-d_6	0.032	8.9 (2)
(dfppe)Pt(p-tol)$_2$	90	DMSO-d_6	0.032	20.6 (4)

acetone. The primary (ca. 50%) thermolysis product of **3** in dichloromethane is the dichloride **2**. Thermolysis of **3** in the presence of 2 equiv of dfppe in dichloromethane afforded a 2:1 mixture of **7** and **2**, consistent with competitive trapping of a reactive (dfppe)Pt intermediate. In cases where the disproportionation product **7** is formed in the absence of added dfppe, a small amount of insoluble white precipitate is also observed.

Reductive elimination was anticipated to be more facile for (dfepe)Pt(Ph)$_2$ due to the substantially lower net donor ability of dfepe relative to that of dfppe. However, attempts to prepare (dfepe)Pt(Ph)$_2$ were unsuccessful. Treatment of (dfepe)PtCl$_2$ with 2 equiv of PhMgBr at room temperature for 12 h gave a 5:2 mixture of (dfepe)-Pt(Ph)Br (**8**) and the bis chelate (dfepe)$_2$Pt (**9**), presumably formed through the intermediacy of thermally unstable (dfepe)Pt(Ph)$_2$ (Scheme II). Generation of the bromide **8** via halogen exchange with PhMgBr may occur either concurrent with or subsequent to arylation. Monitoring the reaction of **1** with excess PhMgBr in THF by ^{31}P NMR spectroscopy revealed that the conversion of **1** to **8** is complete within minutes at 20 °C and is followed by the slow formation of **9**. No phosphorus resonance attributable to the intermediate (dfepe)Pt(Ph)$_2$ was observed, consistent with a rate-determining final alkylation step prior to elimination and disproportionation. A mixture of **9** and biphenyl was similarly obtained from the reaction of (cod)Pt(Ph)$_2$ with dfepe in refluxing toluene. Although the elimination of biphenyl from (dfepe)Pt(Ph)$_2$ has not been observed directly, the alkylation results suggest that (dfepe)Pt(Ph)$_2$ has a limited thermal stability at ambient temperature, reminiscent of palladium diaryl complexes. This qualitative comparison suggested that ethane elimination from (dfepe)Pt(Me)$_2$ (**6**) might be observable. However, no decomposition was seen for **5** or **6** after prolonged heating to 150 °C in toluene. Slow decomposition of **6** to give a platinum mirror occurred at 180 °C after several days.

Labeling Studies. In view of the quantitative and direct nature of diaryl eliminations found for (dfppe)Pt(Ph)$_2$, a more careful study of the underlying mechanism was undertaken. The intramolecularity of diaryl elimination has been probed by examining the thermolysis of an equimolar mixture of (dfppe)Pt(C$_6$H$_5$)$_2$ and (dfppe)-Pt(C$_6$D$_5$)$_2$ in toluene at 90 °C. After 12 h, mass spectrometry of the product solution indicated that biphenyl-d_0 and biphenyl-d_{10} were produced exclusively, with less than 2% biphenyl-d_5 observed. The regiospecificity of elimination was addressed by examining the thermolysis of (dfppe)Pt(p-tol)$_2$ (**4**). The only organic product detected by ^{1}H NMR spectroscopy in the thermal decomposition of **4** was 4,4′-dimethylbiphenyl. Taken together, these results are consistent with a simple concerted 1,1′-reductive elimination of diaryl in the systems examined.

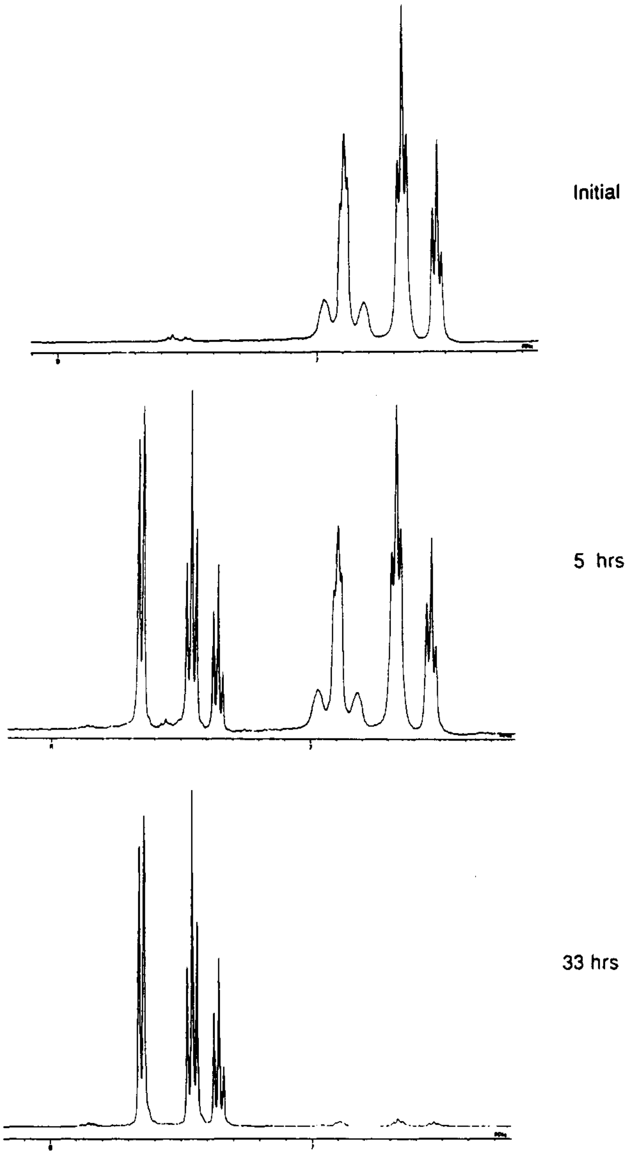

Figure 2. Aryl region of ^{1}H NMR spectra for (dfppe)Pt(Ph)$_2$ thermolysis in DMSO at 100 °C.

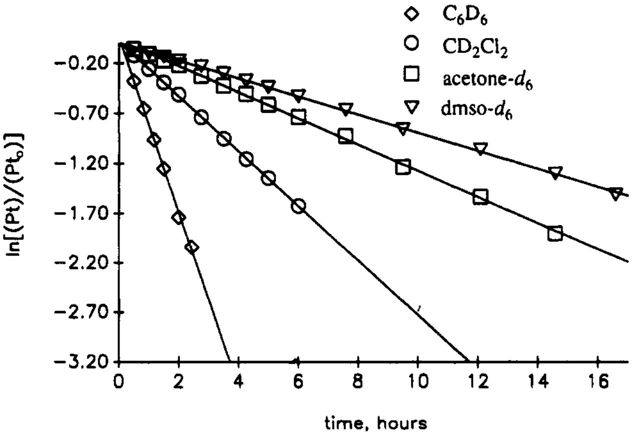

Figure 3. Solvent-dependent thermal decomposition of (dfppe)Pt(Ph)$_2$ (3) at 100 °C.

Kinetic Studies. The aromatic proton resonances for diaryl complexes **3** and **4** are shifted well upfield from those of the biaryl thermolysis products and allow the extent of reaction to be readily monitored by ^{1}H NMR spectroscopy (Figure 2). A particular advantage of the (fluoroaryl)-phosphine ligand is that the aryl region of interest is not obscured by ligand resonances. Kinetic data are summarized in Table III and in Figures 3 and 4. Decomposition

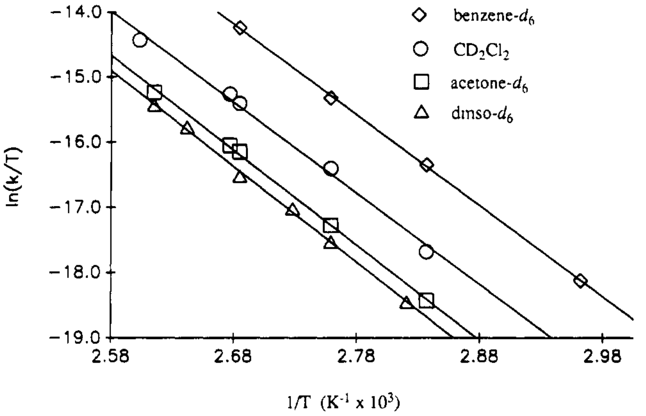

Figure 4. Arrhenius plots for the thermolysis of (dfppe)Pt(Ph)$_2$ (3) in four different solvents. The activation parameters obtained are as follows: for C_6D_6, $\Delta H^\ddagger$ = 27.6 ± 1 kcal mol^{-1}, $\Delta S^\ddagger$ = -1.5 ± 1 eu; for CD_2Cl_2 $\Delta H^\ddagger$ = 27.8 ± 1 kcal mol^{-1}, $\Delta S^\ddagger$ = -3.5 ± 4 eu; for acetone-d_6, $\Delta H^\ddagger$ = 29.0 ± 1 kcal mol^{-1}, $\Delta S^\ddagger$ = -1.8 ± 1.5 eu; for DMSO-d_6, $\Delta H^\ddagger$ = 29.2 ± 1 kcal mol^{-1}, $\Delta S^\ddagger$ = -1.7 ± 2 eu.

of 3 follows first-order behavior in all solvents examined, with no deviation from linearity evident over more than 3 half-lives.

The observed rate of decomposition is only slightly dependent on added dfppe. Enhanced elimination via association to form a higher coordinate species such as (η^1-dfppe)(η^2-dfppe)Pt(Ph)$_2$ is unlikely due to the sterically encumbering nature of the dfppe ligand (θ = 151°) and its intrinsically lower basicity.[14a,27] In a dissociative mechanism, the addition of free dfppe to 3 would not be expected to compete effectively for a coordination site in (η^1-dfppe)Pt(Ph)$_2$ due to the high effective concentration of the pendant phosphine group. However, monitoring 3 by ^{31}P NMR spectroscopy under thermolysis conditions reveals no decrease in the observed $^1J_{PtP}$ coupling constant from its room-temperature value, suggesting that chelate dissociation does not occur to a significant extent. The relative elimination rate observed for the more electron-releasing bis(tolyl) 4 versus the parent diphenyl 3 (k(4)/k(3) = 2.3) is comparable to that reported for $(Ph_3P)_2Pt(Ar)_2$ systems (k(tol)/k(Ph) = 1.6)[6a] and is in accord with prior theoretical and kinetic $L_2M(R)_2$ studies.[3a,6c,9]

Solvent Effects and Activation Parameters. The systematic study of kinetic solvent effects provides a useful probe of reaction mechanism and transition-state properties. Although Stille has previously investigated the role of solvent in $(R_3P)_2Pd(Me)_2$ eliminations,[2] competitive displacement of phosphine by polar solvents to form $(R_3P)(solv)Pd(Me)_2$ intermediates preempts any meaningful interpretation of simple outer-sphere solvent effects. A solvent-dependence study on eliminations from substitutionally inert (dppe)Pd(Me)$_2$ or other related chelated systems would address this question.[28]

As shown in Figure 3, the rate of reductive elimination for (dfppe)Pt(Ph)$_2$ exhibits a moderate solvent dependence. An approximately 10-fold elimination rate enhancement in nonpolar solvents (benzene, ϵ = 2.28, k = [2.44 (5)] × 10^{-4} s^{-1}) over polar solvents (DMSO, ϵ = 45.0, k = [2.50 (2)] × 10^{-5} s^{-1}) at 100 °C is comparable to that reported for $(MePh_2P)_2Pd(Me)_2$. Although Whitesides has observed anomalous promoted reductive elimination behavior for $(Bu_3P)_2Pt(CH_2)_4$ in CH_2Cl_2 due to C–Cl bond oxidative addition,[4b] the relative elimination rate observed for 3 in CH_2Cl_2 is consistent with its intermediate polarity (ϵ = 9.08).[29]

Table IV. Solvent-Dependent ^{31}P NMR Data for (dfppe)Pt(Ph)$_2$ (3)

solvent	dielectric constant, ϵ	δ (ppm)	$^1J_{PtP}$ (Hz)
benzene-d_6	2.28	14.5	1518
chloroform-d	4.81	14.1	1534
dichloromethane-d_2	9.08	14.5	1558
acetone-d_6	20.7	15.6	1574
DMSO-d_6	45.0	15.1	1590

Kinetic solvent effects on the reductive elimination from 3 may be attributable to either inner-sphere (solvent coordination) or outer-sphere (solvent reorganization or solvation) interactions. Direct solvent adduct formation to form the stabilized 5-coordinate complex (dfppe)Pt(Ph)$_2$(solv) in either the ground state or transition state should be reflected in changes of the entropy of activation, $\Delta S^\ddagger$. However, as seen from Figure 4, there is essentially no difference in $\Delta S^\ddagger$ for the thermolysis of 3 in coordinating ($\Delta S^\ddagger$(DMSO) = -1.7 ± 2 eu) and noncoordinating ($\Delta S^\ddagger$(benzene) = -1.5 ± 1 eu) media. Any significant solvent adduct formation in the ground state should also be reflected in the observed $^1J_{PtP}$ coupling constants for 3, which provide a sensitive measure of coordination changes about platinum. As shown in Table IV, a regular monotonic increase in $^1J_{PtP}$ is in fact observed on going from benzene to DMSO solvent. However, the range of variation is less than 5% and can be readily attributed to nonspecific solvent van der Waals interactions.[30]

Theoretical descriptions of reductive elimination from group 8 $L_2M(R)_2$ complexes indicate that the M–C bonds are largely covalent and that elimination occurs via an essentially isopolar transition state. However, since comparable solvent effects have also been observed in isopolar organic transformations, a differential stabilization of ground-state and excited-state complex dipoles may be sufficient to explain the observed solvent trends.[31] A dipole decrease in the transition state relative to the ground state would result in the observed solvent dependence. This change in dipole is consistent with the expected transfer of charge from the donor aryl groups to the metal prior to biaryl loss.[9]

The small negative $\Delta S^\ddagger$ found for 3 in all solvents compares favorably with values reported for a variety of other reductive-elimination systems. C–H coupling activation parameters for $(\eta^5-C_5H_5)_2W(H)Me$ ($\Delta S^\ddagger$ = -4 (1) eu)[32] and $(Ph_3P)_2Pt(H)CH_2CF_3$ ($\Delta S^\ddagger$ = 2–8 (3) eu)[28] and C–C coupling parameters for $(\eta^5-C_5Me_5)Ru(NO)Ph_2$ ($\Delta S^\ddagger$ = -7 (2) eu)[5] and $(Cy_3P)_2Pt(CH_2C(Me)_2CH_2)$ ($\Delta S^\ddagger$ = 4 (2) eu)[4a] fall in the range of ±10 eu. In contrast, activation values reported by Young for *cis*-$(Ph_3P)_2Pt(p\text{-tol})_2$ ($\Delta S^\ddagger$ = -24 (4) eu)[6a] and *cis*-$(py)_2Pt(p\text{-}C_6H_4CF_3)_2$ ($\Delta S^\ddagger$ = -24 (3) eu) are significantly more negative. This difference was attributed to a loss of conformational freedom of the aryl groups in the transition state; however, in view of our results this interpretation does not appear to be reasonable.

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(27) An inverse correlation between phosphine-promoted reductive elimination and phosphine size has been noted in $L_2Ni(Me)(Ar)$ systems.[3b]

(28) For the alkyl hydride $(Ph_3P)_2Pt(H)CH_2CF_3$, a mild inhibition of elimination rate in polar solvents has been observed. In this system phosphine loss does not occur prior to fluoroalkane elimination: Michelin, R. A.; Faglia, S.; Uguagliati, P. *Inorg. Chem.* **1983**, *22*, 1831.

(29) The elimination rate of 3 in $CHCl_3$ (ϵ = 4.81) is also qualitatively observed to be intermediate between those in benzene and CH_2Cl_2.

(30) Jameson, C. J. In *Multinuclear NMR*; Mason, J., Ed.; Plenum Press: New York, 1987; Chapter 4.

(31) For a detailed discussion of kinetic solvent effects for organic systems, see: Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed.; VCH: New York, 1988; Chapter 5.

(32) Bullock, R. M.; Headford, C. E. L.; Hennessy, K. M.; Kegly, S. E.; Norton, J. R. *J. Am. Chem. Soc.* **1989**, *111*, 3897.

Summary

Chelating (perfluoroaryl)phosphine complexes (dfppe)$\mathrm{Pt(Ar)_2}$ have proven to be ideally suited for the study of reductive elimination in 4-coordinate group 10 systems. Kinetic and mechanistic results indicate that, for this system, elimination occurs without phosphine loss or significant solvent association via a simple concerted 1,1′-coupling process. Although both theory and conventional wisdom predict a correlation between lowered ancillary ligand donor ability and ease of reductive elimination, this has not yet been clearly demonstrated for $\mathrm{L_2M(R)_2}$ compounds. Decomposition rates for $\mathrm{(Ph_3P)_2Pt(Ar)_2}$ do not provide a useful comparison with (dfppe)$\mathrm{Pt(Ar)_2}$ due to an energetically unfavorable restriction of the P–Pt–P angle throughout the reaction coordinate.[9] Interestingly, the greater stability of (dppe)$\mathrm{PdMe_2}$ relative to $\mathrm{(MePh_2P)_2PdMe_2}$ has been ascribed to its greater difficulty in achieving a more reactive 3-coordinate geometry but may in fact be at least partially attributable to a restricted coordination geometry.[33] It is unfortunate that no direct kinetic information on a donor chelating system such as (dppe)$\mathrm{Pt(Ar)_2}$ is currently available.[34]

A general goal in inorganic and organometallic coordination chemistry is to predict reactivity and structural trends following broad guidelines. Historically, it is not uncommon to find that conclusions based on a limited array of environmental variables and transition-metal systems are quite specific to the particular complexes examined and often do not afford any general applicability. In particular, a major continuing problem is the separation of steric and electronic effects. Comparisons between sterically unencumbered electron-poor carbonyl systems and more bulky donor phosphine systems are a classic case in point. In the present study we have shown that (fluoroalkyl)phosphine complexes potentially offer a broader spectrum of reactivity for systematic study and comparison with sterically equivalent donor phosphine analogues.

Experimental Section

General Procedures. All manipulations were conducted under an atmosphere of nitrogen using Schlenk, high-vacuum-line, and/or glovebox techniques. Dry, oxygen-free solvents were vacuum-distilled prior to use. Elemental analyses were performed by Desert Analytics. Infrared spectra were recorded on a Mattson Cygnus 100 or Perkin-Elmer 1600 FTIR instrument as Nujol mulls. NMR spectra were obtained with a JEOL JNM-FX270 or GSX-400 instrument. ^{31}P spectra were referenced to an 85% $\mathrm{H_3PO_4}$ external standard. ^{19}F spectra were referenced to $\mathrm{CF_3CO_2Et}$ as an internal standard (−75.32 ppm vs $\mathrm{CFCl_3}$, with downfield chemical shifts taken to be positive). Mass spectral analyses were performed using a Hewlett-Packard 5995A GC/MS instrument. (cod)$\mathrm{PtCl_2}$[35] and $\mathrm{(R_f)_2PCH_2CH_2P(R_f)_2}$ ($\mathrm{R_f = C_6F_5, CF_3CF_2}$)[14a] were prepared by following literature procedures.

(dfepe)PtCl$_2$ (1). A solution of (cod)$\mathrm{PtCl_2}$ (1.058 g, 2.84 mmol) and dfepe (1.76 g, 3.12 mmol) in 70 mL of xylene was refluxed under nitrogen. After 5 days the reaction mixture was cooled to room temperature and the insoluble white crystalline product was filtered off and washed several times with ether in order to remove a small amount of a green impurity. The yield of **1** after drying was 2.158 g (92%). (dfepe)$\mathrm{PtCl_2}$ is air-stable and is only sparingly soluble in polar organic solvents. Anal. Calcd for $\mathrm{C_{20}H_4F_{20}PtP_2Cl_2}$: C, 14.44; H, 0.48. Found: C, 14.85; H, 0.51. IR (cm^{-1}): 1296 s, 1217 s, 1129 s, 975 s, 753 m, 520 m. ^{1}H NMR (acetone-d_6, 269.7 MHz, 22 °C): δ 3.39 (m, $\mathrm{PC}H_2$). ^{31}P NMR (acetone-d_6, 109.1 MHz, 22 °C): δ 68.3 (m, $^1J_{\mathrm{PtP}}$ = 3362 Hz). ^{19}F NMR (acetone-d_6, 376.05 MHz, 22 °C): δ −77.05 (s, $\mathrm{CF_2C}F_3$), −108.10 (ABX pattern, $^2J_{\mathrm{FF}}$ = 314 Hz, $\mathrm{C}F_2\mathrm{CF_3}$).

(dfppe)PtCl$_2$ (2). A solution of (cod)$\mathrm{PtCl_2}$ (1.190 g, 3.19 mmol) and dfppe (2.424 g, 3.19 mmol) in 70 mL of toluene was refluxed under nitrogen. After 24 h, workup identical with that described for **1** gave 2.699 g of white crystalline **2** (83%). Anal. Calcd for $\mathrm{C_{22}H_4F_{20}PtP_2Cl_2}$: C, 27.07; H, 0.41. Found: C, 26.84; H, 0.69. IR (cm^{-1}): 1682 s, 1519 m, 1296 m, 1096 s, 978 s, 532 m. ^{1}H NMR (acetone-d_6, 269.7 MHz, 22 °C): δ 3.28 (m, $\mathrm{PC}H_2$). ^{31}P NMR (acetone-d_6, 109.1 MHz, 22 °C): δ 17.4 (s, $^1J_{\mathrm{PtP}}$ = 3656 Hz).

(dfppe)Pt(Ph)$_2$ (3). A slurry of **2** (0.450 g, 0.439 mmol) in 25 mL of ether was cooled to −78 °C, and a 3.0 M solution of PhMgBr (0.33 mL, 1.0 mmol) was added slowly by syringe. The reaction mixture was warmed to room temperature over a period of 8 h. The ether was removed and the residue taken up in dichloromethane and filtered. The volume of the dichloromethane was reduced, and ether was slowly added to give **3** as a white precipitate (0.200 g, 41%). Note: Attempts to prepare **3** from **2** and PhMgBr in tetrahydrofuran gave a 1:1 solvated product. Anal. Calcd for $\mathrm{C_{38}H_{14}F_{20}PtP_2}$: C, 41.21; H, 1.27. Found: C, 41.51; H, 1.11. IR (cm^{-1}): 1643 m, 1518 s, 1299 m, 1096 s, 980 s. ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 269.7 MHz, 22 °C): δ 6.96 (ps t, $^3J_{\mathrm{HH}}$ = 6 Hz, $^3J_{\mathrm{PtH}}$ = 61 Hz, 4 H, o-Pt($\mathrm{C_6}H_5$)), 6.72 (ps t, $^3J_{\mathrm{HH}}$ = 7 Hz, 4 H, m-Pt($\mathrm{C_6}H_5$)), 6.60 (ps t, $^3J_{\mathrm{HH}}$ = 7 Hz, 2 H, p-Pt($\mathrm{C_6}H_5$)), 2.81 (m, 4 H, $\mathrm{PC}H_2$). ^{31}P NMR ($\mathrm{CDCl_3}$, 109.1 MHz, 22 °C): δ 14.1 (s, $^1J_{\mathrm{PtP}}$ = 1534 Hz). ^{19}F NMR (benzene-d_6, 376.05 MHz, 22 °C): δ −128.8 (d, $^3J_{\mathrm{FF}}$ = 18 Hz; o-$\mathrm{C_6}F_5$), −146.0 (t, $^3J_{\mathrm{FF}}$ = 20 Hz; p-$\mathrm{C_6}F_5$), −158.9 (br t, $^3J_{\mathrm{FF}}$ ≈ 22 Hz, m-$\mathrm{C_6}F_5$).

(dfppe)Pt(C$_6$D$_5$)$_2$ (3a) was prepared as described above for **3** from **2** and $\mathrm{C_6D_5MgBr}$ (0.5 M in ether, 99+ atom %, Aldrich). The chemical purity of **3a** was verified by ^{1}H and ^{31}P NMR spectroscopy. The isotopic purity was confirmed by mass spectroscopy.

(dfppe)Pt(p-C$_6$H$_4$Me)$_2$ (4). Using the procedure described for **3**, the reaction of **2** (0.252 g, 0.271 mmol) with 0.55 mL of 1.0 M p-$\mathrm{MeC_6H_4MgBr}$ in ether afforded 0.190 g (67%) of **4**. Anal. Calcd for $\mathrm{C_{40}H_{18}F_{20}PtP_2}$: C, 42.31; H, 1.59. Found: C, 42.13; H, 1.40. ^{1}H NMR ($\mathrm{CDCl_3}$, 269.7 MHz, 22 °C): δ 6.83 (m, $^3J_{\mathrm{PtP}}$ = 64 Hz, 4 H; o-$\mathrm{C_6}H_4\mathrm{Me}$), 6.58 (br d, $^3J_{\mathrm{HH}}$ = 6 Hz, 4 H, m-$\mathrm{C_6}H_4\mathrm{Me}$), 2.78 (m, 4 H, $\mathrm{PC}H_2$), 2.02 (br s, 6 H; $\mathrm{C_6H_4}Me$). ^{31}P NMR ($\mathrm{CDCl_3}$, 109.1 MHz, 22 °C): δ 13.8 (s, $^1J_{\mathrm{PtP}}$ = 1527 Hz).

(dfppe)PtMe$_2$ (5). A slurry of **2** (0.522 g, 0.510 mmol) in 30 mL of diethyl ether at −78 °C was treated with 0.39 mL of 3.0 M MeMgBr, and the mixture was warmed to ambient temperature. After 2 h the reaction mixture was quenched with aqueous $\mathrm{NH_4Cl}$ and the volatiles were removed under vacuum. Extraction of the residue with $\mathrm{CH_2Cl_2}$ and precipitation from $\mathrm{CH_2Cl_2/Et_2O}$ gave 0.323 g (58%) of **5** as a pure white solid. Anal. Calcd for $\mathrm{C_{28}H_{10}F_{20}PtP_2}$: C, 34.20; H, 1.03. Found: C, 34.26; H, 0.86. ^{1}H NMR (acetone-d_6, 400 MHz, 22 °C): δ 3.01 (m, 4 H, $\mathrm{PC}H_2$), 0.64 (br s, $^2J_{\mathrm{PtH}}$ = 76 Hz, 6 H, $\mathrm{PtC}H_3$). ^{31}P NMR (acetone-d_6, 109.1 MHz, 22 °C): δ 20.5 (br s, $^1J_{\mathrm{P5P}}$ = 1608 Hz). ^{13}C NMR (acetone-d_6, 100.60 MHz, 22 °C): δ 148.1 (d, $^1J_{\mathrm{CF}}$ = 250 Hz), 144.2 (d, $^1J_{\mathrm{CF}}$ = 257 Hz), 138.9 (d, $^1J_{\mathrm{CF}}$ = 253 Hz), 105.9 (s), 30.4 (tt, $^1J_{\mathrm{CH}}$ = 136 Hz, J_{PH} = 24 Hz, $\mathrm{P}C\mathrm{H_2}$), 3.1 (partially resolved AA′XX′M$_3$, $^2J_{\mathrm{CP}}$(trans) + $2J_{\mathrm{CP}}$(cis) ≈ 120 Hz, $^1J_{\mathrm{PtC}}$ = 326 Hz, $^1J_{\mathrm{CH}}$ = 127 Hz, $\mathrm{Pt}C\mathrm{H_3}$). ^{19}F NMR (acetone-d_6, 376.05 MHz, 22 °C): δ −129.1 (d, $^3J_{\mathrm{FF}}$ = 17 Hz, o-$\mathrm{C_6}F_5$), −149.1 (t, $^3J_{\mathrm{FF}}$ = 20 Hz, p-$\mathrm{C_6}F_5$), −160.7 (br t, $^3J_{\mathrm{FF}}$ ≈ 18 Hz, m-$\mathrm{C_6}F_5$).

(dfepe)PtMe$_2$ (6). By the procedure described for **5**, 0.490 g of **1** in diethyl ether was treated with 0.41 mL of 3.0 M MeMgBr. After quenching and extraction of the reaction mixture with $\mathrm{CH_2Cl_2}$, precipitation from a $\mathrm{CH_2Cl_2}$/pentane mixture at −78 °C afforded 0.465 g (60%) of **6**. Anal. Calcd for $\mathrm{C_{12}H_{10}F_{20}PtP_2}$: C, 18.22; H, 1.27. Found: C, 18.21; H, 1.28. ^{1}H NMR (acetone-d_6, 269.7 MHz, 22 °C): δ 2.87 (m, 4 H, $\mathrm{PC}H_2$), 1.06 (t, $^2J_{\mathrm{PtH}}$ = 79 Hz, $^3J_{\mathrm{PH}}$ = 6 Hz, 6 H, $\mathrm{PtC}H_3$). ^{31}P NMR (acetone-d_6, 109.1 MHz, 22 °C): δ −74.2 (m, $^1J_{\mathrm{PtP}}$ = 1403 Hz).

(dfppe)$_2$Pt (7). A mixture of 210 mg (0.190 mmol) of **3** and 178 mg (0.235 mmol) of dfppe was heated to reflux in 20 mL of toluene for 3 days. After the reaction mixture was cooled, the volatiles were removed under vacuum and the solid residue was

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(33) Note: A pronounced chelate ring size effect has been observed for elimination rates of $\mathrm{(Ph_2P(CH_2)_nPPh_2)NiMe_2}$.[3d]

(34) Photoassisted reductive elimination from $(\overset{\frown}{\mathrm{P\;P}})\mathrm{Pt(Ar)_2}$ systems has been reported by Brune: (a) Brune, H. A.; Hupfer, E.; Schmidtberg, G.; Baur, A. *J. Organomet. Chem.* **1992**, *424*, 225. (b) Klotzbücher, R.; Brune, H. A. *J. Organomet. Chem.* **1986**, *299*, 1986.

(35) McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6521.

kept under dynamic vacuum for 12 h to remove the biphenyl side product. The remaining solid was extracted with several portions of CH_2Cl_2, filtered, and concentrated to ca. 3 mL. Slow addition of diethyl ether at −78 °C precipitated **7** as a light yellow powder. The isolated yield after drying in vacuo was 263 mg (81%). Anal. Calcd for $C_{38}H_{14}F_{20}P_2Pt$: C, 36.30; H, 0.52. Found: C, 36.49; H, 0.47. ^1H NMR ($CDCl_3$, 269.7 MHz, 22 °C): δ 2.98 (m, PCH_2). ^{31}P NMR (acetone-d_6, 109.1 MHz, 22 °C): δ −7.8 (s, $^1J_{PtP}$ = 4240 Hz). ^{19}F NMR (acetone-d_6, 376.05 MHz, 22 °C): δ −130.7 (br s, o-C_6F_5), −152.5 (t, $^3J_{FF}$ = 20 Hz, p-C_6F_5), −162.4 (t, $^3J_{FF} \approx$ 20 Hz, m-C_6F_5).

(dfepe)Pt(Ph)Br (8). A 0.42-mL amount of PhMgBr in ether (3.0 M, 1.3 mmol) was added dropwise to a slurry of 0.500 g of (dfepe)$PtCl_2$ (0.602 mmol) in 15 mL of THF at −78 °C. After the addition was complete, the solution was slowly warmed to ambient temperature and stirred an additional 1 h. The excess Grignard reagent was quenched with NH_4Cl/THF, and the volatiles were removed under vacuum. The residue was extracted with CH_2Cl_2, and the filtrate was concentrated to ca. 2 mL and cooled to −78 °C. The resulting white precipitate was filtered off, washed twice with ether, and then dried under vacuum; crude yield 0.420 g (80%). Recrystallization from CH_2Cl_2 afforded an analytically pure sample of **8**. Anal. Calcd for $C_{16}H_9BrF_{20}P_2Pt$: C, 20.93; H, 0.99. Found: C, 20.96; H, 0.92. ^1H NMR (acetone-d_6, 269.7 MHz, 22 °C): δ 7.23 (m, 2 H, o-Pt(C_6H_5)), 7.14 (m, 2 H, m-Pt(C_6H_5)), 6.95 (m, 1 H, p-Pt(C_6H_5)), 2.90–3.40 (m, 4 H, PCH_2). ^{31}P NMR (C_6D_6, 109.1 MHz, 22 °C): δ 68.5 (m, $^1J_{PtP}$ = 1275 Hz), 57.8 (m, $^1J_{PtP}$ = 4130 Hz). ^{19}F NMR (acetone-d_6, 376.05 MHz, 22 °C): δ −78.13 (s, PCF_2CF_3), −78.51 (s, PCF_2CF_3), −105 to −110 (overlapping ABX multiplets, PCF_2CF_3).

(dfepe)$_2$Pt (9). A mixture of (cod)Pt(Ph)$_2$ (0.517 g, 1.13 mmol) and dfepe (0.673 g, 1.19 mmol) in toluene was heated to reflux. After 72 h, the solvent was removed under vacuum. Sublimation of the residue (50 °C, 10^{-4} Torr) yielded biphenyl (104 mg, 67% of theoretical yield). The remaining unsublimed material was taken up in hexane and filtered. When the solution was cooled to −78 °C, a small amount of **9** was obtained as a white precipitate. Anal. Calcd for $C_{20}H_8F_{40}P_4Pt$: C, 18.10; H, 0.61. Found: C, 18.31; H, 0.60. ^1H NMR ($CDCl_3$, 269.7 MHz, 22 °C): δ 2.33 (m, PCH_2). ^{31}P NMR (acetone-d_6, 109.1 MHz, 22 °C): δ 52.5 (m, $^1J_{PtP}$ = 4150 Hz).

Kinetic Studies. Kinetic runs were followed by ^1H NMR spectroscopy. In a typical experiment, 14 mg of recrystallized **3** was placed in a dry 5-mm medium-wall NMR tube (Wilmad), 0.4 mL of dried and degassed deuterated solvent was added by vacuum transfer at −78 °C, and the tube was sealed off under 200 Torr of N_2 with a torch. A concurrent series of NMR samples were completely immersed in an insulated oil bath fitted with a Braun Thermomix 1480 heater circulator. Temperatures were maintained constant to within ±0.1 °C. ^1H NMR spectra were obtained on a JEOL GSX 400-MHz instrument at regular intervals, and thermolyses were generally followed for a minimum of 2 half-lives. Product distributions of t_∞ samples were analyzed by ^1H, ^{19}F, and ^{31}P NMR spectroscopy. Kinetic rate and statistical data were obtained using the programs KINANN and KINPAR 3.01, which were kindly provided by Prof. Jack R. Norton.

Crystal Structure of (dfppe)$_2$Pt·3C_6H_6. X-ray data were collected on a Nicolet R3m/V automated diffractometer system with a dedicated MicroVAX II computer system. The radiation used was Mo Kα monochromatized by a highly ordered graphite crystal. All computations used the SHELXTL PLUS (Version 3.4) program library (Nicolet Corp., Madison, WI).

A yellow prism (0.28 × 0.50 × 0.88 mm) of **7** was obtained by slow evaporation from benzene solution. Triclinic unit cell dimensions were derived from a least-squares fit of 50 random reflections ($20° \leq 2\theta \leq 30°$). The calculated unit cell density was consistent with a centrosymmetric triclinic cell, which was confirmed by the subsequent solution and refinement. Data were collected between 4 and 45° using the 2θ–θ scan technique with a variable scan rate of 5.0–30.0° min^{-1}. Three standard reflections monitored after every 100 data collected showed no systematic vibration; the R value for averaging 472 redundant data was 0.015. Data were corrected for absorption using an empirical ellipsoidal model based on ψ scans for 12 reflections with $8° \leq 2\theta \leq 45°$, with T_{max}/T_{min} = 0.069/0.038.

The structure of **7** was solved using the SHELXTL PLUS direct methods program, which revealed almost all the non-hydrogen atoms on the initial E map. All remaining non-hydrogen atoms were located in subsequent difference Fourier maps. With the exception of the chelate backbone, all carbon atoms were refined isotropically. All other non-hydrogen atoms were refined anisotropically. A total of three benzene molecules of crystallization were located, with one residing on a center of symmetry. Chelate backbone hydrogen atom positions were added in ideal calculated positions with d(C–H) = 0.96 Å and common isotropic thermal parameters fixed at 0.07. Each benzene molecule was refined using a separate free-variable common isotropic carbon thermal parameter with hydrogen thermal parameters set at 1.1 times this free variable. In the final refinement all shift/esd ratios were less than 0.036 with no unusually high variable correlations apparent. The final R indices were R = 3.89% and R_w = 4.70%, with a goodness of fit of 1.50. The largest electron density peak observed on the final Fourier difference map was 1.19 e/Å^3 and was due to uncompensated absorption for the heavy platinum atom.

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Supplementary Material Available: A complete tabulation of thermolysis rate data for **3** (Table S1) and complete X-ray data collection parameters (Table S2), atomic coordinates (Table S3), bond distances (Table S4), bond angles (Table S5), anisotropic thermal parameters (Table S6), and hydrogen atom coordinates and isotropic thermal parameters (Table S7) for **7** (11 pages). Ordering information is given on any current masthead page.

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