Organometallics **2004,** *23,* 1089−1097 1089

C−F Activation Reactions of (Pentafluorophenyl)cyclopentadiene and 3-(Pentafluorophenyl)indene with Tetrakis(dimethylamido)titanium(IV)

Paul A. Deck,* Mariam M. Konaté,† Bryte V. Kelly,† and Carla Slebodnick

Department of Chemistry, Virginia Tech, Blacksburg, Virginia 24061

Received December 18, 2003

Reactions of either 3-(pentafluorophenyl)indene (**1a**) or (pentafluorophenyl)cyclopentadiene (**1b**) with $Ti(NMe_2)_4$ afford products in which one or both of the *ortho* fluorines of the C_6F_5 group are replaced with a dimethylamino group. The *ortho* selectivity suggests a titanium-mediated, intramolecular nucleophilic aromatic substitution mechanism. The organic products 3-[2-(dimethylamino)tetrafluorophenyl]indene (**4a**), 3-[2,6-bis(dimethylamino)-trifluorophenyl]indene (**7a**), and 1-[2,6-bis(dimethylamino)trifluorophenyl]cyclopentadiene (**7b**) were isolated upon hydrolytic workup. The substituted cyclopentadiene (**7b**) was converted to the corresponding ferrocene derivative (**12**) by treatment first with sodium hydride and then with iron dibromide in THF. Three compounds (**4a**, **7b**, and **12**) were characterized crystallographically.

Introduction

Selective activation of polyfluorinated organic compounds is an important synthetic challenge and a rapidly advancing area of investigation.[1] Transition metal complexes offer diverse mechanisms for CF activation.[2−17] In both C−H and C−F activation studies, aromatic substrates are used more commonly than aliphatic substrates for three main reasons. First, metal aryls are often more stable and more readily isolated than corresponding alkyls, allowing stepwise mechanistic exploration, especially of late transition metal oxidative addition pathways.[11,18,19] Second, substituents can impart rational activating/directing effects without encumbering the reactive bonds. Finally, the desired outcome of "activation" is usually formal substitution rather than elimination, and although elimination is known for arenes,[20] the selectivity for substitution is generally better.

As part of our investigation of perfluoroaryl-substituted metallocenes and related complexes,[21−25] we want to synthesize group 4 complexes of the 1-(pentafluorophenyl)indenyl ligand. Certain zirconium and hafnium complexes of the isomeric 2-(pentafluorophenyl)-indenyl ligand are stable and useful as catalysts for olefin polymerization.[26−29] Using established methods[30−32]

---

* Corresponding author. E-mail: pdeck@vt.edu. Fax: (540)-231-3255.

† Undergraduate research participant.

[1] Kiplinger, J. L.; Richmond, T. G.; Osterberg, C. E. *Chem. Rev.* **1994**, *94*, 373−431.

[2] Braun, T.; Noveski, D.; Neumann, B.; Stammler, H. G. *Angew. Chem., Intl. Ed.* **2002**, *41*, 2745−2747.

[3] Albietz, P. J.; Houlis, J. F.; Eisenberg, R. *Inorg. Chem.* **2002**, *41*, 2001−2003.

[4] Fujiwara, M.; Ichikawa, J.; Okauchi, T.; Minami, T. *Tetrahedron Lett.* **1999**, *40*, 7261−7265.

[5] Hughes, R. P.; Zhang, D.; Zakharov, L. N.; Rheingold, A. L. *Organometallics* **2002**, *21*, 4902−4904.

[6] Hughes, R. P.; Smith, J. M.; Incarvito, C. D.; Lam, K. C.; Rhatigan, B.; Rheingold, A. L. *Organometallics* **2002**, *21*, 2136−2144.

[7] Kraft, B. M.; Jones, W. D. *J. Organomet. Chem.* **2002**, *658*, 132−140.

[8] Kraft, B. M.; Jones, W. D. *J. Am. Chem. Soc.* **2002**, *124*, 8681−8689.

[9] Edelbach, B. L.; Rahman, A. K. F.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **1999**, *18*, 3170−3177.

[10] Edelbach, B. L.; Jones, W. D. *J. Am. Chem. Soc.* **1997**, *119*, 7734−7742.

[11] Braun, T.; Perutz, R. N. *Chem. Commun.* **2002**, 2749−2757.

[12] Godoy, F.; Higitt, C. L.; Klahn, A. H.; Oelckers, B.; Parsons, S.; Perutz, R. N. *J. Chem. Soc., Dalton Trans.* **1999**, 2039−2047.

[13] Cronin, L.; Higgitt, C. L.; Karch, R.; Perutz, R. N. *Organometallics* **1997**, 4920−4928.

[14] Rausch, M.; Bruhn, C.; Steinborn, D. *J. Organomet. Chem.* **2001**, *622*, 172−179.

[15] Aizenberg, M.; Milstein, D. *J. Am. Chem. Soc.* **1995**, *117*, 8674−8675.

[16] Schrock, R. R.; Adamchuk, J.; Ruhland, K.; Lopez, L. P. H. *Organometallics* **2003**, *22*, 5079−5091.

[17] Cochran, F. V.; Bonitatebus, P. J.; Schrock, R. R. *Organometallics* **2000**, *19*, 2414−2416.

[18] Sladek, M. L.; Braun, T.; Neumann, B.; Stammler, H. G. *J. Chem. Soc., Dalton Trans.* **2002**, 297−299.

[19] Böhm, V. P. W.; Gstöttmayr, C. W. K.; Weskamp, T.; Herrmann, W. A. *Angew. Chem., Intl. Ed.* **2001**, *40*, 3387−3389.

[20] Kraft, B. M.; Lachiotte, R. J.; Jones, W. D. *Organometallics* **2002**, *21*, 727−731.

[21] Deck, P. A.; Jackson, W. F.; Fronczek, F. R. *Organometallics* **1996**, *15*, 5287−5291.

[22] Deck, P. A.; Fronczek, F. R. *Organometallics* **2000**, *19*, 327−333.

[23] Thornberry, M. P.; Slebodnick, C.; Deck, P. A.; Fronczek, F. R. *Organometallics* **2000**, *19*, 5352−5369.

[24] Deck, P. A.; Maiorana, C. R. *Macromolecules* **2001**, *34*, 9−13.

[25] Thornberry, M. P.; Slebodnick, C.; Deck, P. A.; Fronczek, F. R. *Organometallics* **2001**, *20*, 920−926.

[26] Waymouth, R. M.; Kravchenko, R. L.; Maciejewski; Petoff, J. (Stanford University) US, 6169151, Jan 2, 2001.

[27] Hauptman, E.; Waymouth, R. M.; Ziller, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 11586−11587.

[28] Bruce, M. D.; Coates, G. W.; Hauptman, E.; Waymouth, R. M.; Ziller, J. W. *J. Am. Chem. Soc.* **1997**, *119*, 11174−11182.

[29] Lin, S.; Hauptman, E.; Lal, T. K.; Waymouth, R. M.; Quan, R. W.; Ernst, A. B. *J. Mol. Catal. A Chem.* **1998**, *136*, 23−33.

[30] Morris, R. J.; Shaw, S. L.; Jefferis, J. M.; Storhoff, J. J.; Goedde, D. M. *Inorg. Synth.* **1998**, *32*, 215−221.

[31] Diamond, G. M.; Rodewald, S.; Jordan, R. F. *Organometallics* **1995**, *14*, 5−7.

10.1021/om034385g CCC: $27.50 © 2004 American Chemical Society
Publication on Web 01/27/2004

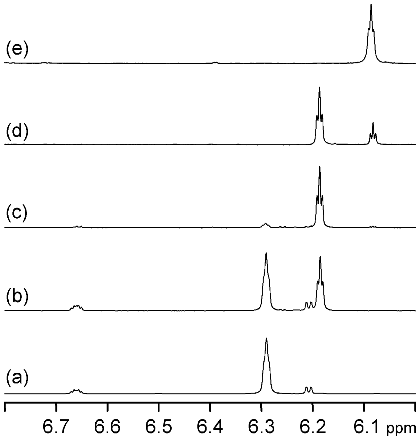


Figure 1. Partial ^{1}H NMR spectra (Cp and vinylic region) for the reaction of **1a** with 2 equiv of $Ti(NMe_2)_4$ in C_6D_6 recorded at the following intervals: (a) 15 min at 25 °C, (b) 18 h at 25 °C, then 3 h at 50 °C, (c) 17 h at 50 °C, (d) 40 h at 65 °C, (e) 3 days at 80 °C.

for the synthesis of indenyl complexes, our initial attempts to isolate stable C_6F_5-substituted indenyl complexes largely failed. However, in an amine elimination reaction of 3-(pentafluorophenyl)indene with $Ti(NMe_2)_4$, we observed the formation of products consistent with intramolecular S_NAr substitution of C−F at the *ortho* positions of the C_6F_5 substituent.[33−36] We describe here our initial exploration of this unexpected C−F activation pathway.

Results and Discussion

Reactions of 3-(Pentafluorophenyl)indene (1a) with $Ti(NMe_2)_4$. A solution of **1a** and $Ti(NMe_2)_4$ (1:2 ratio) in benzene-d_6 in a flame-sealed NMR tube was examined using ^{1}H and ^{19}F NMR spectroscopy at several intervals (Figures 1−3). The initial ^{1}H NMR spectrum (Figures 1a, 2a) was consistent with a mixture of unreacted arylindene (**1a**) and the corresponding η^5-indenyltitanium complex (**2a**) along with unreacted $Ti(NMe_2)_4$ (singlet at 3.11 ppm) and free Me_2NH (doublet at 2.20 ppm, broad singlet at 0.1 ppm, 6:1 intensity ratio). The initial ^{19}F NMR spectrum (Figure 3a) likewise showed three signals each for **1a** (major) and **2a** (minor). After 18 h at 25 °C, the ratio of **1a** and **2a** was essentially unchanged, suggesting the initial equilibrium shown in Scheme 1. After warming the same sample at 50 °C for 3 h, a new indene product (**4a**) was identified by a slightly shifted vinyl signal (Figure 1b) and a new aryl-NMe_2 signal (Figure 2b) in the ^{1}H NMR spectrum, as well as four signals of mutually equal intensity in the ^{19}F NMR spectrum (Figure 3b). The formation of **4a** is nearly complete after an additional 17 h at 50 °C (Figures 1c, 3c). After an additional 40 h at 65 °C, the triplet and doublet (1:2 ratio) in the ^{19}F NMR spectrum (Figure 3d) and the upfield-shifted vinylic hydrogen signal (Figure 1d) clearly indicated formation of indene **7a**. The ^{1}H NMR spectrum showed numerous signals in the upfield region (Figure 2d), some of which appear exchange-broadened. The methylene signals of **4a** and **7a** were not well resolved, but their presence was confirmed using a 1D-TOCSY experiment by irradiating the corresponding vinylic hydrogens at 6.1 ppm. Complete conversion to the diaminated arylindene (**7a**) was essentially complete after 3 days at 80 °C (Figures 1e, 2e, 3e).

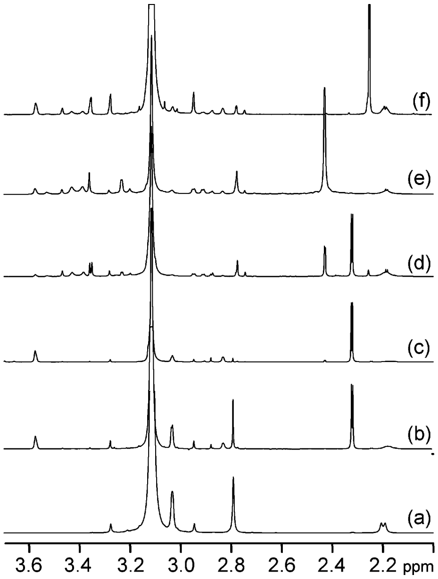


Figure 2. Partial ^{1}H NMR spectra (methyl region) for the reaction of **1a** with 2 equiv of $Ti(NMe_2)_4$ in C_6D_6 recorded at the following intervals: (a) 15 min at 25 °C, (b) 18 h at 25 °C, then 3 h at 50 °C, (c) 17 h at 50 °C, (d) 40 h at 65 °C, (e) 3 days at 80 °C, (f) TsF + $Ti(NMe_2)_4$ in C_6D_6 after 18 h at 65 °C.

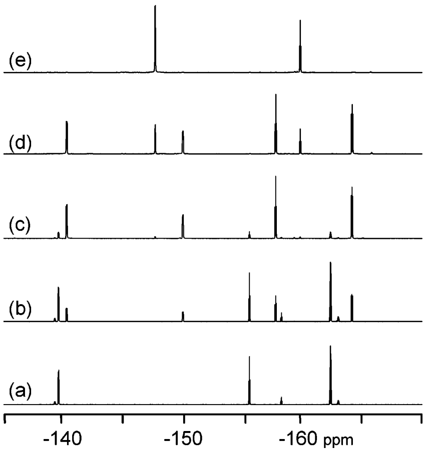


Figure 3. ^{19}F NMR spectra (aromatic region) for the reaction of **1a** with 2 equiv of $Ti(NMe_2)_4$ in C_6D_6 recorded at the following intervals: (a) 15 min at 25 °C, (b) 18 h at 25 °C, then 3 h at 50 °C, (c) 17 h at 50 °C, (d) 40 h at 65 °C, (e) 3 days at 80 °C.

Whereas the ^{19}F NMR spectra suggest a clean, highly selective reaction with respect to the indenyl moiety, the coordination environment about titanium in general and the fate of the “activated” fluoride ions in particular are unclear. Formally, removal of NMe_2 groups from titanium leaves vacant coordination sites for fluoride, affording $(Me_2N)_3TiF$ and $(Me_2N)_2TiF_2$. Examination of

---

(32) Diamond, G. M.; Jordan, R. F.; Petersen, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 8024−8033.

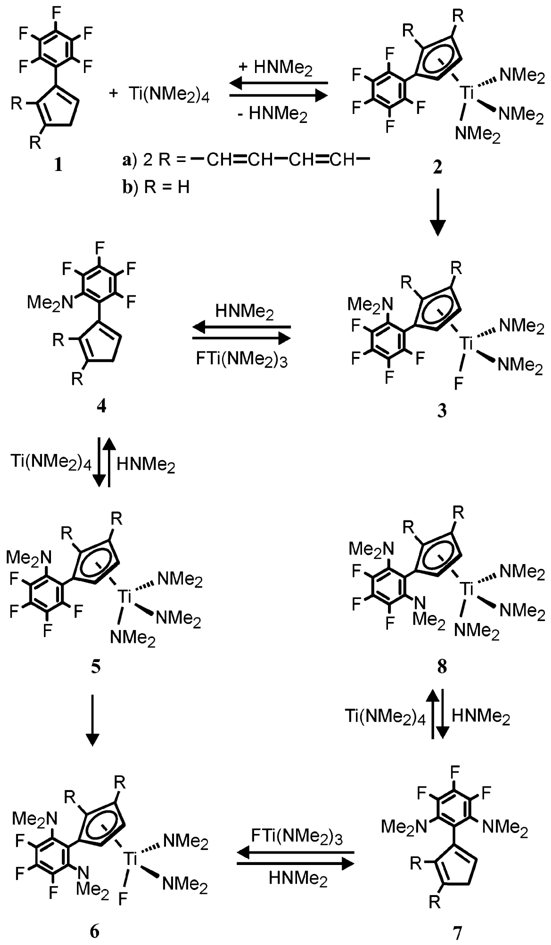
(33) O'Connor, P. E.; Berg, D. J.; Barclay, T. *Organometallics* **2002**, *21*, 3947−3954.

(34) Barrio, P.; Castarlenas, R.; Esterualas, M. A.; Lledós, A.; Maseras, F.; OZate, E.; TomBs, J. *Organometallics* **2001**, *20*, 442−452.

(35) Hughes, R. P.; Lindner, D. C.; Rheingold, A. L.; Yap, G. P. A. *Organometallics* **1996**, *15*, 5678−5686.

(36) Bellabarba, R. M.; Nieuwenhuyzen, M.; Saunders, G. C. *J. Chem. Soc., Dalton Trans.* **2001**, 512−514.

Scheme 1



the ^{19}F NMR spectrum from +250 to −250 ppm showed only the intense aryl CF groups and two weak, broadened, unassigned complex doublets ($J \approx 200$ Hz) around 0 ppm. In a small minority of duplicate experiments, weak/broadened signals were sometimes observed, but these signals would then disappear again after additional reaction time. The additional ^{19}F signals accounted for only about 20% of the expected signal intensity for the abstracted fluoride. Longer relaxation delays (20 s) did not change integration data significantly. The samples do slowly deposit a small amount of a fine precipitate that is insoluble in common solvents.

We tried to identify $(Me_2N)_3TiF$ spectroscopically by preparing it in situ from *p*-toluenesulfonyl fluoride (TsF) with excess $Ti(NMe_2)_4$ in C_6D_6. Slow formation of *N*,*N*-dimethyl-*p*-toluenesulfonamide[37] was confirmed by comparison to authentic samples. We hypothesized that the putative byproduct $(Me_2N)_3TiF$ would meet the same fate as in the reaction of **1a** with $Ti(NMe_2)_4$, and indeed the ^{1}H NMR spectra of the two reactions (Figure 2e,f) are strikingly similar in the region 2.5−3.7 ppm, whereas neither ^{19}F NMR spectrum shows signals in the range +250 to −250 ppm that we could assign to titanium fluorides. Furthermore the diethylamido analogues $(Et_2N)_3TiF$ and $(Et_2N)_2TiF_2$ are known to exhibit complex, broadened, concentration- and temperature-dependent NMR spectra, suggesting extensive aggregation and ligand scrambling, presumably through bridging fluorides.[38] Aggregation would probably be even more likely for our less encumbered dimethylamido analogues, whereas for the more encumbered TiF moiety of $[^tBuN(3,5\text{-}Me_2C_6H_3)]_3TiF$, a clear signal was reported at −71.6 ppm.[39]

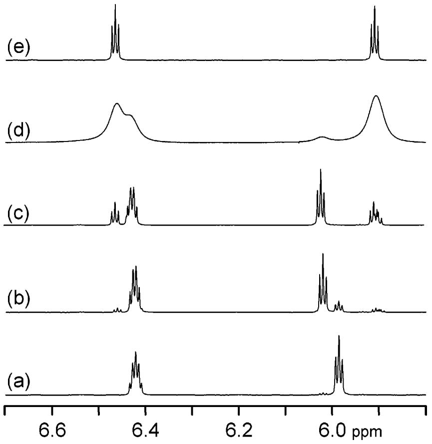


Figure 4. Partial ^{1}H NMR spectra (Cp region) for the reaction of **1b** with 2 equiv of $Ti(NMe_2)_4$ in C_6D_6 recorded at the following intervals: (a) 15 min at 25 °C, (b) 17 h at 25 °C, (c) 3 h at 50 °C, (d) 24 h at 50 °C. (e) $Ti(NMe_2)_4$ + **7b** (2:1) in C_6D_6.

When arylindene (**1a**) reacted with 2.0 equiv of $Ti(NMe_2)_4$ on a preparative scale, the diaminated arylindene (**7a**) was obtained selectively in 71% crude yield after hydrolytic workup. Likewise, a preparative-scale reaction of arylindene (**1a**) with 0.5 equiv of $Ti(NMe_2)_4$ gave the monoaminated arylindene (**4a**) in 93% crude yield as the major product, although subsequent chromatographic purification was rather inefficient. NMR spectroscopic analyses of the pure substances (**4a** and **7a**) confirmed their assignment in the spectra of the reaction mixtures (Figures 1−3). Two related negative findings are noteworthy: In reactions conducted in flame-sealed NMR tubes, arylindene (**1a**) did not react with either $Ti(O^iPr)_4$ (80 °C, benzene-d_6, 18 h) or $CpTi(NMe_2)_3$ (80 °C, benzene-d_6, 18 h).

Reactions of (Pentafluorophenyl)cyclopentadiene (1b) with Ti(NMe$_2$)$_4$. When the arylcyclopentadiene (**1b**) was treated with 2.0 equiv of $Ti(NMe_2)_4$ in C_6D_6 at 25 °C, the initial ^{1}H NMR spectrum (Figures 4a, 5a; $t < 15$ min) showed that all of the diene (**1b**) had been consumed to form **2b** and 1 equiv of Me_2NH cleanly. Generally, monosubstituted Cp complexes show ^{1}H NMR splitting patterns that resemble two triplets because the vicinal ($^3J_{HH}$) and distal ($^4J_{HH}$) coupling constants are nearly the same (about 2 Hz).[40] The signal at 6.42 ppm in **2b** showed a pentet instead, and we assigned this additional splitting to long-range H−F coupling to the two *ortho* fluorines of the C_6F_5 group ($^5J_{HF} \approx {}^3J_{HH} \approx {}^4J_{HH} \approx 2$ Hz). A similar observation was reported for $[\eta^5\text{-}C_5H_4(C_6F_5)]_2Fe$.[21] The accidental equivalence of the three coupling constants provided a means to assign C−F activated species in the ^{1}H NMR spec-

---

(37) Steinkopf, W.; Buchheim, K.; Beythien, K.; Dudek, H.; Eisold, J.; Gall, J.; Jaeger, P.; Beumuth, H.; Semenoff, A.; Wemme, A. *J. Prakt. Chem.* **1927**, *117*, 1−82.

(38) Bürger, H.; Wiegel, K. *Z. Anorg. Allg. Chem.* **1973**, *398*, 257−272.

(39) Agapie, T.; Diaconescu, P. L.; Mindiola, D. J.; Cummins, C. C. *Organometallics* **2002**, *21*, 1329−1340.

(40) Gamboa, J. A.; Sundararaman, A.; Kakalis, L.; Lough, A. J.; Jäkle, F. *Organometallics* **2002**, *21*, 4169−4181.

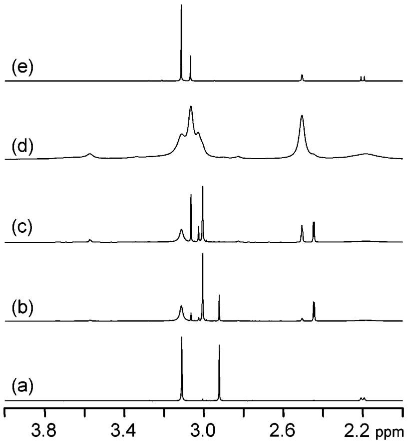


Figure 5. Partial ^{1}H NMR spectra (methyl region) for the reaction of **1b** with 2 equiv of $Ti(NMe_2)_4$ in C_6D_6 recorded at the following intervals: (a) 15 min at 25 °C, (b) 17 h at 25 °C, (c) 3 h at 50 °C, (d) 24 h at 50 °C. (e) $Ti(NMe_2)_4$ + **7b** (2:1) in C_6D_6.

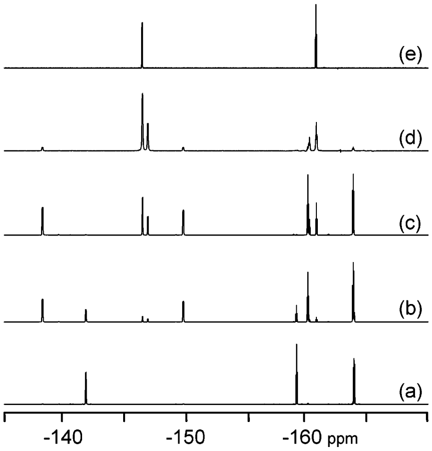


Figure 6. ^{19}F NMR spectra (aromatic region) for the reaction of **1b** with 2 equiv of $Ti(NMe_2)_4$ in C_6D_6 recorded at the following intervals: (a) 15 min at 25 °C, (b) 17 h at 25 °C, (c) 3 h at 50 °C, (d) 24 h at 50 °C. (e) $Ti(NMe_2)_4$ + **7b** (2:1) in C_6D_6.

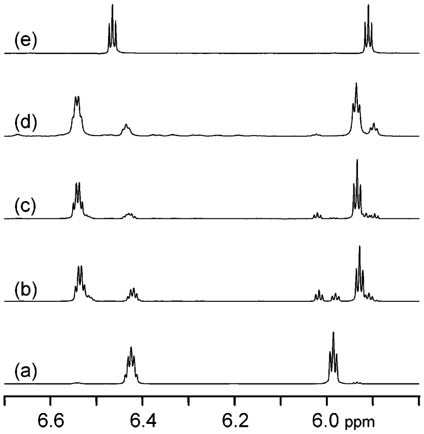


Figure 7. Partial ^{1}H NMR spectra (Cp region) for the reaction of **1b** with 1 equiv of $Ti(NMe_2)_4$ in C_6D_6 recorded at the following intervals: (a) 15 min at 25 °C, (b) 17 h at 25 °C, (c) 3 h at 50 °C, (d) 24 h at 50 °C. (e) $Ti(NMe_2)_4$ + **7b** (2:1) in C_6D_6.

trum as the reaction ensued. The ^{19}F NMR spectrum of **2b** (Figure 6a) shows the expected three signals.

After 17 h at 25 °C, analysis of the mixture using ^{19}F NMR (Figure 6b) showed about 75% conversion to the *ortho*-CF-activated intermediate **3b** (four equally integrating signals). In the downfield ^{1}H NMR spectrum (Figure 4b), the quartet at 6.42 ppm (Figure 4b) is consistent with coupling of Cp hydrogens to only one *ortho* fluorine. In the upfield ^{1}H NMR spectrum (Figure 5b), a new doublet (J = 2 Hz) appears at 2.45 ppm for the aryl dimethylamino group coupled to the fluorine at position 3. (Corresponding dd-septet coupling is observed in the signal at −150 ppm in the ^{19}F NMR spectrum.) However compound **3b** requires a 1:2 integration ratio for the aryl- and Ti-bound NMe_2 groups, respectively, whereas a 1:3 ratio is observed instead. We propose that the reaction has proceeded by exchange with unreacted $Ti(NMe_2)_4$ to give intermediate **5b** instead, possibly by bimolecular ligand exchange or via the free diene **4b**. In this scenario, the signal at 3.11 corresponding to $Ti(NMe_2)_4$ should be depleted, because 2 equiv of the starting titanium complex is formally consumed. Instead the signal is broadened. The putative byproduct $FTi(NMe_2)_3$ probably does not have the same chemical shift based on data obtained for the corresponding Et_2N derivatives.[38] The presence of this signal, its intensity (equal to that of **5b**), and its broadened appearance may arise from aggregation and disproportionation of $FTi(NMe_2)_3$ as discussed earlier, but we have no additional evidence to support that speculation. As in the reactions of **1a**, Ti−F signals were not identified in any of the ^{19}F spectra in the expected range,[21,41] and again we must concede that the fate of the displaced fluoride remains unknown.

After an additional 3 h at 50 °C, all of the initial complex (**2b**) has been consumed, and after 24 h at 50 °C, the intermediate **5b** is nearly completely consumed as well. The corresponding ^{19}F NMR spectra (Figure 6c,d) show that the four-line pattern of **5b** is gradually replaced by two new doublets at about −146 ppm and two new triplets at about −160 ppm. These observations, together with the appearance of a new triplet in the downfield ^{1}H NMR spectrum (Figure 4c), suggest new complexes in which both *ortho* fluorines are replaced by Me_2N groups. One of these was assigned by treating an authentic sample of **7b** with $Ti(NMe_2)_4$ to afford **8b** (Figures 4e, 5e, 6e). The other is presumably intermediate **6b**, although the extensive broadening of the NMR signals (Figures 4d, 5d) suggests ligand-scrambling at titanium on the NMR time scale.

When an essentially identical reaction is conducted—except that a 1:1 ratio of **1b** and $Ti(NMe_2)_4$ is used—a qualitatively analogous process occurs, except that the chemical shifts of the major intermediates are different. Complex **2b** is still obtained cleanly (Figures 7a, 8, and 9a), and free $Ti(NMe_2)_4$ is consumed. However after 17 h at 25 °C, two quartets are observed in the downfield ^{1}H NMR spectrum (Figure 7b) along with two four-line systems in the ^{19}F NMR spectrum (Figure 9b), perhaps indicating a mixture of **3b** and **5b**. After 24 h at 50 °C, a small amount of doubly activated species is indicated by the triplet at 6.43 ppm in the downfield ^{1}H NMR spectrum (Figure 7d) and the two-line pattern in the ^{19}F NMR spectrum (Figure 9d). This species is not complex **8b** (compare to Figures 7e and 9b) but corre-

---

(41) Kaminsky, W.; Lenk, S.; Scholz, V.; Roesky, H. W.; Herzog, A. *Macromolecules* **1997**, *30*, 7647−7650.

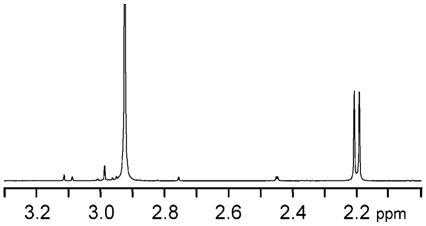


Figure 8. Partial ^{1}H NMR spectra (methyl region) for the reaction of **1b** with 1 equiv of Ti(NMe$_2$)$_4$ in C$_6$D$_6$ recorded after 15 min at 25 °C.

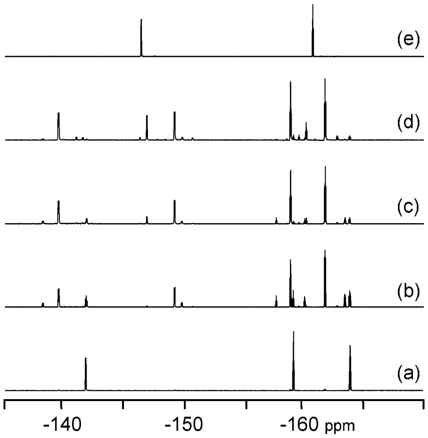


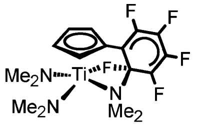
Figure 9. ^{19}F NMR spectra (aromatic region) for the reaction of **1b** with 1 equiv of Ti(NMe$_2$)$_4$ in C$_6$D$_6$ recorded at the following intervals: (a) 15 min at 25 °C, (b) 17 h at 25 °C, (c) 3 h at 50 °C, (d) 24 h at 50 °C. (e) Ti(NMe$_2$)$_4$ + **7b** (2:1) in C$_6$D$_6$.

sponds to the signals we tentatively assigned to intermediate **6b** above. An increase in the relative concentrations of fluorine-rich intermediates is consistent with the change in reaction stoichiometry.

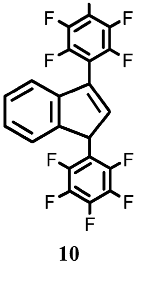
The *ortho* selectivity of the CF activation processes suggests an intramolecular substitution pathway, perhaps via an intermediate like **9**. Reactions of **1a** with either excess LiNMe$_2$ in THF or excess Me$_2$NH in aqueous THF resulted in *para*-selective substitutions characterized by the appearance of two new equally integrating signals in the ^{19}F NMR spectrum. Bimolecular reactions of C$_6$F$_5$-substituted ferrocenes with "external" nucleophiles such as alkoxides and alkyllithiums are also *para*-selective.[15,42] Pentafluorotoluene (CH$_3$C$_6$F$_5$), which cannot bind titanium in the same manner as **1a** or **1b**, did not react with Ti(NMe$_2$)$_4$ (toluene, 100 °C, 24 h).

Berg and co-workers observed a similar formal intramolecular *ortho* CF substitution in zirconium(III) aryldiamides, which they theorized might proceed by oxidative addition to Zr(II) following disproportionation.[33] Redox chemistry is unlikely in our reactions. More relevant here are the analogous intermolecular S$_N$Ar pathway proposed[43] for dehydrofluorination of C$_6$H$_5$F by (Me$_5$C$_5$)$_2$ZrH$_2$ and the dehydrofluorinative couplings of Me$_5$C$_5$ and fluoroaryl ligands observed in some late transition metal complexes.[35,36] The most compelling predecent for our findings is the observation of analogous fluoride/amide exchanges upon complexation of fluoroaryl-substituted tripodal amine ligands to molybdenum[17] and to hafnium.[16] In the latter example the hafnium source was Hf(NMe$_2$)$_4$, and the product was a well-characterized quasi-octahedral hafnium monofluoride complex in which an erstwhile 2,6-difluorophenyl group was converted to a 2-fluoro-6-(dimethylamino)phenyl substituent. This result suggests that our C−F activation reaction might also proceed with less highly fluorinated aryl substituents.

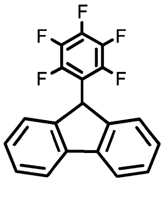
The equilibrium between free and complexed indenes (**1a** and **2a**) warrants more discussion. As the aminated indenes (**4a** and **7a**) are formed, they are observed only as free indenes (Figure 1, Scheme 1); indenyltitanium complexes **3a**, **5a**, and **8a** were not observed. The Me$_2$N groups might disrupt indenyl−titanium bonding by changing the conformation of the aryl groups (see "Structural Studies" below), although steric effects should be relatively minor especially for the monoaminated indene (**3**). Indenes **4** and **7** are probably also less acidic than **1**. More acidic indenes should be more reactive toward the basic Ti−NMe$_2$ moiety. However, variations in Ti−indenyl bond strengths would also need to be considered in a complete thermodynamic treatment, and one might expect indenyl anions bearing electron-withdrawing substituents to form weaker Ti−indenyl bonds. When the diarylated indene (**10**, 12.2 mg) was treated with 1 equiv of Ti(NMe$_2$)$_4$ (15.4 mg) in benzene-*d*$_6$, we observed a qualitatively similar equilibrium, even though **10** is about 7 p*K* units more acidic than **1a** in THF.[44] Similarly, when unsubstituted indene, which has a p*K* about 6 units higher than that of **1a**,[44] was treated with 1 equiv of Ti(NMe$_2$)$_4$ at 80 °C for 18 h in benzene-*d*$_6$ *in a sealed tube*, ^{1}H NMR spectroscopic analysis (at 25 °C) showed a mixture of uncomplexed indene and (Ind)Ti(NMe$_2$)$_3$. Martins and coworkers reported a high-yielding synthesis of (Ind)Ti(NMe$_2$)$_3$ from the same two reactants in toluene at 80 °C, but their procedure called for a continuous stream of inert gas to carry away the Me$_2$NH byproduct.[45] In contrast, cyclopentadienyl ligands generally form stronger bonds to transition metals than indenyl ligands. Thus, even though the p*K* of **1b** lies between that of the two arylindenes **1a** and **10**,[44] the free dienes (**1b**, **4b**, **7b**) were not observed in our reactions with excess Ti(NMe$_2$)$_4$. Also, 9-(pentafluorophenyl)fluorene (**11**),[46] which is about 2 p*K* units less acidic than **1a**,[47] does not react at all with 2 equiv of Ti(NMe$_2$)$_4$ (C$_6$D$_6$, 80 °C, 18 h).



9



10



11

---

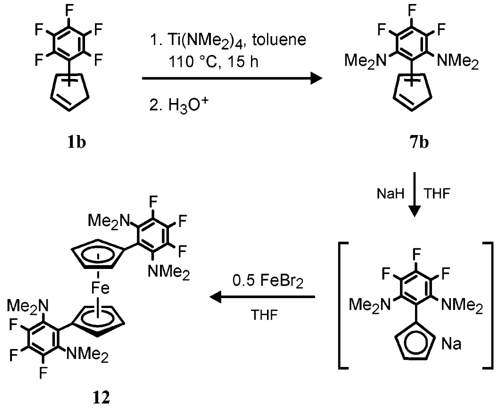
[42] Deck, P. A.; Lane, M. J.; Montgomery, J. L.; Slebodnick, C.; Fronczek, F. R. *Organometallics* **2000**, *19*, 1013−1024.

[43] Kraft, B. M.; Lachiotte, R. J.; Jones, W. D. *J. Am. Chem. Soc.* **2001**, *123*, 10973−10979.

Table 1. Crystallographic Data

	4a	**7b**	**12**
empirical formula	$C_{17}H_{13}F_4N$	$C_{15}H_{17}F_3N_2$	$C_{30}H_{32}F_6FeN_4$
fw	307.28	282.31	618.45
diffractometer	Oxford Diffraction X2	Oxford Diffraction X2	Oxford Diffraction X2
cryst dimens (mm)	0.14 × 0.10 × 0.08	0.25 × 0.19 × 0.17	0.18 × 0.18 × 0.12
cryst system	monoclinic	monoclinic	monoclinic
a (Å)	7.5668(8)	10.7977(18)	6.0695(5)
b (Å)	16.3012(15)	8.0970(13)	34.001(2)
c (Å)	11.2873(13)	15.816(2)	13.2317(12)
α (deg)	90	90	90
β (deg)	92.976(9)	94.422(12)	92.535(7)
γ (deg)	90	90	90
V (Å^3)	1390.4(3)	1378.6(4)	2727.9(4)
space group	$P2_1/c$	$P2_1/n$	$P2_1/c$
Z	4	4	4
D_{calc} (Mg m^{-3})	1.468	1.360	1.506
abs coeff (mm^{-1})	0.123	0.109	0.622
F_{000}	632	592	1280
radiation	Mo Kα	Mo Kα	Mo Kα
λ (Kα) (Å)	0.71073	0.71073	0.71073
temp (K)	100(2)	100(2)	100(2)
θ range for collection (deg)	2.97 to 27.60	3.35 to 30.07	3.08 to 27.50
no. of reflns colld	8270	15733	18700
no. of indep reflns	3213	4032	2513
abs corr method	none	none	none
no. of data/restrts/params	3213/0/201	4032/0/185	6250/0/378
R [$I > 2\sigma(I)$]	0.0439	0.0494	0.0463
R_w [$I > 2\sigma(I)$]	0.1099	0.1477	0.1004
GoF on F^2	1.139	1.157	1.171
largest diff peak, hole (e A^{-3})	0.572, −0.662	0.417, −0.372	0.440, −0.368

Scheme 2



Isolation of the (Diaminoaryl)cyclopentadiene (7b) and its Use as a Ligand. As shown in Scheme 2, when the arylcyclopentadiene (**1b**) was treated with excess $Ti(NMe_2)_4$ on a preparative scale, hydrolytic workup gave **7b** in 71% yield. Treatment of **7b** with sodium hydride followed by 0.5 equiv of $FeBr_2$ in THF gave the substituted ferrocene derivative (**12**) in 74% yield as a deep red solid. The NMR spectrum of **12** in $CDCl_3$ at 25 °C shows free rotation of the aryl substitutents (1 Me_2N signal in ^1H NMR spectrum and 2 sharp aryl CF signals in the ^{19}F NMR spectrum).

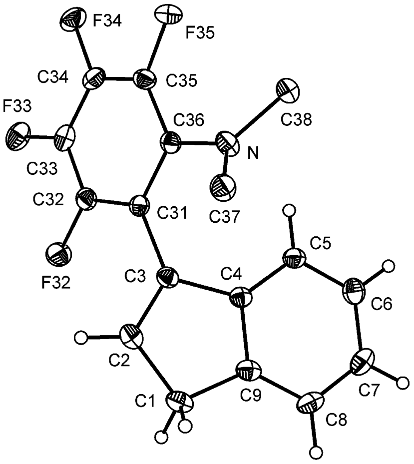


Figure 10. Thermal ellipsoid plot (50% probability) of **4a**. Methyl hydrogens omitted for clarity. Selected interatomic distances (Å) and angles (deg): C1−C2, 1.507(3); C2−C3, 1.348(2); C3−C4, 1.481(2); C4−C9, 1.395(2); C9−C1, 1.508(3); C3−C31, 1.487(2); N−C36, 1.389(2); N−C37, 1.456(2); N−C38, 1.456(2); C36−N−C37, 120.96(14); C37−N−C38, 115.82(15); C38−N−C36, 121.62(14).

Structural Studies. Compounds **4a**, **7b**, and **12** were subjected to single-crystal X-ray diffraction studies (Table 1), and their solid-state molecular structures (Figures 10−12) exhibited some noteworthy features. In **4a**, the indene−aryl torsion angle is about 55°, whereas in **7b** and **12**, the aryl substituents are approximately perpendicular to their respective cyclopentadienyl moieties, presumably because of the steric effects of the Me_2N groups. In contrast, 1,4-bis(pentafluorophenyl)-cyclopentadiene, which lacks bulky *ortho* substituents, is a nearly planar molecule.[23] This strong conformational preference of the aryl groups in **12** apparently precludes intramolecular arene stacking of the type reported elsewhere for 1,1′-diarylferrocenes.[23,25,48] The packing diagram of **4a**, which has only one Me_2N group,

---

[44] Thornberry, M. P.; Warren, A. D.; Deck, P. A.; McKeown, A. E.; Hasayan, F.; Streitwieser, A. Manuscript in preparation.

[45] Martins, A. M.; Ascenso, J. R.; de Azevedo, C. G.; Calhorda, M. J.; Dias, A. R.; Rodrigues, S. S.; Toupet, L.; de Leonardis, P.; Veiros, L. F. *J. Chem. Soc., Dalton Trans.* **2000**, 4332−4338.

[46] Andrews, A. F.; Mackie, R. K.; Walton, J. C. *J. Chem. Soc., Perkin Trans. 2* **1980**, 96−102.

[47] Bordwell, F. G.; Branca, J. C.; Bares, J. E.; Filler, R. *J. Org. Chem.* **1988**, *1988*, 780−782.

[48] Blanchard, M. D.; Hughes, R. P.; Concolino, T. E.; Rheingold, A. L. *Chem. Mater.* **2000**, *12*, 1604−1610.

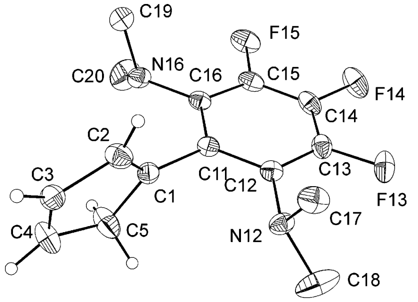


Figure 11. Thermal ellipsoid plot (50% probability) of **7b**. Methyl hydrogens omitted for clarity. Selected interatomic distances (Å) and angles (deg): C1−C2, 1.357(2); C2−C3, 1.450(2); C3−C4, 1.376(2); C4−C5, 1.470(2); C5−C1, 1.458(2); C1−C11, 1.480(2); C2−C1−C5, 108.4(1); C2−C1−C11, 128.4(1); C5−C1−C11, 128.2(1); C11−C12−N12, 119.2(1); C11−C16−N16, 118.6(1); C2−C1−C11−C12, 82.1(2).

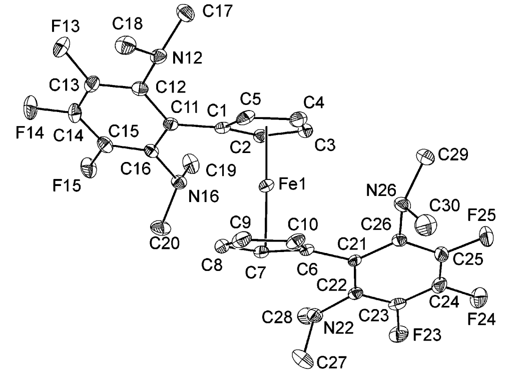


Figure 12. Thermal ellipsoid plot (50% probability) of **12**. Hydrogens omitted for clarity. Selected interatomic distances (Å) and angles (deg): Fe1−C1, 2.069(2); Fe1−C2, 2.051(2); Fe1−C3, 2.051(2); Fe1−C4, 2.040(2); Fe1−C5, 2.035(2); Fe1−C6, 2.074(2); Fe1−C7, 2.032(2); Fe1−C8, 2.035(2); Fe1−C9, 2.051(2); Fe1−C10, 2.051(2); C2−C1−C11−C16, 34.3(3); C10−C6−C21−C26, −35.0(3).

reveals an arene stacking motif in which the Me_2N groups are in an *anti* arrangement. The distance between arene centroids is 3.53 Å, and the orthogonal interplanar distance is 3.27 Å, indicating a moderately strong stacking interaction. The ferrocene (**12**) also exhibits some strain, reflected in slightly longer Fe−C distances to the *ipso* carbons of the (η^5-C_5H_4R) groups, a distortion not observed in $(C_5H_4C_6F_5)_2Fe$.[48] The Fe−N distances (3.72 Å) are far too long to consider the Me_2N group to be a pendant donor group in this system. We have considered the possibility that species such as **4b** might serve as "hybrid" ligands in a manner similar to Saunders's Cp-linked phosphines[49,50] or Rothwell's indenyl-linked phenoxides,[51,52] but the fluoroaromatic substituent probably renders the Me_2N moiety a rather unwilling electron pair donor.

Conclusions

$Ti(NMe_2)_4$ reacts with 3-(pentafluorophenyl)indene and (pentafluorophenyl)cyclopentadiene via intramolecular, nucleophilic substitution of the *ortho* C−F groups by Ti−NMe_2 groups to afford aminated arylindenes and arylcyclopentadienes. NMR-scale experiments demonstrate the indermediacy of indenyltitanium and cyclopentadienyltitanium compounds. Taken in context of complementary work published by others, it is clear that aryl CF bonds positioned in close proximity to the inner coordination sphere of early transition metal amides are subject to nucleophilic CF activation. The scope and mechanism of these processes are under continued investigation in our laboratories.

Experimental Section

General Procedures. All reactions were carried out using standard inert-atmosphere techniques. NMR spectra were recorded on Varian Unity-400 or Inova-400 instruments. ^{19}F NMR spectra were referenced externally to C_6F_6 in $CDCl_3$ (δ_F = −163.0 ppm). Elemental microanalyses were performed by Desert Analytics (Tuscon AZ). $Ti(NMe_2)_4$ was used as received from Aldrich. The arylindene (**1a**) was prepared as previously reported[22] and purified by repeated fractional crystallization from methanol followed by sublimation at 100 °C (0.1 Torr). Indene was distilled at 20 mmHg. The monoarylated cyclopentadiene (**1b**) was prepared by treating hexafluorobenzene with sodium cyclopentadienide and sodium hydride at 0 °C in THF following our "improved" procedure given on the last page of the Supporting Information for ref 23. After hydrolytic workup, the diene (**1b**) is obtained as a mixture of double-bond regioisomers. The diene dimerizes slowly even when stored in a freezer (−10 °C), so all samples of **1b** used for these experiments were freshly sublimed at 50 °C (0.1 Torr). When highly pure, both **1a** and **1b** are white solids. Common solvents were purified by published methods. Benzene-d_6 was vacuum-transferred from NaK alloy and stored in the glovebox.

NMR-Scale Reaction of 3-(Pentafluorophenyl)indene (1a) and $Ti(NMe_2)_4$. In a nitrogen glovebox, a solution of **1a** (9.4 mg, 33 μmol) and $Ti(NMe_2)_4$ (15.0 mg, 67 μmol) in benzene-d_6 (about 0.7 mL) was prepared in an NMR tube, which was then flame-sealed. After initial NMR spectroscopic analysis, the tube was allowed to stand for the following intervals and temperatures and reanalyzed after each interval: 18 h at 25 °C, 3 h at 50 °C, 17 h at 50 °C, 10 h at 65 °C, 30 h at 65 °C, 12 h at 80 °C, and 60 h at 80 °C. Representative NMR data are presented in Figures 1−3. A concurrent experiment in which **1a** (18.8 mg, 66 μmol) was treated instead with 1 equiv of $Ti(NMe_2)_4$ (15.0 mg, 67 μmol) gave qualitatively similar results. Components of the reaction mixture were assigned as follows: Unreacted $Ti(NMe_2)_4$: ^1H NMR (C_6D_6) δ 3.11(s). Me_2NH: ^1H NMR (C_6D_6) δ 2.20 (d, 6 H), 0.1 (br s). Complex **2a**: ^1H NMR (C_6D_6) δ 7.26 and 7.00 (m, 2 H each, C_6H_4), 6.66 (m, 1 H_2), 6.21 (dd, 1 H_3), 2.80 (s, 18 H, $Ti[NMe_2]_3$); ^{19}F NMR (C_6D_6) δ −139.2 (d, 2 F_o), −158.2 (t, 1 F_p), −163.0 (m, 2 F_m). Data for **4a** and **7a** are provided below.

NMR-Scale Reaction of (Pentafluorophenyl)cyclopentadiene (1b) and $Ti(NMe_2)_4$. In a nitrogen glovebox, a solution of **1b** (15 mg, 67 μmol) and $Ti(NMe_2)_4$ (30 mg, 132 μmol) in benzene-d_6 (about 0.7 mL) was prepared in an NMR tube, which was then flame-sealed. After initial NMR analysis, the tube was allowed to stand for the following intervals and temperatures and reanalyzed after each interval: 17 h at 25 °C, 3 h at 50 °C, and 24 h at 50 °C. Representative NMR data are presented in Figures 4−6. Spectra from a concurrent experiment in which **1b** (15 mg, 67 μmol) was treated instead with 1 equiv of $Ti(NMe_2)_4$ (15 mg, 67 μmol) are shown in Figures 7−9. Spectral assignments are presented in the Results and Discussion.

---

(49) Ballabarba, R. M.; Saunders, G. C. *J. Fluorine Chem.* **2001**, *112*, 139−144.

(50) Bellabarba, R. M.; Niewenhuyzen, M.; Saunders, G. C. *Organometallics* **2002**, *21*, 5726−5737.

(51) Turner, L. E.; Thorn, M. G.; Fanwick, P. E.; Rothwell, I. P. *Chem. Commun.* **2003**, 1034−1035.

(52) Thorn, M. G.; Parker, J. R.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **2003**, *22*, 4658−4664.

NMR-Scale Reaction of Indene and Ti(NMe$_2$)$_4$. In a nitrogen glovebox, a solution of indene (20 mg, 170 μmol) and Ti(NMe$_2$)$_4$ (38.5 mg, 172 μmol) in benzene-d_6 (about 0.7 mL) was prepared in an NMR tube, which was then flame-sealed. The tube was placed in an 80 °C oil bath for 18 h. ^{1}H NMR spectroscopic analysis showed unreacted indene and (Ind)Ti(NMe$_2$)$_3$ (verified by comparison with published data[45]) in a ratio of about 4:1.

NMR-Scale Reaction of 1,3-Bis(pentafluorophenyl)indene (10) and Ti(NMe$_2$)$_4$. In a nitrogen glovebox, a solution of diarylindene[22] (**10**, 13.5 mg, 30.1 mmol) and Ti(NMe$_2$)$_4$ (13.5 mg, 60.3 μmol) in benzene-d_6 (about 0.7 mL) was prepared in an NMR tube, which was then flame-sealed. Immediate ^{19}F NMR spectroscopic analysis (t < 15 min) showed unreacted **10** and [1,3-(C$_6$F$_5$)$_2$Ind]Ti(NMe$_2$)$_3$ in a ratio of about 2:1. Data for **10** compared well with published data obtained in CDCl$_3$.[22] Data for [1,3-(C$_6$F$_5$)$_2$Ind]Ti(NMe$_2$)$_3$: ^{19}F NMR (C$_6$D$_6$) δ −142.3 (d, 2 F), −157.3 (t, 2 F), −162.6 (m, 2 F). ^{1}H NMR assignments were unclear because of apparent exchange broadening. After several hours at room temperature a C−F activation process analogous to the reaction of **1a** and Ti(NMe$_2$)$_4$ was evident from ^{19}F NMR spectroscopic analysis but was not pursued further.

NMR-Scale Reaction of Arylcyclopentadiene (7b) with Ti(NMe$_2$)$_4$. In a nitrogen glovebox, a solution of arylindene (**7b**, 9.3 mg, 33 μmol) and Ti(NMe$_2$)$_4$ (14.8 mg, 66 μmol) in benzene-d_6 (about 0.7 mL) was prepared in an NMR tube, which was then flame-sealed. After 4 h at 25 °C, NMR analysis showed dimethylamine, unreacted Ti(NMe$_2$)$_4$, and complex **8b**. Data for **8b**: ^{1}H NMR (C$_6$D$_6$) δ 6.45 (t, $J = 2$ Hz, 2 H), 5.90 (t, $J = 2$ Hz, 2 H), 3.06 (s, 18 H), 2.50 (d, $J_{FH} = 1.6$ Hz, 6 H); ^{19}F NMR (C$_6$D$_6$) δ −146.4 (d, $^3J_{FF} = 20$ Hz, 2 F), −160.7 (d, $^3J_{FF} = 20$ Hz, 1 F).

NMR-Scale Reaction of 9-(Pentafluorophenyl)fluorene (11) with Ti(NMe$_2$)$_4$. In a nitrogen glovebox, a solution of 9-(pentafluorophenyl)fluorene[47] (10.8 mg, 32 μmol) and Ti(NMe$_2$)$_4$ (14.6 mg, 65 μmol) in benzene-d_6 (about 0.7 mL) was prepared in an NMR tube, which was then flame-sealed. After 4 h at 25 °C, NMR spectroscopic analysis showed only unreacted starting materials. Data for **11**: ^{1}H NMR (C$_6$D$_6$) δ 7.57 (d, 2 H), 7.20 (d, 2 H), 7.08 (d, 2 H), 7.00 (d, 2 H), 5.09 (s, 1 H); ^{19}F NMR (C$_6$D$_6$) δ −140.0 (br s, 1 F), −145.4 (br s, 1 F), −156.0 (t, $^3J_{FF} = 21$ Hz, 1 H), −161.7 (br s, 1 F), −162.6 (br s, 1 F).

NMR-Scale Reaction of 3-(Pentafluorophenyl)indene with CpTi(NMe$_2$)$_3$. In a nitrogen glovebox, a solution of **1a** (20 mg, 76 μmol) and CpTi(NMe$_2$)$_3$[53] in benzene-d_6 (about 1 mL) was prepared in an NMR tube, which was then flame-sealed. After immersion in an oil bath for 18 h at 80 °C, analysis by ^{1}H and ^{19}F NMR spectroscopy showed only unreacted starting materials.

NMR-Scale Reaction of 3-(Pentafluorophenyl)indene with Ti(O^{i}Pr)$_4$. In a nitrogen glovebox, a solution of **1a** (about 20 mg) and Ti(O^{i}Pr)$_4$ (about 50 mg) in toluene-d_8 (about 1 mL) was prepared in a J-Young NMR tube. After immersion in an oil bath for 18 h at 80 °C, analysis by ^{1}H and ^{19}F NMR spectroscopy showed only unreacted starting materials and a small amount of ^{i}PrOH from the hydrolysis of Ti(OiPr)$_4$ by adventitious moisture.

NMR-Scale Reaction of *p*-Toluenesulfonyl Fluoride (TsF) with Ti(NMe$_2$)$_4$. In a nitrogen glovebox, a solution of TsF (8.7 mg, 50 μmol) and Ti(NMe$_2$)$_4$ (22.7 mg, 100 μmol) in C$_6$D$_6$ (about 0.8 mL) was prepared in an NMR tube, which was then flame-sealed. Initial ^{1}H and ^{19}F NMR spectra showed only unreacted starting materials. Data for TsF: ^{1}H NMR (C$_6$D$_6$) δ 7.51 (d, 2 H), 6.50 (d, 2 H), 1.72 (s, 3 H); ^{19}F NMR (C$_6$D$_6$) δ +66.7 (s). After 18 h at 65 °C, the sample contained about 25% of *N*,*N*-dimethyl *p*-toluenesulfonamide (TsNMe$_2$). Data for TsNMe$_2$: ^{1}H NMR (C$_6$D$_6$) δ 7.59 (d, 2 H), 6.78 (d, 2 H), 2.26 (s, 6 H), 1.91 (s, 3 H). These chemical shifts were confirmed by comparison to an authentic sample of TsNMe$_2$ prepared by adding excess 40% aqueous dimethylamine to a solution of tosyl chloride in benzene followed by aqueous workup.[54] The ^{1}H NMR spectrum also contained several unassigned signals in the NMe$_2$ region (see Figure 8), whereas the ^{19}F NMR spectrum showed only unreacted TsF at 66.7 ppm.

Synthesis of 3-[2-(Dimethylamino)tetrafluorophenyl]indene (4a). A solution of **1a** (1.13 g, 4.00 mmol), Ti(NMe$_2$)$_4$ (450 mg, 2.00 mmol), and toluene (50 mL) was stirred at 100 °C under a nitrogen atmosphere for 5 days and then cooled. The volatile components were evaporated. Hexane (50 mL) and water (20 mL) were added. The biphasic mixture was filtered through Celite, and the filter was rinsed with 50 mL of hexane. The biphasic filtrate was separated, and the aqueous layer was washed with 50 mL of hexane. The organic layers were combined, washed with saturated sodium bicarbonate solution (2 × 20 mL), dried over anhydrous MgSO$_4$, filtered, and evaporated to afford 1.14 g (3.71 mmol, 93%) of a red oil that crystallized upon standing. ^{1}H NMR analysis showed the crude product to be about 85% pure, with **7a** as the primary impurities. An analytical sample was obtained by flash chromatography on silica gel, eluting with hexane ($R_f = 0.24$) followed by sublimation (60−80 °C, 0.1 mmHg) to afford a pale yellow solid: ^{1}H NMR (C$_6$D$_6$) δ 7.28 (d, $^3J = 8$ Hz, 1 H), 7.20 (t, $^3J = 8$ Hz,1 H), 7.15 (t, $^3J = 8$ Hz, 1 H), 6.97 (d, $^3J = 8$ Hz, 1 H), 6.18 (t, $^3J = 2$ Hz, 1 H), 3.12 (d, $^3J = 2$ Hz, 2 H), 2.32 (d, $^5J_{FH} = 2$ Hz, 6 H); ^{19}F NMR (C$_6$D$_6$) δ −140.7 (dd, $^3J = 24$ Hz, $^5J = 9$ Hz, 1 F, F$_6$), −150.9 (dd of sept, $^3J = 20$ Hz, $^5J = 9$ Hz, $^5J_{HF} = 2$ Hz, F$_3$), −158.1 (td, $^3J = 21$ Hz, $^4J = 2$ Hz, F$_4$), −164.5 (dd, $^3J = 24$ Hz, $^3J = 21$ Hz, F$_5$). Anal. Calcd (found) for C$_{17}$H$_{13}$F$_4$N: C, 66.45 (66.27); H, 4.26 (4.17); N, 4.56 (4.69).

Synthesis of 3-[2,6-Bis(dimethylamino)trifluorophenyl]indene (7a). A solution of **1a** (564 mg, 2.00 mmol), Ti(NMe$_2$)$_4$ (900 mg, 4.00 mmol), and toluene (50 mL) was stirred at 100 °C under a nitrogen atmosphere for 5 days and then cooled. The volatile components were evaporated. Hexane (50 mL) and water (20 mL) were added. The dark biphasic mixture was filtered through Celite, and the filter was rinsed with 50 mL of hexane. The biphasic filtrate was separated, and the aqueous layer was washed with 50 mL of hexane. The organic layers were combined, washed with saturated sodium bicarbonate solution (2 × 20 mL), dried over anhydrous MgSO$_4$, filtered, and evaporated to afford 471 mg (1.42 mmol, 71%) of a yellow-orange crystalline solid, which was found to be about 90% pure by ^{1}H NMR spectroscopic analysis. An analytical sample was obtained by flash chromatography on silica gel, eluting with hexane ($R_f = 0.11$) followed by sublimation (90 °C, 0.1 mm): ^{1}H NMR (C$_6$D$_6$) δ 7.30 (d, $^3J = 8$ Hz, 1 H), 7.22 (t, $^3J = 8$ Hz, 1 H), 7.15 (t, $^3J = 8$ Hz, 1 H), 6.90 (d, $^3J = 8$ Hz, 1 H), 6.07 (t, $^3J = 2$ Hz, 1 H), 3.24 (d, $^3J = 2$ Hz, 2 H), 2.44 (d, $^5J_{FH} = 1.5$ Hz, 12 H); ^{19}F NMR (C$_6$D$_6$) δ −148.0 (d, $^3J = 21$ Hz, 2 F), −161.2 (t, $^3J = 21$ Hz, 1 F). Anal. Calcd (found) for C$_{19}$H$_{19}$F$_3$N$_2$: C, 68.66 (68.38); H, 5.76 (5.40), N 8.43 (8.30).

Synthesis of [2,6-Bis(dimethylamino)trifluorophenyl]cyclopentadiene (7b). In a Teflon-valved glass tube, a solution of freshly sublimed (pentafluorophenyl)cyclopentadiene (1.15 g, 4.96 mmol) and Ti(NMe$_2$)$_4$ (1.11 g, 4.96 mmol) in toluene (2 mL) was sealed and stirred at 110 °C for 15 h. After cooling, the resulting solution was added to a rapidly stirred mixture of ice-cold water (100 mL) and hexane (50 mL). The resulting mixture was filtered through Celite. The biphasic filtrate was separated, and the organic phase was washed with water, dried over anhydrous MgSO$_4$, filtered, and evaporated to afford 1.02 g (3.61 mmol, 73%) of a dark solid. An analytical sample was obtained by chromatography on silica gel, eluting with hexanes, followed by sublimation (0.1 mmHg,

---

(53) Bürger, H.; Dämmgen, U. *J. Organomet. Chem.* **1975**, *101*, 295−306.

(54) Briscoe, P. A.; Challenger, F.; Duckworth, P. S. *J. Chem. Soc.* **1956**, 1755−1768.

80 °C) to obtain a pale yellow solid. The product was found to be a nearly equimolar mixture of double-bond regioisomers. Data for 1-[2,6-$C_6(Me_2N)_2F_3$]C_5H_5: ^{1}H NMR ($CDCl_3$) δ 6.62 (m, 1 H), 6.54 (m, 1 H), 6.38 (m, 1 H), 3.36 (m, 2 H), 2.65 (d, $^5J_{FH}$ = 2 Hz, 12 H); ^{19}F NMR ($CDCl_3$) δ −147.6 (d, ^3J = 21 Hz, 2 F) −161.0 (t, ^3J = 21 Hz, 1 F). Data for 2-[2,6-$C_6(Me_2N)_2F_3$]C_5H_5: ^{1}H NMR ($CDCl_3$) δ 6.57 (m, 1 H), 6.46 (m, 1 H), 6.38 (m, 1 H), 3.18 (m, 2 H), 2.64 (d, $^5J_{FH}$ = 2 Hz, 12 H); ^{19}F NMR (C_6D_6) δ −148.4 (d, ^3J = 21 Hz, 2 F), −161.1 (t, ^3J = 21 Hz, 1 F). Anal. Calcd (found) for $C_{15}H_{17}F_3N_2$: C, 64.08 (63.80); H, 6.09 (5.99); N, 9.96 (9.91).

1,1′-Bis(2,6-bis(dimethylamino)trifluorophenyl)ferrocene (12). A mixture of arylcyclopentadiene (**7b**, 564 mg, 2.00 mmol), sodium hydride (96 mg, 4.00 mmol), and THF was stirred under nitrogen for 15 h. To the resulting purple solution was added iron dibromide (216 mg, 1.00 mmol) in one portion. The resulting mixture was stirred at 65 °C for 4 h and then cooled. The solvent was evaporated, and the mixture was hydrolyzed by adding toluene (50 mL) and water (40 mL) with stirring. After filtration through Celite, the biphasic mixture was separated, dried over anhydrous $MgSO_4$, filtered, and evaporated to afford 460 mg (0.74 mmol, 74%) of a red solid. An analytical sample was obtained by recrystallization from hexane: ^{1}H NMR ($CDCl_3$) δ 5.11 (t, $^3J = {}^4J$ = 2 Hz, 2 H), 4.18 (t, $^3J = {}^4J$ = 2 Hz, 2 H), 2.72 (s, 24 H); ^{19}F NMR ($CDCl_3$) δ −146.2 (d, ^3J = 21 Hz, 4 F), −162.5 (t, ^3J = 21 Hz, 2 F). Anal. Calcd (found): C, 58.26 (58.65); H, 5.22 (5.40); N, 9.06 (8.85).

Crystallographic Studies. Crystal data are presented in Table 1. Colorless prisms of **4a** were obtained by sublimation at ambient conditions over an 18-month period. Colorless plates of substituted cyclopentadiene **7b** were crystallized from ethanol at 25 °C. Red needles of substituted ferrocene **12** were crystallized from hexanes at −10 °C. Crystals were cut prior to mounting on nylon CryoLoops (Hampton Research) with Krytox Oil (DuPont) and centering on the goniometer of an Oxford Diffraction XCalibur2 diffractometer equipped with a Sapphire 2 CCD detector. The data collection routines, unit cell refinements, and data processing were carried out with the program CrysAlis.[55] Structure solution (direct methods), refinement, and molecular graphics generation used the SHELXTL NT program package.[56] The Laue symmetry and systematic absences were consistent with the monoclinic space group $P2_1/n$ for indene **4a**, $P2_1/n$ for diene **7b**, and $P2_1/c$ for ferrocene **12**. The final refinement models for both structures involved anisotropic displacement parameters for non-hydrogen atoms and a riding model for all hydrogen atoms.

Acknowledgment. This work was supported by the National Science Foundation (CHE-9875446). We also thank NSF for funding the purchase of the Oxford Diffraction Xcalibur2 single crystal diffractometer (CHE-0131128) and the Varian Inova 400 MHz NMR spectrometer (CHE-0131124).

Supporting Information Available: X-ray crystallographic data, including thermal ellipsoid plots of **4a**, **7a**, and **12**, and a partial packing diagram of **4a** showing the arene stacking motif (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

OM034385G

---

(55) *CrysAlis* v1.170; Oxford Diffraction: Wrocław, Poland, 2002.

(56) Sheldrick, G. M. *SHELXTL NT* v 6.12; 2001.