1,2-Bis{(pentafluorophenyl)phenylphosphino}ethane: A Probe for Configurational Stability in Three-Legged Piano Stool Complexes

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The pentafluorophenyl-substituted diphosphine $(C_6F_5)PhPCH_2CH_2PPh(C_6F_5)$ has been prepared, as a 1:1.7 mixture of *rac* (**1a**) and *meso* (**1b**) isomers, in four steps from dppe. The reaction between $[Cp^*RhCl(\mu\text{-}Cl)]_2$ and **1** in the presence of tetrafluoroborate yielded a mixture of racemic diastereoisomers of $[Cp^*RhCl(\kappa P,\kappa P\text{-}\mathbf{1a})][BF_4]$ (**4a·BF$_4$**) and *trans* and *cis* isomers of $[Cp^*RhCl(\kappa P,\kappa P\text{-}\mathbf{1b})][BF_4]$ (**4b·BF$_4$** and **4c·BF$_4$**, respectively). On addition of Proton Sponge, **4a** and **4c**, in which at least one pentafluorophenyl group is close to the pentamethylcyclopentadienyl ligand, underwent rapid dehydrofluorinative carbon−carbon coupling giving *trans*- and *cis*-$[\{\eta^5,\kappa P,\kappa P\text{-}C_5Me_4CH_2C_6F_4\text{-}2\text{-}PPhCH_2CH_2PPh(C_6F_5)\}RhCl]^+$ (**5** and **6**), respectively. The latter underwent further dehydrofluorinative carbon−carbon coupling to give two isomers of $[\{\eta^5,\kappa P,\kappa P\text{-}C_5Me_3[CH_2C_6F_4\text{-}2\text{-}PPhCH_2]_2\}RhCl]^+$ (**7**). Isomerization of **4b** to **4c** was observed in chloroform and dimethlysulfoxide. Neither isomerization of **4a** to **4b** or **4c** nor isomerization of **5** to **6** was observed at ambient or elevated temperature in dimethyl sulfoxide. The results provide the first evidence that complexes of $\eta^5,\kappa P,\kappa L$-cyclopentadienyl-phosphine-donor ligands are configurationally stable at high temperature.

Introduction

The study of the epimerization of three-legged piano stool complexes containing stereogenic metal centers, $[(\eta^n\text{-}C_nR_n)MX(LL')]^{m+}$ ($n = 5$ or 6),[1−6] is important to the development of their use as stereoselective catalysts.[7,8] These complexes have been shown to undergo inversion at the metal with widely different rates, and two types of mechanism have been proposed.[2,9−13] One type involves hemidissociation, dissociation of one of the ligating moietes of LL′ (Scheme 1, mechanism A),[8,12] or complete dissociation of LL′, and in the other type both moieties remain bound with inversion occurring via a two- or four-legged piano stool intermediate (Scheme 1, mechanism B) and involving dissociation of ligand X.[10,13] Either or both of these may operate depending on the complex and the conditions.

Complexes of chelating ligands in which one moiety is labile often undergo inversion at the metal more rapidly than those of ligands that are nonlabile, and it is inferred that in such cases mechanism A dominates.[9] For complexes in which the chelating ligand is nonlabile, inversion at the metal still occurs by mechanism B. For example, inversion at the metal has been observed in complexes of chelating diphosphines, which are typically considered as nonlabile, such as $[Cp^*RuCl(Ph_2PCHMeCH_2PPh_2)]$,[14] $[Cp^*RhCl(Ph_2PCHMeCH_2PPh_2)]^+$,[10] and $[Cp^*RhCl\{Ph_2PCH_2CH_2PPh(C_5F_4N\text{-}4)\}]^+$,[15] and this is presumed to occur by mechanism B. Calculations and mechanistic studies reveal that the barrier to inversion of $[(\eta^n\text{-}C_nR_n)M(LL')]^{n+}$ is less than 15 kcal mol^{-1}.[16] However, to our knowledge a mechanism involving phosphine dissociation has not been unequivocally ruled out.

In complexes in which the carbocylic ligand is joined to the chelating ligand by a short, rigid linkage, giving an $\eta^n,\kappa L^1,\kappa L^2$ bound ligand, mechanism B is prevented. Brunner has postulated that complexes of this type of ligand are configurationally stable at the metal.[17] Indeed, room-temperature configurational stability has been confirmed for $[\{\eta^6,\kappa P,\kappa N\text{-}C_6H_4(CH_2CH_2PPh_2)(pyr)\text{-}3\}Ru(OH_2)](OTf)_2$ (pyr = bis(trifluoromethyl)pyrazole or camphorpyrazole), but decomposition occurred on heating.[18] No other studies to confirm configurational stability have been

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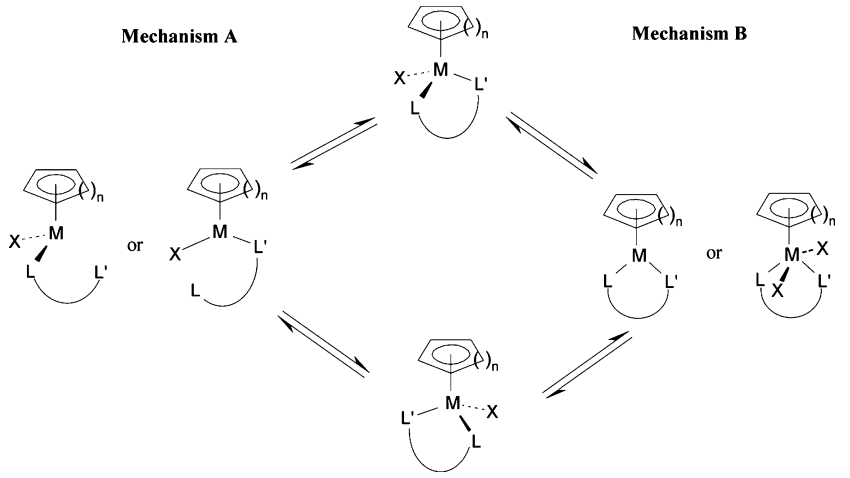
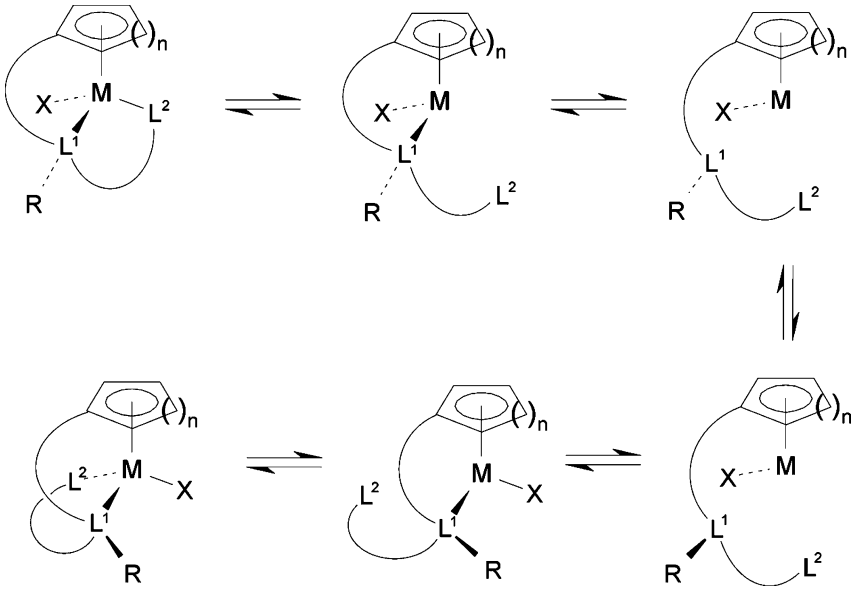
Scheme 1



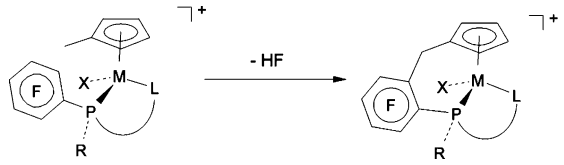
Scheme 2



carried out at elevated temperature. However, if L^1 is the bridgehead and both L^1 and L^2 can dissociate, then inversion at the metal is still possible. Thus, despite the three-point attachment of the ligand, a mechanism for inversion at the metal can be proposed. For ligands in which L^1 is a stereogenic center, inversion at the metal requires inversion at L^1 (Scheme 2).

We are interested in η^5,κP,κL-cyclopentadienyl-phosphine-donor (Cp−PL) ligands as a means of providing chiral, potentially configurationally stable metal complexes as precatalysts for organic transformations. This ligand type includes L groups that are considered as nonlabile, such as phosphines,[9,15,19,20] and that are labile, such as thioether.[9] The latter are of particular interest since configurational stability would be combined with ligand hemilability,[21] which provides a latent coordination site at the metal, allowing a greater range of reactivity. For inversion at the metal to occur, the phosphine must dissociate and inversion at phosphorus occur. Thus, if the phosphine is insufficiently labile or the barrier to inversion at the phosphorus atom of the dissociated phosphine is sufficiently high, then configurational stability will result.

Scheme 3



Although phosphine moieties of chelating Cp−P ligands are expected to be typically nonlabile, their dissociation is not without precedent.[22] Furthermore, the synthetic strategy we have developed for complexes of these ligands (Scheme 3) necessitates a strongly electron-withdrawing polyfluoroaryl phosphine substituent, which reduces the basicity and increases the cone angle of the phosphine compared to the nonfluorinated analogue.

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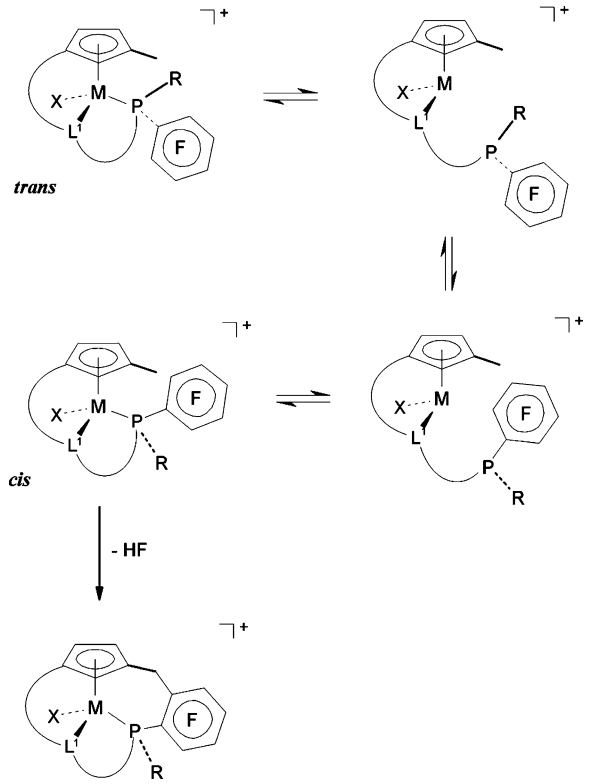
Scheme 4

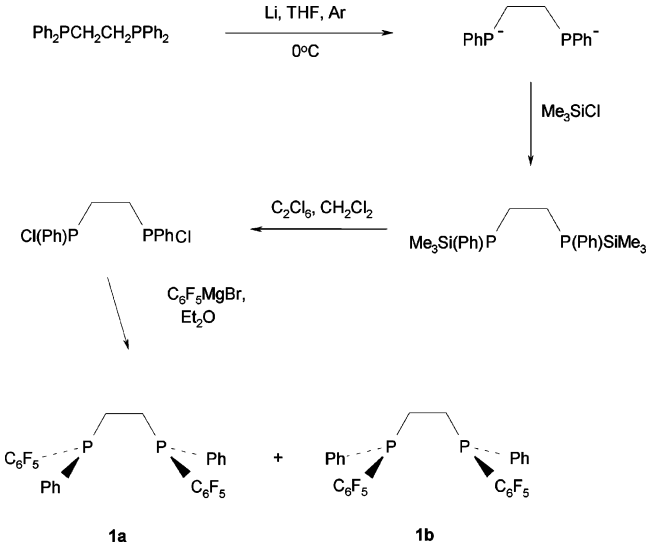


On the basis of past observations[23] both of these effects are expected to increase the lability of the phosphine moiety.

Although the barrier to inversion at phosphorus in phosphines is typically high, 25 to 36 kcal mol^{-1},[24] this is lowered by electron-withdrawing substituents. For example, $\Delta G^{\ddagger}$ is 20 kcal mol^{-1} for $MeOP(Ph)CHMe_2$[25] and 18.9 kcal mol^{-1} for $Me_3SiP(Ph)CHMe_2$.[26] The presence of a polyfluoroaryl substituent is also expected to reduce the barrier to inversion at the phosphorus.

We wished to determine experimentally whether rhodium complexes of Cp−PL ligands can undergo inversion. Two methods were considered. One involves enantiomeric enrichment of a complex and measurement of its optical rotation or CD spectrum over time. The other involves the investigation of phosphine dissociation and inversion by employing a phosphine with one polyfluoroaryl substituent as the L^2 moiety (Scheme 4). Two pairs of enantiomers exist for complexes of these ligands. The cyclopentadienyl ring and polyfluoroaryl substituent are either on the same side (*cis*) or on opposite sides (*trans*) of the RhL^1P plane. If phosphine dissociation and inversion do occur, then an equilibrium of the *cis* and *trans* pair of enantiomers would be established. Although the *cis* and *trans* isomers are expected to have different spectroscopic properties and thus be readily observed by ^{31}P NMR spectroscopy, it would not be possible to observe the isomerization if the equilibrium has been established under the conditions of the synthesis. However, in the case of the *cis* stereoisomers intramolecular dehydrofluorinative carbon−carbon coupling can occur to give a complex of a double-linked Cp═L^1P ligand,

Scheme 5



which is expected to possess spectroscopic properties different from those of both the *cis* and *trans* isomers.[9,19] The coupling reaction is rapid in the presence of a suitable base or at high temperature. Observation of a decrease in the concentration of the complex of the Cp−L^1P ligand and a concomitant increase in the concentration of the complex of the Cp═L^1P ligand would establish unequivocally that phosphine dissociation and inversion at phosphorus have occurred. Ultimately this establishes whether complexes of Cp−PL^2 ligands are configurationally stable under the conditions of investigation. It is noteworthy that this method does not require enantiomeric enrichment. The latter method was chosen for our study.

We wished to use a rhodium complex of a Cp−P^1P^2 ligand. This is prepared by an intramolecular coupling of the η^5-C_5R_5 and a polyfluoroaryl substituent on P^1 disphosphine. Since P^2 is also to bear a polyfluoroaryl substitutent, the diphosphine selected for this study was $(C_6F_5)PhPCH_2CH_2PPh(C_6F_5)$, **1**. It was expected that the *rac* isomer of **1** would provide a complex suitable for the study, and that the *meso* isomer would produce a complex of the double-linked Cp═PP ligand and a complex in which the cyclopentadienyl ring and diphosphine are not linked. Here we report the synthesis of **1** and its rhodium piano stool complexes and a determination of the configurational stability of a Cp−P^1P^2 rhodium complex.

Results and Discussion

The four-step synthesis of diphosphine **1** is outlined in Scheme 5. Treatment of $Ph_2PCH_2CH_2PPh_2$ (dppe) with a 10-fold excess of lithium in THF at 0 °C produced a yellow solution of $(Li^+)_2[PhPCH_2CH_2PPh]^{2-}$,[27] which on subsequent treatment with chlorotrimethylsilane, then hexachloroethane, gave $PhClPCH_2CH_2PPhCl$.[28] Addition of an excess of C_6F_5MgBr in diethyl ether gave **1**, as a 1:1.7 mixture of *rac* (**1a**) and *meso* (**1b**) isomers, which was isolated as a white solid in 54.5% yield. (The identity of the major isomer was determined from the spectroscopic data of [Cp*RhCl(*κP,κP*-**1**)][BF_4] (vide infra).) It is presumed that **1a** is formed as a racemic mixture of the *RR* and *SS* enantiomers. The ratio of isomers is in contrast to that of 1.7:1 *rac*:*meso* reported for 1,2-bis[(2-quinolinemethyl)-

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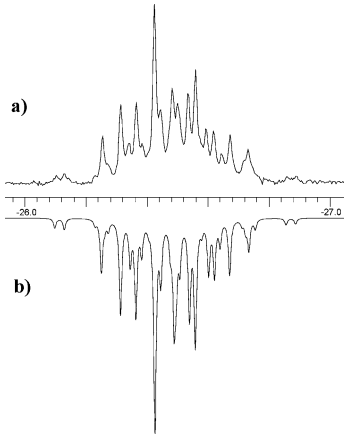

Figure 1. (a) Experimental and (b) simulated $^{31}P\{^1H\}$ NMR spectrum of **1**.

phenylphosphino]ethane, which is synthesized by a similar route.[28] The identity of **1** was confirmed by elemental analysis, high-resolution mass spectrometry, and NMR spectrosocopy. The $^{31}P\{^1H\}$ NMR spectrum of **1** contains a complicated asymmetric pattern, consistent with two overlapping patterns arising from A parts of $AA'X_2X_2'$ spin systems (Figure 1). The spectrum was simulated using relative values of the $^3J_{PP}$, $^3J_{PF}$, $^6J_{PF}$, and $^9J_{PF}$ coupling constants of 43.0, 33.0, 2.0, and 0 Hz, respectively, for resonances centered at δ −26.56 for **1a** and at δ −26.43 for **1b**. These coupling constants are similar to those of $(C_6H_3F_2\text{-}2,6)_2PCH_2CH_2P(C_6H_3F_2\text{-}2,6)_2$ ($^3J_{PP}$ 47.2, $^3J_{PF}$ 30.1, $^6J_{PF}$ 1.2, and $^9J_{PF}$ −0.4 Hz),[20] and the chemical shifts are similar to that of $PPh_2(C_6F_5)$ (δ −24.7).[29] The ^{19}F NMR spectrum shows only four resonances. Those of the *ortho* fluorine atoms of **1a** and **1b** are coincident at δ −129.68, as are those of the *meta* fluorine atoms at δ −160.70. Two resonances for the *para* fluorine atoms (δ −150.46 and −150.70) are consistent with the two isomers of **1**. Unfortunately to date attempts to separate **1a** and **1b** have been unsuccessful.

A small amount of a 1:1 mixture of isomers of the phosphine monoxide **2**, characterized by mass spectrometry and NMR spectroscopy, was also obtained from the preparation of **1**. The $^{31}P\{^1H\}$ NMR spectrum exhibits two sets of doublets of triplets at ca. δ 30 and doublet of doublets at ca. δ −25, consistent with two pairs of enantiomers. The former resonances are assigned to the phosphine by comparison with those of **1** and the latter to the phosphine oxide by comparison to those of the phosphine dioxide, **3**, formed by oxidation of an NMR sample of **1** with hydrogen peroxide. The identity of **3** was confirmed by mass spectrometry. Two resonances are observed in the $^{31}P\{^1H\}$ NMR spectrum consistent with *meso* and *rac* isomers.

Scheme 6

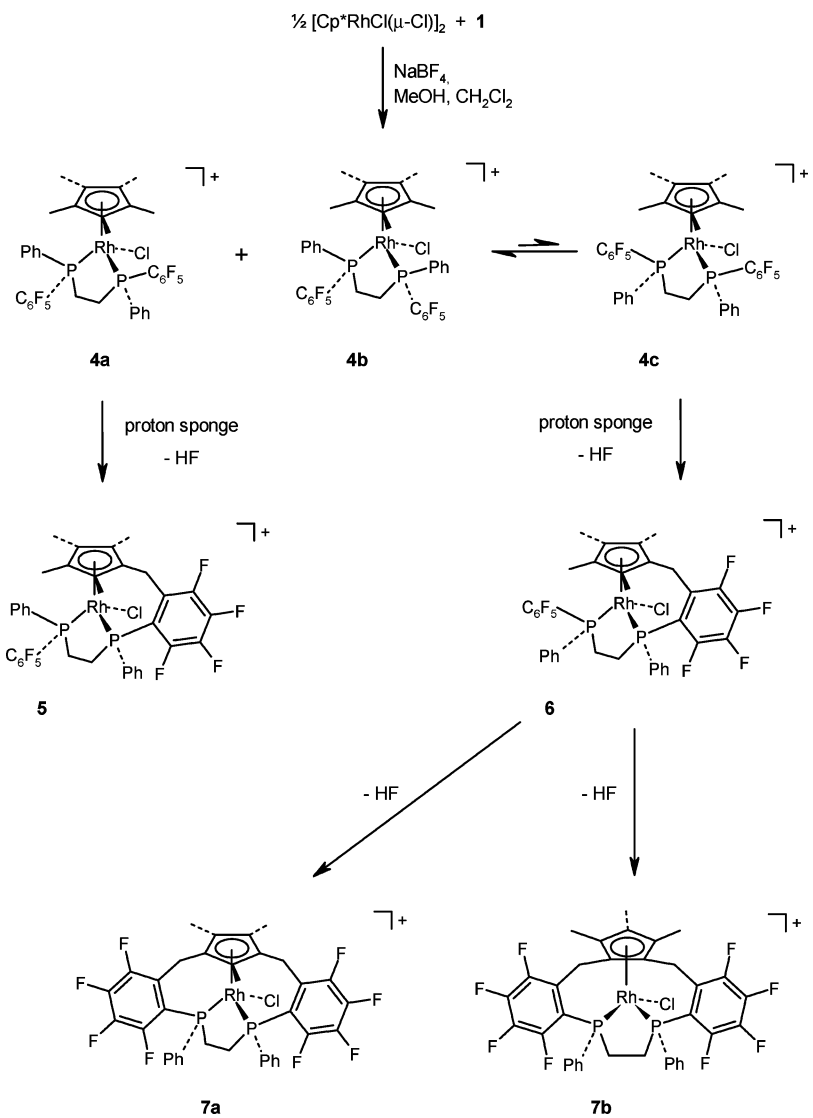

Table 1. Selected NMR and Mass Spectral Data for 4·BF$_4$, 5·BF$_4$, 6·BF$_4$, and 7·BF$_4$[a]

	δ_P ($^1J_{RhP}$/Hz)	δ_F	δ_H	LSIMS
4a·BF$_4$[b]	64.6 (138)[c] 54.4 (146)[d]	−125.10 (2F, d, $^3J_{FF}$ = 21.7 Hz, F_{ortho}), −126.40 (2F, d, $^3J_{FF}$ = 25.3 Hz, F_{ortho}), −145.80 (2F, t, $^3J_{FF}$ = 20.7 Hz, F_{para}), −143.24 (2F, t, $^3J_{FF}$ = 20.2 Hz, F_{para}), −157.15 (4F, m, F_{meta}), −159.12 (4F, m, F_{meta})	1.61 (t, $^4J_{PH}$ = 3.9 Hz, CH_3)	851 (M^+), 816 ([M − Cl]$^+$) calcd for $C_{36}H_{29}ClF_{10}P_2Rh$, 851.032841; found M^+, 851.032267
4b·BF$_4$[b]	60.1 (142)	−126.5 (4F, br s, F_{ortho}), −144.85 (2F, t, $^3J_{FF}$ = 21.8 Hz, F_{para}), −158.55 (4F, br s, F_{meta})	1.46 (t, $^4J_{PH}$ = 3.8 Hz, CH_3)	
4c·BF$_4$[b]	51.1 (141 Hz)	−127.46 (2F, d, $^3J_{FF}$ = 18.1 Hz, F_{ortho}), −143.60 (2F, t, $^3J_{FF}$ = 20.5 Hz, F_{para}), −157.59 (4F, m, F_{meta})	1.51 (t, $^4J_{PH}$ = 4.2 Hz, CH_3)	
5·BF$_4$	74.5 (140)[e] 53.8 (140) [d]	−123.80 (m), −134.93 (m), −144.13 (td, J = 22.4, 9.0 Hz), −145.17 (t, J = 22.4 Hz), −151.16 (t, J = 22.5 Hz)	4.35 (dd, $^2J_{HH}$ = 17.8 Hz, $^4J_{PH}$ = 17.8 Hz, $C_5CHHC_6F_4$), 3.29 (d, $^2J_{HH}$ = 17.8 Hz, $C_5CHHC_6F_4$), 1.80 (d, $^4J_{PH}$ = 4.8 Hz, CH_3), 1.63 (d, $^4J_{PH}$ = 8.8 Hz, CH_3), 0.76 (d, $^4J_{PH}$ = 1.7 Hz, CH_3)	831 (M^+), 895 ([M − Cl − H]$^+$) calcd for $C_{36}H_{28}ClF_9P_2Rh$, 831.026613; found M^+, 831.022610
6·BF$_4$[f]	85.1 (142) 63.5 (142)			
7·BF$_4$	72.0 (134)[g] 67.4 (137)[h]	−121.77 (m), −134.02 (m)[g], −134.75 (m)[h], −144.71 (td, J = 22.3, 9.0 Hz),[g] −145.55 (td, J = 22.4, 9.0 Hz)[h], −151.97 (t, J = 22.4 Hz)[h], −153.21 (t, J = 22.4 Hz)[g]	4.60 (m), 3.59 (m),2.13 (d, $^4J_{PH}$ = 6.5 Hz, CH_3), 0.71 (s, CH_3)	811 (M^+), 875 ([M − Cl − H]$^+$) calcd for $C_{36}H_{27}ClF_8P_2Rh$, 811.020385; found M^+, 811.018631

[a] NMR spectra recorded in $CDCl_3$ except where stated. Many of the ^1H and ^{19}F resonances of **5·BF$_4$**, **6·BF$_4$**, and **7·BF$_4$** are obscured, and only those resonances that can be positively assigned to the complexes are given. [b] Data common to **4a·BF$_4$**, **4b·BF$_4$**, and **4c·BF$_4$**. ^1H: δ 7.4−8.0 (m, C_6H_5), 2.5−3.5 (m, CH_2). ^{19}F: δ −153.88 (0.8F, $^{10}BF_4^-$), −153.93 (3.2F, $^{11}BF_4^-$). [c] P(*cis*-C_6F_5), $^2J_{PP}$ = 22 Hz. [d] P(*trans*-C_6F_5). [e] P(C_6F_4). [f] NMR spectrum recorded in $(CD_3)_2SO$. [g] Major isomer. [h] Minor isomer.

Treatment of [Cp*RhCl(μ-Cl)]$_2$ with 2 equiv of **1** in the presence of ammonium tetrafluoroborate yielded, after recrystallization, the salt [Cp*RhCl(κP,κP-**1**)][BF$_4$], **4·BF$_4$**, as an orange solid in moderate yield (Scheme 6). The analytical and spectral data of **4·BF$_4$** (Table 1) are entirely consistent with the formulation. The ^1H and ^{19}F NMR spectra, although consistent with the formulation, are far from simple. In contrast the $^{31}P\{^1H\}$ NMR spectrum is simple and indicates the presence of the three expected isomers. A pair of mutually coupled resonances at δ 64.6 and 54.4 are consistent with [Cp*RhCl(κP,κP-**1a**)][BF$_4$], **4a·BF$_4$**, and are assigned on the basis of the reaction with Proton Sponge (vide infra) to the phosphorus atoms with the pentafluorophenyl substituents respectively *cis* and *trans* to the pentamethylcyclopentadienyl ring. Two doublets of multiplet resonances at δ 60.1 and 51.1 are assigned to *trans*-[Cp*RhCl(κP,κP-**1b**)][BF$_4$], **4b·BF$_4$**, and *cis*-[Cp*RhCl(κP,κP-**1b**)][BF$_4$], **4c·BF$_4$**, respectively, on the basis of the reaction with Proton Sponge (vide infra). The ratio of **4a**:**4b**:**4c** is ca. 12:17:1. An in situ NMR study revealed that the reaction between [Cp*RhCl(μ-Cl)]$_2$ and **1** in the presence of tetrafluoroborate forms **4·BF$_4$** in virtually quantitative yield with a ratio of **4a**:**4b**:**4c** of 10:16:1, confirming the assignments of **1a** and **1b** and consistent with the steric congestion in **4c** due to the greater bulk of pentafluorophenyl compared to phenyl substituents. Attempts to separate the isomers by fractional crystallization were unsuccessful, but a crystal of **4a·BF$_4$** suitable for a single-crystal X-ray diffraction study was obtained (Figure 2). The geometry, Rh−P and Rh−Cl distances, and P−Rh−P angles of **4a·BF$_4$** are consistent with those of [Cp*RhCl(P$_2$)]BF$_4$, in which the diphosphine bears at least one fluoroaryl substituent.[15,19,20]

The dehydrofluorinative coupling reactions of **4·BF$_4$** were studied by in situ NMR experiments in $CDCl_3$ and $(CD_3)_2SO$ at room temperature. Although the ^1H and ^{19}F NMR spectra were complicated, the $^{31}P\{^1H\}$ NMR spectra were simple and gave data from which assignments and the course of the reaction could be determined. The identity of the products of the reaction in $CDCl_3$ were supported by ^1H and ^{19}F NMR data where possible and high-resolution mass spectrometry (Table 1). In both solvents **4a·BF$_4$** and **4c·BF$_4$**, but not **4b·BF$_4$**, underwent rapid reactions on addition of Proton Sponge. The rapid reactions of **4a** and **4c** and lack of reaction of **4b** are consistent with observations of the treatment of *cis*- and *trans*-[Cp*RhCl{Ph$_2$PCH$_2$CH$_2$PPh(C$_5$F$_4$N-4)}][BF$_4$] with Proton Sponge.[15] The data indicated that, as expected, the single-linked product **5** was formed from **4a**. Over time isomerization of **4b** to **4c**, and subsequent reaction, was observed (Figures 3 and 4). Ultimately two products with similar spectroscopic properties were formed in a ratio of ca. 3:2. The spectroscopic data strongly suggest that one of these is the expected 1,3-double-linked product **7a**, which is similar to that formed exclusively on coupling dfppe and Cp*.[19] On the basis of the similarity of the data, it is proposed that the other is the 1,2-linked product, **7b**, which is similar to that formed exclusively on coupling dfppe and η^5-C_5Me_4H.[30] In $CDCl_3$ the reaction occurred with less than the stoichiometric quantity of Proton Sponge. In $(CD_3)_2SO$ the

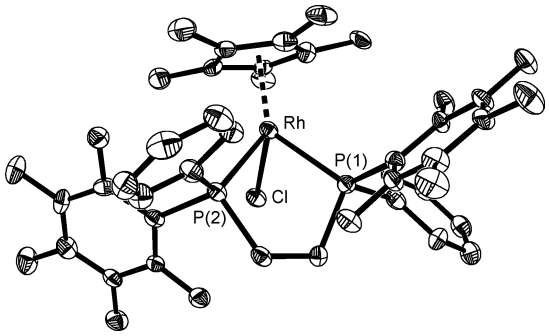

Figure 2. Structure of the *SS* enantiomer of the cation of [Cp*RhCl{κP,κP-*rac*-(C$_6$F$_5$)PhPCH$_2$CH$_2$PPh(C$_6$F$_5$)}][BF$_4$], **4a·BF$_4$**. Thermal ellipsoids are at the 30% level. Hydrogen atoms are omitted for clarity. Cp†−Rh 1.867(10) Å, Rh−Cl 2.395(2) Å; Rh−P(1) 2.339(3) Å; Rh−P(2) 2.322(3) Å; Cp†−Rh−Cl 120.7(3)°; Cp†−Rh−P(1) 134.2(3)°; Cp†−Rh−P(2) 131.4(3)°; Cl−Rh−P(1) 84.99(9)°; Cl−Rh−P(2) 84.63(9)°; P(1)−Rh−P(2) 84.08(9)°.

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(30) Nieuwenhuyzen, M.; Saunders: G. C. *J. Organomet. Chem.* **2000**, *595*, 292.

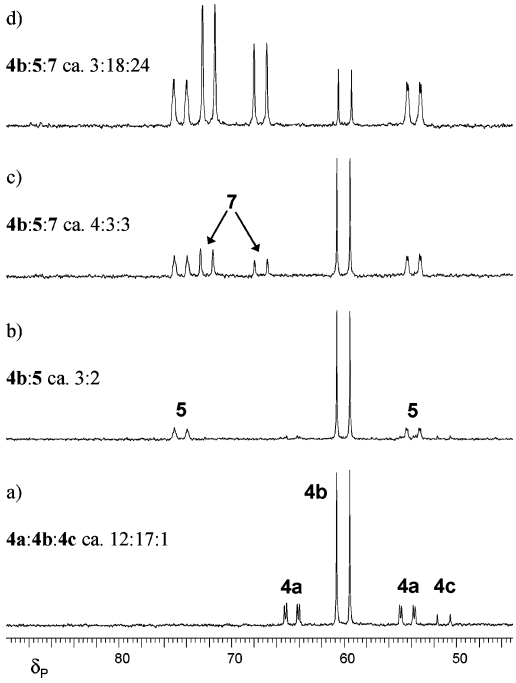

Figure 3. (a) $^{31}P\{^1H\}$ NMR spectrum of **4·BF₄** in $CDCl_3$ at 25 °C: (b) 3 h, (c) 66 h, and (d) 238 h after addition of Proton Sponge.

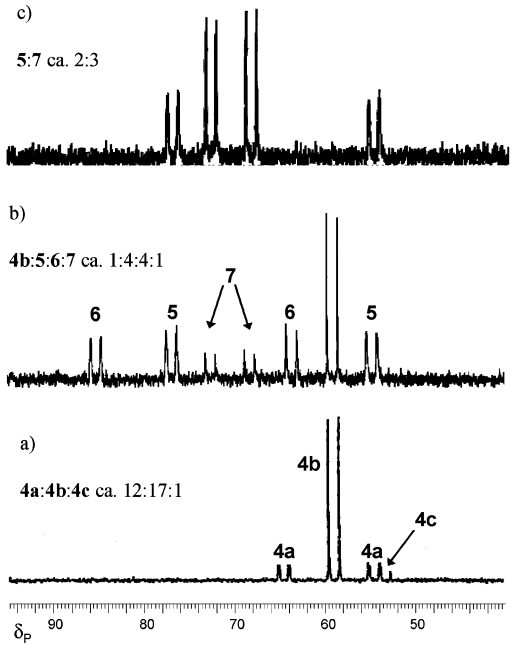

Figure 4. (a) $^{31}P\{^1H\}$ NMR spectrum of **4·BF₄** in $(CD_3)_2SO$ at 25 °C: after addition of (b) less than stoichiometric amount and (c) excess of Proton Sponge.

reaction required more Proton Sponge, which allowed the observation of the intermediate **6** as a pair of doublet resonances of equal integration in the $^{31}P\{^1H\}$ NMR spectrum (Figure 4). The increase in intensity of these doublets as **4b** was consumed and their decrease in intensity as **7a** and **7b** were formed confirms the intermediacy of **6** and supports the identities of **7a** and **7b**. In the presence of an excess of Proton Sponge the reaction reached completion within 24 h, indicating rapid isomerization of **4b** to **4c**. In contrast the isomerization in $CDCl_3$ was slow, allowing analysis of the kinetics. As expected, a first-order rate law was obeyed with $k \approx 2.5 \times 10^{-6}$ s^{-1}. This is comparable to the rate of epimerization of $[Cp^*RhCl(Ph_2PCHMeCH_2PPh_2)]^+$ in dimethyl sulfoxide at 85 °C ($k = 6.18 \times 10^{-5}$ s^{-1}).[10]

The difference in the rates of isomerization of **4b** is consistent with the difference in solvation properties. Chloride dissociation and ion separation is favored in dimethyl sulfoxide, which is polar with a large relative permittivity and is both a strong donor and moderate acceptor ($\mu = 3.96$ D, $\epsilon_r = 46.6$ at 20 °C,[31] donor number = 29.8, acceptor number = 19.3[32]), but not in chloroform, which is much less polar, is only a moderate acceptor, and is not a donor ($\mu = 1.01$ D, $\epsilon_r = 4.8$ at 20 °C,[31] acceptor number = 23.1[32]). Since it might be expected that if mechanism A predominates in both solvents, the rates would be comparable, we suggest that mechanism B, which involves chloride dissociation, predominates in dimethyl sulfoxide. The slower rate of isomerization in chloroform is consistent with either mechanism operating in that solvent.

The reaction between $[Cp^*RhCl(\mu\text{-}Cl)]_2$ and 2 equiv of **1** in refluxing benzene was carried out as an attempt to prepare pure **5** or **7**. It was hoped that either product would be precipitated. Unfortunately, although after 50 h a precipitate was apparent, this was not of a single compound. The mass spectrum of the solid showed the presence of the cations of the single- and double-linked products **5** and **7**, and NMR spectroscopy confirmed the mixture and the presence of minor amounts of other rhodium phosphine complexes.

To assess the configurational stability of **5**, the NMR sample resulting from the reaction between **4a·BF₄** and an excess of Proton Sponge was heated at 100 °C and the $^{31}P\{^1H\}$ NMR spectrum recorded periodically. No change in the ratio of **5** to **7** was observed, even after 2 months. The result indicates that neither both nor one of phosphine dissociation and inversion at phosphorus occurs under these conditions.

Conclusion

In summary, the pentafluorophenyl-substituted diphosphine $(C_6F_5)PhPCH_2CH_2PPh(C_6F_5)$ (**1**) was prepared as a 1:1.7 mixture of the *rac* and *meso* isomers from dppe. In situ NMR studies of intramolecular dehydrofluorinative coupling reactions of the salt $[Cp^*RhCl(\kappa P,\kappa P\text{-}\mathbf{1})][BF_4]$ reveal that inversion at the metal occurs slowly in chloroform and more rapidly in dimethyl sulfoxide. Subsequent NMR studies establish that phosphine dissociation and inversion at phosphorus do not occur in $[\{\eta^5,\kappa P,\kappa P\text{-}C_5Me_4CH_2C_6F_4\text{-}2\text{-}PhPCH_2CH_2PPh(C_6F_5)\}RhCl][BF_4]$ in dimethyl sulfoxide at 100 °C. This observation provides evidence that complexes of Cp−PL ligands are configurationally stable at elevated temperature.

Experimental Section

General Considerations. The compounds dppe, lithium (Aldrich), bromopentafluorobenzene (Apollo), and hexachloroethane (Lancaster) were used as supplied. Chlorotrimethylsilane (Aldrich) was purified by vaccum distillation and stored under dinitrogen. $[Cp^*RhCl(\mu\text{-}Cl)]_2$ was prepared as described.[33] The preparation of **1** was performed under argon and dintrogen using diethyl ether, THF, and dichloromethane dried by distillation under dinitrogen from sodium/benzophenone, potassium/benzophenone, and calcium hydride, respectively, and stored over molecular sieves (4 Å). No precautions to exclude air or moisture were taken for the other preparations.

(31) *Solvent Recovery Handbook*, 2nd ed.; Smallwood, I. M., Ed.; Blackwell Science: Oxford, 2002.

(32) *The Donor*-Acceptor *Approach to Molecular Interactions*; Gutmann, V., Ed.; Plenum Press: New York, 1978.

(33) White, C.; Yates, A.; Maitlis, P. M. *Inorg. Synth.* **1992**, *29*, 228.

^{1}H, ^{19}F, and ^{31}P NMR spectra were recorded using Bruker DPX300 or DRX500 spectrometers. ^{1}H NMR spectra (300.01 or 500.13 MHz) were referenced internally using the residual protio solvent resonance relative to $SiMe_4$ (δ 0), ^{19}F (282.26 MHz) externally to $CFCl_3$ (δ 0), and ^{31}P (121.45 or 202.46 MHz) externally to 85% H_3PO_4 (δ 0). All chemical shifts are quoted in δ (ppm), using the high-frequency positive convention, and coupling constants in Hz. Simulations were carried out using the gNMR simulation package.[34] EI and LSIMS mass spectra were recorded on a VG Autospec X series mass spectrometer. Elemental analyses were carried out by ASEP, The School of Chemistry, Queen's University Belfast.

(C_6F_5)PhPCH$_2$CH$_2$PPh(C_6F_5) (1). A solution of dppe (2.9 g, 7.3 mmol) in THF (50 cm^3) at 0 °C was added to an excess of lithium shot (2.9 g, 0.42 mmol) under argon. The mixture was stirred vigorously at 0 °C for 1 h, allowed to warm to ambient temperature, and stirred for a further 72 h. The resulting yellow-brown solution was decanted from the lithium, and chlorotrimethylsilane was added dropwise by syringe until the color disappeared. The volatiles were removed under reduced pressure, affording an off-white solid, which was extracted with dichloromethane (150 cm^3). Hexachloroethane (3.5 g, 15.0 mmol) in dichloromethane (50 cm^3) was added slowly to the extract and the solution left at ambient temperature for 72 h. The volatiles were removed under reduced pressure, affording ClPhPCH$_2$CH$_2$PPhCl as a colorless oil, which solidified on standing in vacuo. The identity of the chlorophosphine was confirmed by mass spectrometry and ^{31}P{^{1}H} NMR spectroscopy. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 93.1. HRLSIMS: calcd for $C_{14}H_{14}{}^{35}Cl_2P_2$, 313.99431; found for M$^+$, 313.99478.

Pentafluorophenylmagnesium bromide in diethyl ether (100 cm^3), freshly prepared from C_6F_5Br (3.5 cm^3 g, 0.03 mol) and magnesium (1.0 g, 0.04 mol), was added to a slurry of the ClPhPCH$_2$CH$_2$-PPhCl in diethyl ether (50 cm^3) with vigorous stirring. A color change from black to dark brown was observed. The mixture was stirred for 16 h at ambient temperature. The solution was opened to the atmosphere, water (30 cm^3) and dichloromethane (30 cm^3) were added, and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 × 30 cm^3). The combined extracts and organic layer were washed with water (3 × 30 cm^3) and dried over magnesium sulfate. The solution was filtered and the solvent removed by rotary evaporation to afford a brown solid. Product **1**, as a 1:1.7 mixture of **1a** and **1b**, was obtained as a white crystalline solid following chromatography on neutral alumina (6% H_2O) with hexane/dichloromethane (9:1) as eluant. Yield: 2.3 g (54.5%). ^{1}H NMR ($CDCl_3$): δ 7.46 (4H, m), 7.34 (6H, m), 2.41 (4H, m). ^{19}F NMR ($CDCl_3$): δ −129.68 (4F, m, F_{ortho}), −150.46 (1.2F, t, $^3J_{FF}$ = 19.8 Hz, F_{para}), −150.70 (0.8F, t, $^3J_{FF}$ = 19.8 Hz, F_{para}), −160.70 (4F, m, F_{meta}). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −26.56 (0.63, 2nd order pattern from AA′X$_2$X′$_2$ spin system: $^3J_{PP}$ = 43.0 Hz, $^3J_{PF}$ = 33.0 Hz, $^6J_{PF}$ = 2.0 Hz), −26.43 (0.37, 2nd order pattern from AA′X$_2$X′$_2$ spin system: $^3J_{PP}$ = 43.0 Hz, $^3J_{PF}$ = 33.0 Hz, $^6J_{PF}$ = 2.0 Hz). LSIMS, *m*/*z*: 578 (100%, M$^+$), 411 (58%, [M − C_6F_5]$^+$). HRLSIMS: calcd for $C_{26}H_{14}F_{10}P_2$, 578.041110; found M$^+$, 578.041806. Anal. Calcd for $C_{26}H_{14}F_{10}P_2$: C, 54.03; H, 2.44. Found: C, 53.69; H, 2.61.

A small amount (<0.05 g) of monoxide **2**, as a 1:1 mixture of *meso* and *rac* isomers, was obtained by elution with dichloromethane. ^{1}H NMR ($CDCl_3$): δ 7.4−7.8 (10H, m), 2.54 (3H, m), 2.35 (1H, m). ^{19}F NMR ($CDCl_3$): δ −129.40 (4F, m, F_{ortho}), −130.47 (2F, m, F_{ortho}), −130.73 (2F, m, F_{ortho}), −145.84 (2F, m, F_{para}), −150.13 (2F, m, F_{para}), −158.78 (4F, m, F_{meta}), −160.51 (4F, m, F_{meta}). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 30.1 (dm, $^3J_{PP}$ = 59 Hz, PO), 29.6 (dm, $^3J_{PP}$ = 59 Hz, PO), −25.3 (dt, $^3J_{PP}$ = 59 Hz, $^3J_{PF}$ = 33 Hz, P), −25.8 (dt, ^3JPP = 59 Hz, $^3J_{PF}$ = 33 Hz, P). LSIMS, *m*/*z*: 595 (100%, [M + H]$^+$), 427 (25%, [M − C_6F_5]$^+$), 303 (72%, [M − $C_6H_5(C_6F_5)PO$]$^+$). HRLSIMS: calcd for $C_{26}H_{15}F_{10}OP_2$, 595.043850; found [M + H]$^+$, 595.044586.

Table 2. Crystal Data and Structure Refinement for 4a·BF$_4$

formula	$C_{36}H_{29}BClF_{14}P_2Rh\cdot 1/2CH_2Cl_2$
fw	981.17
cryst dimens, mm	0.42 × 0.18 × 0.08
T, K	293(2)
cryst syst	monoclinic
space group	*P*2(1)/*n*
unit cell dimens	
a, Å	17.220(4)
b, Å	12.682(3)
c, Å	19.14655
β, deg	110.082(5)
U, Å^3	3927.0(17)
Z	4
calc density, g cm^{-3}	1.660
F(000)	1956
θ, deg	2.54−23.23
abs coeff, mm^{-1}	0.747
total no. of data	33 406
no. of unique data, R_{int}	6913, 0.1497
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0832
	wR2 = 0.2035
R indices (all data)	R1 = 0.1430
	wR2 = 0.2338
GoF on F^2	0.956
largest diff peak and hole, e Å^{-3}	1.375, −0.826

(C_6F_5)PhP(O)CH$_2$CH$_2$P(O)Ph(C_6F_5) (3). Dioxide **3** was formed on addition of hydrogen peroxide to an NMR sample of **1** in $CDCl_3$. ^{1}H NMR ($CDCl_3$): δ 7.74 (4H, m), 7.55 (6H, m), 2.82 (2H, m), 2.58 (2H, m). ^{19}F NMR ($CDCl_3$): δ −130.25 (4F, m, F_{ortho}), −145.31 (2F, m, F_{para}), −158.64 (4F, m, F_{meta}). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 30.1 (2s). LSIMS, *m*/*z*: 611 (100%, M$^+$), 443 (17%, [M − C_6F_5 − H]$^+$). HRLSIMS: calcd for $C_{26}H_{14}F_{10}O_2P_2$, 611.038764; found M$^+$, 611.036133.

[Cp*RhCl{$\kappa P,\kappa P$-rac-(C_6F_5)PhPCH$_2$CH$_2$PPh(C_6F_5)}][BF$_4$] (4a·BF$_4$), *trans*-[Cp*RhCl{$\kappa P,\kappa P$-*meso*-(C_6F_5)PhPCH$_2$CH$_2$PPh(C_6F_5)}][BF$_4$] (4b·BF$_4$), and *cis*-[Cp*RhCl{$\kappa P,\kappa P$-*meso*-(C_6F_5)PhPCH$_2$CH$_2$PPh(C_6F_5)}][BF$_4$] (4c·BF$_4$). A slurry of [Cp*RhCl(μ-Cl)]$_2$ (0.075 g, 0.12 mmol), **1** (0.14 g, 0.24 mmol), and NH_4BF_4 (0.5 g, 4.8 mmol) was treated as for the synthesis of [Cp*RhCl(dfppe)][BF$_4$].[19] A mixture of **4a·BF$_4$**, **4b·BF$_4$**, and **4c·BF$_4$** (ca. 12:17:1) was obtained as an orange solid. Yield: 0.07 g (31%). Anal. Calcd for $C_{36}H_{29}BClF_{14}P_2Rh\cdot CH_2Cl_2$: C, 43.41; H, 3.05. Found: C, 43.58; H, 3.54. NMR and mass spectral data are given in Table 1.

X-ray Crystallography. A crystal of **4a·BF$_4$**·0.5CH_2Cl_2 (0.42 × 0.18 × 0.08 mm) was obtained by slow evaporation of solvent from a solution of **4a·BF$_4$** in dichloromethane. Crystal data are listed in Table 2. Diffraction data were collected on a Bruker SMART diffractometer using the SAINT-NT[35] software with graphite-monochromated Mo Kα radiation. Lorentz and polarization corrections were applied. Empirical absorption corrections were applied using SADABS.[36] The structure was solved by direct methods and refined with the program package SHELXTL version 5.[37] The non-hydrogen atoms, except those of the anion (B(1), B(1′), F(11), F(11′), F(12), F(12′), F(13), F(13′), F(14), and F(14′)) and solvent (C(1S), Cl(1S), and Cl(2S)), were refined with anisotropic thermal parameters. Hydrogen atom positions were added and idealized, and a riding model with fixed thermal parameters (U_{ij} = 1.2U_{eq} for the atom to which they are bonded (1.5 for CH_3)) was used for subsequent refinements. The function minimized was $\sum[w(|F_o|^2 - |F_c|^2)]$ with reflection weights $w^{-1} = [\sigma^2|F_o|^2 + (g1P)^2 + (g2P)]$ where $P = [\max|F_o|^2 + 2|F_c|^2]/3$. CCDC 286537 contains the supplementary crystallographic data for this paper. These data can

(34) *gNMR*, version 4.0; Cherwell Scientific Publishing Ltd.: Oxford, 1995.

(35) *SAINT-NT*; Bruker AXS Inc.: Madison, WI, 1998.

(36) Sheldrick, G. M. *SADABS*; University of Göttingen: Germany 1996.

(37) Sheldrick, G. M. *SHELXTL* version 5; Bruker AXS Inc.: Madison, WI, 1998.

be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information Available: A listing of atomic coordinates, anisotropic displacement parameters, bond distances, and bond angles for **4a·BF_4·**$0.5CH_2Cl_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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