

# Characterization of Intermediates in the C-F Activation of Tetrafluorobenzenes using a Reactive Ni(PEt<sub>3</sub>)<sub>2</sub> Synthon: Combined Computational and Experimental Investigation

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The reaction of the anthracene adduct  $(PEt_3)_2Ni(\eta^2-C_{14}H_{10})$  with 1,2,3,4-tetrafluorobenzene revealed NMR spectroscopic evidence for the immediate equilibrium production of the dinuclear adduct  $[(PEt_3)_2Ni]_2(\mu-\eta^2:\eta^2-C_6F_4H_2)$  and mononuclear adducts  $(PEt_3)_2Ni(\eta^2-C_6F_4H_2)$ . Similarly, the reaction of  $(PEt_3)_2Ni(\eta^2-C_{14}H_{10})$  with 1,2,4,5- and 1,2,3,5-tetrafluorobenzene revealed NMR spectroscopic evidence for the equilibrium production of the dinuclear adducts and mononuclear adducts and also the C-H activation products (PEt<sub>3</sub>)<sub>2</sub>NiH( $C_6F_4H$ ). The conversions to both the adducts and C-H activation products were too minimal to allow for isolation, and the low concentrations hampered complete NMR spectroscopic characterization. The reaction of the readily prepared (PEt<sub>3</sub>)<sub>2</sub>NiMe<sub>2</sub> with isobutene allowed for the in situ generation of (PEt<sub>3</sub>)<sub>2</sub>Ni( $\eta^2$ - $H_2C=CMe_3$ ) as a more reactive Ni(PEt\_3)<sub>2</sub> synthon. The reaction of (PEt\_3)<sub>2</sub>Ni( $n^2$ -H<sub>2</sub>C=CMe<sub>2</sub>) with tetrafluorobenzenes also generates small equilibrium concentrations of adducts and C-H activation products, but the equilibrium can be driven by the removal of isobutene. The dinuclear adducts  $[(PEt_3)_2Ni]_2(\mu-\eta^2:\eta^2-1,2,3,4-C_6F_4H_2)$  and  $[(PEt_3)_2Ni]_2(\mu-\eta^2:\eta^2-1,2,4,5-C_6F_4H_2)$  were isolated and fully characterized by X-ray crystallography. The isolation of the dinuclear adduct of 1,2,3,5tetrafluorobenzene was hampered by its rapid C-F activation and the generation of the less soluble aryne adduct  $[(PEt_3)_2Ni]_2(\mu-\eta^2;\eta^2-3,4,6-C_6F_3H)$ , which was fully characterized. The spectroscopic characterization of all the tetrafluorobenzene mononuclear and dinuclear adducts as well as C-H activation products was accomplished by variable-temperature NMR spectroscopy and aided by DFT calculations on the proposed intermediates. The observation of equilibrium concentrations of the intermediates in solution allowed for the determination of the thermodynamic parameters for their interconversion.

### Introduction

The inclusion of fluorine substituents has become a common trend in modern pharmaceuticals<sup>1</sup> and agrochemicals.<sup>2</sup> These fluorinated compounds are believed to have increased resistance to metabolic degradation relative to their C–Hcontaining analogues and increased lipophilicity, among other biologically relevant properties that affect binding in receptor sites.<sup>1,3</sup> A common current synthetic approach to these compounds involves using a fluorinating agent to introduce the fluorine substituent.<sup>4</sup> Although numerous electrophilic and nucleophilic fluorination methodologies have been devised,<sup>5</sup> this approach has limitations in the possible product substitution patterns, and the cost of some of these reagents discourages large-scale application.<sup>6</sup> An alternate approach that has been suggested is to start with commercially available fluorinated starting materials, such as fluorinated aromatics, and then functionalize these directly, by either  $C-H^{7,8}$  or C-F bond activation.<sup>9</sup> This approach allows for the possibility of introducing multiple fluorine substituents with substitution patterns inaccessible by other methods. Nickel complexes have shown great promise in the functionalization of fluorinated aromatics; they have been shown to react not only with the most reactive substrates, such as the perfluorinated arenes,<sup>10–14</sup> pyridines,<sup>12,15</sup> and pyrimidines,<sup>16</sup> but also with the less reactive partially fluorinated arenes<sup>12,14,17</sup> of particular interest in pharmaceutical synthesis. Remarkably, given the decreased thermodynamic

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propensity of Ni complexes to undergo C–H bond oxidative addition compared to its heavier congeners,<sup>18</sup> nickel complexes have also been shown to facilitate not only C–F bond activation but also stoichiometric C–H bond activation<sup>17,19,20</sup> and catalytic functionalization with partially fluorinated substrates, with examples including C–H bond alkenylation<sup>8,20</sup> and an unprecedented C–H bond stannylation.<sup>21</sup>

To rationalize and predict the reactivity and selectivity of substrates in C-F and/or C-H bond activations using nickel complexes, it is necessary to understand the intermediates and mechanisms involved. The activation of both aromatic C-H and C-F bonds is commonly accepted to proceed through intermediate mononuclear  $\eta^2$ -bound adducts.<sup>11–13,18,22</sup> However, the reaction of hexafluorobenzene with the anthracene complex (PEt<sub>3</sub>)<sub>2</sub>Ni( $\eta^2$ -C<sub>14</sub>H<sub>10</sub>) generated the unexpected dinuclear adduct [(PEt<sub>3</sub>)<sub>2</sub>Ni]<sub>2</sub>- $(\mu - \eta^2 : \eta^2 - C_6 F_6)$  as a thermally stable isolable solid.<sup>17</sup> Only a trace amount of mononuclear adduct,  $(PEt_3)_2Ni(\eta^2-C_6F_6)$ , was observed by NMR spectroscopy in the presence of excess  $C_6F_6$ . Similarly, the reaction of  $(PEt_3)_2Ni(\eta^2-C_{14}H_{10})$  with pentafluorobenzene provided the isolable dinuclear adduct  $[(\text{PEt}_3)_2\text{Ni}]_2(\mu-\eta^2:\eta^2-\text{C}_6\text{F}_5\text{H});$  however, in the presence of excess pentafluorobenzene both a mononuclear adduct and the C-H activation product  $(PEt_3)_2NiH(C_6F_5)$  were found to be in equilibrium. Solutions of  $[(PEt_3)_2Ni]_2(\mu-\eta^2:\eta^2-C_6F_5H)$ with added  $C_6F_5H$  convert with > 97% selectivity to the *o*-F

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(21) Doster, M. E.; Hatnean, J. A.; Jeftic, T.; Modi, S.; Johnson, S. A. J. Am. Chem. Soc. 2010, 28, 11923–11925. activated compound *trans*-(PEt<sub>3</sub>)<sub>2</sub>NiF(2,3,4,5-C<sub>6</sub>F<sub>4</sub>H). This is unique selectivity for a transition-metal-mediated C–F activation, with all previous reports of selective activation occurring at the para position. It has not been ascertained if the dinuclear intermediate plays a role in this selectivity.

The C-H activation products and adducts of  $Ni(PEt_3)_2$ with the tetrafluorobenzenes have proven more difficult to isolate and characterize. Even the reaction of  $(PEt_3)_2Ni(\eta^2 C_{14}H_{10}$ ) with pentafluorobenzene to form the dinuclear adduct was found to be in equilibrium,<sup>17</sup> so that with stoichiometric amounts of pentafluorobenzene the anthracene adduct  $(PEt_3)_2Ni(\eta^2 \cdot C_{14}H_{10})$  was still observed by NMR spectroscopy. Good yields of the dinuclear adduct were obtained by adding a slight excess of C<sub>6</sub>F<sub>5</sub>H. With less fluorinated aromatics such as the tetrafluorobenzenes, which are worse  $\pi$  acceptors, the equilibrium strongly disfavors the products, as shown in Scheme 1. For example, we previously communicated that the reaction of the phenanthrene adduct of Ni(PEt<sub>3</sub>)<sub>2</sub> with 1,2,4,5-tetrafluorobenzene yielded only slight equilibrium amounts of the C-H activation product  $(PEt_3)_2NiH(C_6F_4H)$ as the major product.<sup>17</sup> Smaller resonances were observed that could conceivably be dinuclear or mononuclear adducts, but their full multinuclear NMR spectroscopic characterization was not possible, due to their low relative concentrations in solution, and isolation proved impossible.

The characterization of these intermediates is of interest because the Ni(PEt<sub>3</sub>)<sub>2</sub> moiety appears to be unique in having C-H activation products as well as mononuclear and dinuclear adducts that are similar in energy and because the pentafluorobenzene adduct demonstrated unprecedented regioselectivity in C-F activation. To characterize the adducts and C-H activation products that serve as intermediates to C-F activation of the tetrafluorobenzenes requires a Ni(PEt<sub>3</sub>)<sub>2</sub> synthon more reactive than the previously reported anthracene and phenanthrene adducts. In this report, we outline such a reactive source of Ni(PEt<sub>3</sub>)<sub>2</sub> and its utility in both C-H activation and the generation of intermediates to both C-H and C-F activation.

## **Results and Discussion**

Reaction of  $(PEt_3)_2Ni(\eta^2-C_{14}H_{10})$  with Tetrafluorobenzenes. The anthracene adduct  $(PEt_3)_2Ni(\eta^2-C_{14}H_{10})$  provided a reactive source of the Ni(PEt<sub>3</sub>)<sub>2</sub> moiety in previous reactions with C<sub>6</sub>F<sub>6</sub> and C<sub>6</sub>F<sub>5</sub>H, which resulted in the isolation of dinuclear adducts. Similar reactions were attempted with 1,2,4,5-, 1,2,3,5-, and 1,2,3,4-tetrafluorobenzene. In all cases, very minor equilibrium conversions to adducts were observed by NMR spectroscopy. The majority of the anthracene adduct remains unreacted, presumably because anthracene is a better  $\pi$ -acceptor than any of the three isomers of tetrafluorobenzene. These solutions slowly undergo slow C-F activation. For all three reactions relatively broad resonances were observed immediately after mixing in the <sup>19</sup>F NMR spectra that could be tentatively assigned to mono and dinuclear adducts. In the case of 1,2,4,5- and 1,2,3,5- $C_6F_4H_2$ , sharper resonances that could be assigned as the C-H activation products were also observed. The largest equilibrium conversion was observed for the C-H activation product of 1,2,4,5-C<sub>6</sub>F<sub>4</sub>H<sub>2</sub>, which allowed for its complete spectroscopic identification;<sup>19</sup> however, even this species was present in far too small amounts to isolate. A summary of the room-temperature <sup>19</sup>F NMR spectroscopic assignments is shown in the right column of Table 1. Although studies of the

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| Table 1 | . Summary | of Calculated | and Experimental | <sup>19</sup> F NMR Shifts |
|---------|-----------|---------------|------------------|----------------------------|
|---------|-----------|---------------|------------------|----------------------------|

| compd | <sup>19</sup> F NMR shift (ppm)   |  |  |  |  |  |
|-------|---|--|--|--|--|--|
|       | predicted slow exchange   | exptl slow exchange  | predicted fast exchange                            | 293 K exptl  |  |  |
| 3     | $-138 (F_{1,2})$  | $-136.0(F_{1,2})$  | $-146(F_{1,2,4,5})$                                | similar to slow exchange   |  |  |
| 4     | $-134 (F_{4,5})$<br>$-134 (F_1)$<br>$-144 (F_2)$<br>$-145 (F_4)$                                | -140./(F <sub>4,5</sub> )  | $-145 (F_{1,2,4,5})$                               | -144.7 (F <sub>1,2,4,5</sub> )   |  |  |
| 5     | -159 (F <sub>5</sub> )<br>-125 (F <sub>2,6</sub> )<br>-146 (F <sub>3,5</sub> )                  |  |  | -117.8 (F <sub>2,6</sub> )<br>-143.7 (F <sub>3,5</sub> )   |  |  |
| 6     | $-137 (F_4)  -139 (F_1)  -155 (F_3)  -182 (F_2)$  | $-132.8 (F_4)$<br>$-141.5 (F_1)$<br>$-158.9 (F_3)$<br>$-189.2 (F_2)$ | $-138 (F_1 + F_4) -169 (F_2 + F_3)$                | $-134.8 (F_1+F_4)$<br>-171.3 (F_2+F_3)   |  |  |
| 7     | $-133 (F_{1,4})$<br>$-170 (F_{2,3})$  |  |  | $-128.9$ (d. $F_{1,4}$ )<br>$-172.1$ (d, $F_{2,3}$ )   |  |  |
| 9     | $-123 (F_5)$<br>$-135 (F_3)$<br>$-161 (F_2)$<br>$-169 (F_1)$                                    | $-113.7 (F_5)$<br>$-137.1 (F_3)$<br>$-162.2 (F_2)$<br>$-175.7 (F_1)$ | $-123 (F_5) -152 (F_1 + F_3) -161 (F_2)$           | $-113.7 (F_5)$<br>-137.1 ( $W_{1/2} = 1500$ Hz. F <sub>3</sub> )<br>-162.2 (F <sub>2</sub> )<br>-175.7 ( $W_{1/2} = 1500$ Hz, F <sub>1</sub> )                                 |  |  |
| 10    | $-113(F_5)$<br>$-141(F_3)$<br>$-152(F_2)$   | $-104 (F_5)$<br>$-147 (F_3)$<br>$-151 (F_2)$                         | $-113 (F_5)$<br>$-147 (F_1 + F_3)$<br>$-166 (F_2)$ | -106.0 (br d, F <sub>5</sub> )<br>-149.9 (br d, F <sub>1</sub> + F <sub>3</sub> )<br>-161.5 (br dt F <sub>2</sub> )  |  |  |
| 11    | $\begin{array}{c} -166 (F_2) \\ -100 (F_6) \\ -116 (F_2) \\ -146 (F_4) \\ -172 F_3 \end{array}$ | $-160(F_2)$  | 100 (1 2)  | $\begin{array}{c} -90.5 \text{ (br dt, } F_{2}) \\ -90.5 \text{ (br dt, } F_{6}) \\ -110.0 \text{ (} F_{2}) \\ -144.6 \text{ (} F_{4}) \\ -170.2 \text{ (} F_{3}) \end{array}$ |  |  |
|       |   |  |  |  |  |  |

effect of added tetrafluorobenzene were used to assess equilibria and discriminate which <sup>19</sup>F NMR resonances are due to the mononuclear and dinuclear adducts by their relative signal intensities, assignment of <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR shifts in these relatively dilute mixtures was unsuccessful. Instead, we decided to search for a more reactive source of the Ni(PEt<sub>3</sub>)<sub>2</sub> moiety in the hopes of providing more concentrated solutions of these adducts for complete spectroscopic characterization, or even isolation.

 $(PEt_3)_2NiMe_2$  as a Ni $(PEt_3)_2$  Synthon. The complex  $(PEt_3)_2$ -NiMe<sub>2</sub> (1)<sup>23</sup> has been used previously as an in situ source of the Ni $(PEt_3)_2$  synthon,<sup>24</sup> although the complex has never been fully characterized, due to its reported thermal instability. The species is an attractive synthetic source of the Ni $(PEt_3)_2$  moiety, because it can be made without the use of Na/Hg amalgam or other strong reducing agents. We made (PEt<sub>3</sub>)<sub>2</sub>NiMe<sub>2</sub> by the reaction of (PEt<sub>3</sub>)<sub>2</sub>NiCl<sub>2</sub> with 2 equiv of MeMgBr in ether and crystallized the product in over 70% yield from cold pentane. The pure yellow crystalline complex is reasonably stable as a solid and can be briefly handled at room temperature without obvious degradation but is best stored at -40 °C. Yellow solutions of 1 discolor within hours at room temperature, but complete decomposition takes many days, as monitored by <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy. The pure material yielded a sharp resonance in the room-temperature <sup>31</sup>P{<sup>1</sup>H} NMR spectrum and a well-defined triplet for the methyl group in the <sup>1</sup>H NMR. Previous descriptions<sup>23</sup> of broad spectra may have been due to the presence of impurities. This may also have decreased the thermal stability of the isolated compound, which reportedly was best handled at -30 °C. The solid-state molecular structure was determined by X-ray crystallography and is shown in Figure 1. Crystallographic data are provided in Table 2.

Attempts to react isolated  $(PEt_3)_2NiMe_2$  with 1,2,4,5-, 1,2,3,5-, or 1,2,3,4-tetrafluorobenzene failed to provide a useful route to the desired adducts and C–H activation products.

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Although the <sup>19</sup>F NMR spectra displayed resonances indicative of the anticipated adducts in the reaction with 1,2,3,4-C<sub>6</sub>F<sub>4</sub>H<sub>2</sub>, C–F bond activation products appeared at a similar rate, over the course of weeks, so that the concentration of the intermediates was not appreciable and only a mixture of products was obtained. In the slow room-temperature reaction of either 1,2,4,5- or 1,2,3,5-C<sub>6</sub>F<sub>4</sub>H<sub>2</sub> with (PEt<sub>3</sub>)<sub>2</sub>NiMe<sub>2</sub> a similar major product was observed, which was later identified as the dinuclear aryne complex [(PEt<sub>3</sub>)<sub>2</sub>Ni]<sub>2</sub>( $\mu$ - $\eta$ <sup>2</sup>: $\eta$ <sup>2</sup>-3,4, 6-C<sub>6</sub>F<sub>3</sub>H) (vide infra). This product likely formed from the C–F activation product and once again indicates similar rates of ethane elimination from (PEt<sub>3</sub>)<sub>2</sub>NiMe<sub>2</sub> and C–F activation.

Synthesis of a Reactive Isobutene Adduct of  $(PEt_3)_2Ni$ . The known ethylene adduct  $(PEt_3)_2Ni(\eta^2-C_2H_4)^{25}$  failed to react with 1,2,4,5-C<sub>6</sub>F<sub>4</sub>H<sub>2</sub>, which is consistent with the observation that it is stoichiometrically prepared from the phenanthrene or anthracene adducts,  $(PEt_3)_2Ni(\eta^2-C_{14}H_{10})$ , by the addition of ethylene. In an attempt to make a more sterically bulky alkene adduct that still incorporated a volatile alkene, isobutene was reacted with  $(PEt_3)_2NiMe_2$  in a variety of hydrocarbon solvents, which included benzene, toluene, and pentane. This reaction takes 2 weeks to go to completion under ambient conditions in a C<sub>6</sub>D<sub>6</sub> solution saturated with isobutene, as monitored by <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy. Under similar conditions, but with heating in the NMR



Figure 1. ORTEP depiction of the solid-state molecular structure of 1 as determined by X-ray crystallography. Hydrogen atoms are omitted for clarity, and 30% probability thermal ellipsoids are shown. Selected bond lengths (Å): Ni(1)–C(1), 2.010(2); Ni(1)–P(1), 2.1846(4).

probe to 60 °C, the reaction was complete in 2–3 h, as shown in eq 1. Yellow solutions of  $(PEt_3)_2Ni(\eta^2-H_2C=CMe_2)$  (2) are readily synthesized on a multigram scale in this manner. Resonances associated with Ni $(PEt_3)_4^{-26,27}$  are the only impurity visible in the <sup>31</sup>P{<sup>1</sup>H} NMR spectra and were typically 2–5% of the sample by integration.



The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of (PEt<sub>3</sub>)<sub>2</sub>Ni( $\eta^2$ -H<sub>2</sub>C=CMe<sub>2</sub>) consists of a pair of second-order doublets at  $\delta$  16.0 and 17.2 with a 52 Hz<sup>2</sup> $J_{PP}$  coupling, consistent with a  $C_s$ -symmetric structure with the two alkene carbons in the P<sub>2</sub>Ni plane. The <sup>1</sup>H NMR spectrum displays a distinctive upfield-shifted multiplet for the olefinic hydrogens at  $\delta$  1.78. Attempts to isolate 2 have failed, due to its high solubility in low-polarity solvents such as pentane and hexamethyldisiloxane and because the removal of the excess isobutene and solvent by either vacuum or slow evaporation slowly decomposes the adduct to produce a reddish purple solution that was identified by  ${}^{31}P{}^{1}H$  NMR spectroscopy to consist primarily of PEt<sub>3</sub> complexes of Ni(0).  ${}^{26,27}$  Compound **2** was also prepared from (PEt<sub>3</sub>)<sub>2</sub>NiMe<sub>2</sub> by a less convenient method using neat isobutene as a solvent at room temperature and provided only a thermally sensitive pale yellow oil after slow evaporation of the isobutene solvent at -35 °C. Regardless, 2 can be conveniently prepared in situ in a variety of hydrocarbon solvents and is of sufficient purity to attempt its use in further reactions.

Synthesis and Characterization of the Dinuclear Ni(PEt<sub>3</sub>)<sub>2</sub> Adduct of 1,2,4,5-C<sub>6</sub>F<sub>4</sub>H<sub>2</sub>. There are two potential isomers for the dinuclear adduct of 1,2,4,5-tetrafluorobenzene [(PEt<sub>3</sub>)<sub>2</sub>-Ni]<sub>2</sub>( $\mu$ - $\eta$ <sup>2</sup>: $\eta$ <sup>2</sup>-1,2,4,5-C<sub>6</sub>F<sub>4</sub>H<sub>2</sub>) (3). DFT calculations were performed using the model complexes [(PMe<sub>3</sub>)<sub>2</sub>Ni]<sub>2</sub>( $\mu$ - $\eta$ <sup>2</sup>: $\eta$ <sup>2</sup>-1,2,4,5-C<sub>6</sub>F<sub>4</sub>H<sub>2</sub>) (3<sup>Me</sup>), where the PEt<sub>3</sub> donors are replaced by PMe<sub>3</sub>, to ascertain whether the isomer labeled 3-1623 or

 Table 2. Summary of X-ray Crystallographic Parameters

|   | 1              | 3                        | 6              | 12  |
|---|----------------|--------------------------|----------------|---|
| empirical formula                       | C14H36NiP2     | $C_{30}H_{62}F_4Ni_2P_4$ | C30H62F4Ni2P4  | C <sub>30</sub> H <sub>61</sub> F <sub>3</sub> Ni <sub>2</sub> P <sub>4</sub> |
| formula wt                              | 325.08         | 740.10                   | 740.10         | 720.10  |
| cryst syst                              | monoclinic     | monoclinic               | monoclinic     | triclinic   |
| a (Å)                                   | 7.3541(8)      | 14.8226(16)              | 19.2829(19)    | 10.5150(14)   |
| $b(\dot{A})$                            | 11.6170(12)    | 13.4117(14)              | 9.9632(10)     | 19.138(3)   |
| $c(\dot{A})$                            | 13.1344(10)    | 23.6234(18)              | 41.320(4)      | 20.958(3)   |
| a (deg)                                 | 90             | 90                       | 90             | 116.821(2)  |
| $\beta$ (deg)                           | 123.314(4)     | 126.885(4)               | 105.036(4)     | 90.686(2)   |
| $\gamma$ (deg)                          | 90             | 90                       | 90             | 101.406(2)  |
| $V(Å^3)$                                | 937.71(16)     | 3756.3(6)                | 7666.6(13)     | 3664.7(9)   |
| space group                             | $P2_1/c$       | $P2_1/c$                 | P2/c           | $P\overline{1}$   |
| Ż                                       | 2              | 4                        | 8              | 4   |
| $D_{\text{calcd}}$ (g/cm <sup>3</sup> ) | 1.151          | 1.309                    | 1.282          | 1.305   |
| $\mu(Mo K\alpha) (mm^{-1})$             | 1.189          | 1.211                    | 1.186          | 1.235   |
| temp (K)                                | 173(2)         | 173(2)                   | 173(2)         | 133(2)  |
| $2\theta_{\rm max}$ (deg)               | 50.0           | 55.0                     | 50.0           | 50.0  |
| total no. of rflns                      | 8525           | 42 547                   | 71 177         | 52 4 54   |
| no. of unique rflns; $R_{int}$          | 1645; 0.0202   | 8577; 0.0250             | 13452; 0.0436  | 52 454; twinned   |
| transmissn factors                      | 0.8705-0.7635  | 0.7280-0.6366            | 0.7323-0.6815  | 0.8659-0.6511   |
| no. of rflns with $I \ge 2\sigma(I)$    | 1549           | 7542                     | 11576          | 34628   |
| no. of variables                        | 83             | 381                      | 769            | 740   |
| rflns/params                            | 19.8           | 22.5                     | 17.5           | 70.9 (twinned)  |
| R1; wR2 (all data)                      | 0.0244; 0.0559 | 0.0366; 0.0873           | 0.0474; 0.0881 | 0.067; 0.094  |
| GOF                                     | 1.080          | 1.046                    | 1.064          | 0.865   |
| resid density (e/Å <sup>3</sup> )       | 0.345; -0.167  | 1.509; -0.473            | 0.619;-0.351   | 0.809; -0.464   |

**3-1234** is favored, as shown in Scheme 2. The isomer  $3^{Me}$ -**1623** was found to have the lowest energy, with a  $\Delta G_{298 \text{ K}}$  value of 4.1 kcal mol<sup>-1</sup> for the conversion to  $3^{Me}$ -**1234**. This large value suggests that no significant equilibrium concentration of the **3-1234** isomer should be observed at room temperature. The calculated <sup>19</sup>F NMR shifts for  $3^{Me}$ -**1623** are  $\delta$  -138 and -154 for F<sub>1,2</sub> and F<sub>4,5</sub>, respectively. The adduct [(PEt<sub>3</sub>)<sub>2</sub>Ni]<sub>2</sub>( $\mu$ - $\eta^{2}$ : $\eta^{2}$ -1,2,4,5-C<sub>6</sub>F<sub>4</sub>H<sub>2</sub>) can be

synthesized by the reaction of  $(PEt_3)_2Ni(\eta^2-H_2C=CMe_2)$  (2) with 1,2,4,5-tetrafluorobenzene in toluene, as shown in Scheme 3. The equilibrium exchange of isobutene with 1,2, 4,5-tetrafluorobenzene produced an observable amount of the hydride  $(PEt_3)_2NiH(C_6F_4H)$  in the <sup>19</sup>F NMR spectrum, but the reaction had to be driven to completion to provide more than a small equilibrium amount of the dinuclear adduct. This was accomplished in toluene by applying vacuum but produced considerable PEt<sub>3</sub> adducts of Ni(0) as a significant impurity. A more efficient method was to prepare a solution of  $(PEt_3)_2Ni(\eta^2-H_2C=CMe_2)$  in pentane and then add a slight excess of 1,2,4,5-tetrafluorobenzene and heat to the boiling point of the pentane solution with rapid stirring. Under these conditions minimal conversion to PEt<sub>3</sub> adducts of Ni(0) or the C-F activation product was observed, and the reaction was complete within 1.5 h. After drying under vacuum the <sup>19</sup>F NMR spectrum revealed primarily a single fluorine-containing product.

Crystalline **3** was obtained from the crude product mixture in modest yields by cooling a pentane solution of the product mixture to -40 °C. An ORTEP depiction of the solid-state molecular structure is shown in Figure 2. The structure confirms that the isomer **3-1623** is preferred in the solid state. Similar to the previously reported adducts of C<sub>6</sub>F<sub>6</sub> and C<sub>6</sub>F<sub>5</sub>H, this complex exhibits extensive back-bonding, with a short C(4)–C(5) distance of 1.332(3) Å indicative of a localized double bond, with the remaining bonds of the C<sub>6</sub>F<sub>4</sub>H<sub>2</sub> moiety significantly longer than an aromatic C–C bond and ranging from 1.425(3) to 1.460(2) Å. Unlike other examples of these dinuclear complexes,<sup>17</sup> the Ni–C bond



lengths are identical within error and cover a range of only 1.953(2)-1.959(2) Å.

The <sup>1</sup>H NMR spectrum of the dinuclear adduct 3 in toluene- $d_8$  features a single multiplet resonance for the aromatic <sup>1</sup>H at  $\delta$  3.02, which is not significantly affected by temperature. The 298 K <sup>19</sup>F NMR spectrum is consistent with the X-ray structure and exhibits two multiplets at  $\delta$  -136.0 and -146.7. These resonances can be assigned as  $F_{1,2}$  and F<sub>4.5</sub>, respectively, by their similarity to the chemical shifts calculated using DFT. The <sup>19</sup>F NMR spectrum does not change significantly on cooling. The absence of any low-energy fluxional process that exchanges the <sup>19</sup>F environments in **3** is consistent with our previous observation that, although the  $Ni(PEt_3)_2$  moieties in these dinuclear complexes undergo 1, 3-shifts with modest activation barriers, shifts that change the locations of the double bonds have much higher energy barriers.<sup>17</sup> The thermal instability of 3 at temperatures significantly higher than room temperature prevented hightemperature NMR studies.

The room-temperature 121.5 MHz <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **3** displays only a broad resonance at  $\delta$  19.0, which decoalesces into two very broad resonances at  $\delta$  22.8 and 15.0 below 273 K. These resonances sharpen further on cooling, with the highest resolution spectra obtained at 233 K. The dinuclear adduct resonance at  $\delta$  22.8 features a large 42 Hz <sup>2</sup>J<sub>PP</sub> value, along with additional unresolved couplings. The resonance at  $\delta$  15.0 is as an apparent doublet of triplets, with a large 42 Hz <sup>2</sup>J<sub>PP</sub> value. The apparent triplet has a <sup>2</sup>J<sub>PF</sub> value of 27 Hz and could conceivably be due to coincident doublet coupling constants or to a second-order virtual triplet. Cooling



**Figure 2.** ORTEP depiction of the solid-state molecular structure of  $[(PEt_3)_2Ni]_2(\mu-\eta^2:\eta^2-1,2,4,5-C_6F_4H_2)$  (**3**). Hydrogen atoms not associated with the tetrafluorobenzene moiety are omitted for clarity, and 30% probability thermal ellipsoids are shown. Selected bond lengths (Å): Ni(1)-C(6), 1.957(2); Ni(1)-C(1), 1.953(2); Ni(2)-C(2), 1.959(2); Ni(2)-C(3), 1.959(2); C(1)-C(6), 1.428(3); C(1)-C(2), 1.460(2); C(2)-C-(3), 1.425(3); C(3)-C(4), 1.447(3); C(4)-C(5), 1.332(3); C(5)-C(6), 1.443(3).









to as low as 198 K does not result in the observation of any additional fluxional processes. The observation of two <sup>31</sup>P resonances for the dinuclear adduct at low temperatures confirm that the favored adduct is the  $C_2$ -symmetric isomer **3-1623**, rather than **3-1234**. The energy for <sup>31</sup>P exchange was determined to be 11.9 kcal mol<sup>-1</sup> by modeling the coalescence of the signals from 263 to 283 K. The exact mechanism of the exchange is not evident from the available data, but it possibly involves a series of 1,3-shifts and the **3-1234** isomer as an intermediate.

Spectroscopic Characterization of a Mononuclear Adduct of 1,2,4,5-C<sub>6</sub>F<sub>4</sub>H<sub>2</sub>. There are two possible isomers for the mononuclear adduct of 1,2,4,5-tetrafluorobenzene (PEt<sub>3</sub>)<sub>2</sub>Ni- $(\eta^2-1,2,4,5-C_6F_4H_2)$  (4). DFT calculations were performed using the model complexes (PMe<sub>3</sub>)<sub>2</sub>Ni( $\eta^2$ -1,2,4,5-C<sub>6</sub>F<sub>4</sub>H<sub>2</sub>) (4<sup>Me</sup>), where the two potential isomers are labeled 4<sup>Me</sup>-12 and 4<sup>Me</sup>-23, as shown in Scheme 4. The isomer 4<sup>Me</sup>-23 was found to be the lowest energy, with a  $\Delta G_{298 \text{ K}}$  value of 4.3 kcal mol<sup>-1</sup> for conversion to  $4^{Me}$ -12. This suggests that only the isomer 4-23 should be observable in solution by NMR spectroscopy. The calculated <sup>19</sup>F NMR shifts for the favored isomer of (PMe<sub>3</sub>)<sub>2</sub>- $Ni(\eta^2-1,2,4,5-C_6F_4H_2)$  are  $\delta -134$ , -144, -145, and -159 for F<sub>1</sub>, F<sub>2</sub>, F<sub>4</sub>, and F<sub>5</sub>, respectively. If these environments were in rapid exchange, an average shift of  $\delta$  –145 would be anticipated. The equilibrium reaction of the dinuclear adduct with  $1,2,4,5-C_6F_4H_2$  to form 2 equiv of the mononuclear adduct is predicted to have a  $\Delta G_{298 \text{ K}}$  value of 3.2 kcal mol<sup>-1</sup>, which suggests that 4 should be observable using suitable concentrations of the dinuclear adduct and  $1,2,4,5-C_6F_4H_2$ .

In the equilibrium reaction of excess 1,2,4,5-tetrafluorobenzene with dinuclear adduct **3**, the major new fluorinecontaining product is the C–H activation product (PEt<sub>3</sub>)<sub>2</sub>NiH-2,3,5,6-C<sub>6</sub>F<sub>4</sub>H (**5**); however, the room-temperature <sup>19</sup>F NMR spectrum also displays a broad multiplet resonance at  $\delta$  –144.7 associated with the mononuclear adduct. The room-temperature 300 MHz <sup>1</sup>H NMR spectrum displays a virtual pentet for the upfield-shifted aromatic proton at  $\delta$  4.87, with an apparent  $J_{\rm FH}$  value of 9.0 Hz. The room-temperature <sup>31</sup>P{<sup>1</sup>H} NMR spectrum features only a broad resonance at  $\delta$  17.5 assignable to **4**. The broadening is possibly due to exchange of the Ni(PEt<sub>3</sub>)<sub>2</sub> moieties between the mononuclear complex and hydride **5** or dinuclear complex **3**. When the temperature is lowered to 263 K, this resonance sharpens to reveal a pentet with  $J_{\rm PF} = 12.5$  Hz.





These spectra are consistent with an  $\eta^2$  adduct that is fluxional at room temperature, as shown in Scheme 5. It has been noted in related mononuclear Ni bis(phosphine) adducts of aromatics<sup>28</sup> that the nickel bis(phosphine) moiety spins as it undergoes 1,2-shifts via an  $\eta^3$ -allyl-like intermediate and that such processes occur with low energy barriers.<sup>18</sup> A circumnavigation of the ring in mononuclear adduct 4-23 requires that the complex pass through the isomer 4-12, which was calculated to be 4.3 kcal  $mol^{-1}$  higher in energy; thus, it is expected that further fluxionality should be observed at low temperature. The aromatic <sup>1</sup>H resonance at  $\delta$ 4.87 begins to broaden at 233 K and decoalesces at 183 K to reveal two broad resonances at  $\delta$  3.9 and 5.8. The observation of two <sup>1</sup>H NMR signals confirms that **4-23** is the lowest energy isomer. The interconversion of the 4-23 isomers via the intermediate 4-12 occurs with the rate-determining step labeled with the rate constant  $k_1$  in Scheme 5. This step is estimated to have an Arrhenius activation energy of  $3.5 \pm$ 1.0 kcal mol<sup>-1</sup> from the <sup>1</sup>H NMR spectroscopic data. This data is consistent with the energy difference between isomers estimated from DFT calculation of 4.3 kcal mol<sup>-1</sup>. If the process labeled with the rate constant  $k_2$  was fast compared to the NMR time scale, two environments would be expected in both the  ${}^{31}P{}^{1}H$  and  ${}^{19}F$  NMR spectra. Both the  ${}^{31}P{}^{1}H$ and <sup>19</sup>F NMR resonances broaden significantly at low temperatures, indicative of decoalescence, but slow-exchange spectra with pairs of resonances were not observed as low as 183 K, which indicates exchange is still rapid relative to the NMR time scale.

Spectroscopic Characterization of  $(PEt_3)_2NiH-2,3,5,6-C_6F_4H$ . As previously noted, the predominant new species in the reaction of dinuclear complex **3** with 1,2,4,5-C<sub>6</sub>F<sub>4</sub>H<sub>2</sub> is the C-H activation product  $(PEt_3)_2NiH-2,3,5,6-C_6F_4H$ (**5**).<sup>19</sup> Ab initio DFT calculations on the model complex  $(PMe_3)_2NiH-2,3,5,6-C_6F_4H$  species predict <sup>19</sup>F NMR shifts of  $\delta$  -125 and -146 for the ortho and meta fluorines, respectively. The hydride model complex is predicted by DFT to be 1.7 kcal mol<sup>-1</sup> more favorable than the mononuclear adduct. Experimentally, **5** displays second-order AA'MM' multiplets in the room-temperature <sup>19</sup>F NMR spectrum at  $\delta$  -117.8 and -143.7. The room-temperature <sup>1</sup>H NMR spectrum features a hydridic signal at  $\delta$  -14.3 that

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is a broad triplet and an aromatic resonance at  $\delta$  6.48. When the temperature is lowered to 233 K, the signal for the hydridic proton sharpens and can be resolved as a triplet of triplet of triplets with a  ${}^{2}J_{\rm PH}$  value of 67.7 Hz. The  ${}^{31}{\rm P}\{{}^{1}{\rm H}\}$ NMR spectrum displays a resonance at  $\delta$  23.5. The  ${}^{31}{\rm P}$  NMR spectrum displays a  ${}^{2}J_{\rm PH}$  coupling of 68 Hz, which confirms its assignment.

Thermodynamic Considerations with 1,2,4,5-C<sub>6</sub>F<sub>4</sub>H<sub>2</sub>. Different concentrations of 1,2,4,5-tetrafluorobenzene were reacted with the dinuclear complex 3, to determine equilibrium constants for its conversion to the mononuclear and hydride complexes. The pair of resonances due to the dinuclear complex decreases in relative intensity as the concentration of 1,2,4,5-tetrafluorobenzene is increased. As expected, the ratio of the integral associated with the mononuclear resonance to those associated with the hydride is not greatly affected by 1,2,4,5-tetrafluorobenzene concentration. The equilibrium constant for the conversion of the hydride to the mononuclear complex in benzene- $d_6$  can be estimated from the ratio of integrals to be 4.3(1), which corresponds to a  $\Delta G_{298}$  value of -0.9 kcal mol<sup>-1</sup> for the conversion of mononuclear adduct 4 to hydride 5. Thus, carbon-hydrogen bond activation of 1,2,4,5-tetrafluorobenzene by  $Ni(PEt_3)_2$  is just slightly more thermodynamically favorable than mononuclear adduct formation. The equilibrium constant for the reaction of the binuclear adduct with 1,2,4,5-tetrafluorobenzene to provide 2 equiv of the mononuclear adduct was determined to be 0.027(1), which corresponds to a  $\Delta G_{298}$  value of 2.2 kcal mol<sup>-1</sup>. The equilibrium constant for the conversion of the dinuclear adduct to the hydride is 0.5, which corresponds to a  $\Delta G_{298}$  value of 0.4 kcal  $mol^{-1}$ ; the hydride was observed as the major product of the reaction of the anthracene adduct (PEt<sub>3</sub>)<sub>2</sub>- $Ni(\eta^2-C_{14}H_{10})$  with 1,2,4,5-tetrafluorobenzene<sup>19</sup> only because of the excess 1,2,4,5-tetrafluorobenzene used to drive the reaction to produce spectroscopically observable amounts of product.

Characterization of a Dinuclear Ni(PEt<sub>3</sub>)<sub>2</sub> Adduct of 1,2, 3,4-C<sub>6</sub>F<sub>4</sub>H<sub>2</sub>. There are four possible isomers for the dinuclear adduct of 1,2,3,4-tetrafluorobenzene  $[(PEt_3)_2Ni]_2(\mu-\eta^2:\eta^2-$ 1,2,3,4-C<sub>6</sub>F<sub>4</sub>H<sub>2</sub>) (6). DFT calculations were performed using the model complexes  $[(PMe_3)_2Ni]_2(\mu-\eta^2:\eta^2-1,2,3,4-C_6F_4H_2)$ (6<sup>Me</sup>) to predict which isomer is favored, where the four potential isomers are labeled 6-2345, 6-1645, 6-1234, and 6-1256, as shown in Scheme 6. The isomer 6-2345 was found to be the lowest energy, with a  $\Delta G_{298 \text{ K}}$  value of 2.4 kcal mol<sup>-1</sup> for conversion to the next lowest energy isomer, the 6-1256 isomer. This value suggests that the equilibrium concentration of the other isomers at room temperature should less than 2% and the NMR spectra of the dinuclear adduct should be dominated by the **6-2345** isomer. The calculated <sup>19</sup>F NMR shifts for the **6-2345** isomer of  $[(PMe_3)_2Ni]_2(\mu-\eta^2:\eta^2-1,2,3, 4-C_6F_4H_2)$  for F<sub>1</sub>, F<sub>2</sub>, F<sub>3</sub>, and F<sub>4</sub> are  $\delta$  -139, -182, -155, and -137, respectively.

The adduct [(PEt<sub>3</sub>)<sub>2</sub>Ni]<sub>2</sub>( $\mu$ - $\eta$ <sup>2</sup>: $\eta$ <sup>2</sup>-1,2,3,4-C<sub>6</sub>F<sub>4</sub>H<sub>2</sub>) was synthesized by the reaction of **2** with 1,2,3,4-tetrafluorobenzene in toluene, as shown in eq 3. The equilibrium exchange of isobutene with 1,2,3,4-tetrafluorobenzene in this reaction scarcely produces any of the desired product under ambient conditions, as monitored by <sup>19</sup>F and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy; therefore, vacuum had to be applied to remove isobutene and drive the reaction to completion. As a result, the crude reaction mixture contained Ni(PEt<sub>3</sub>)<sub>4</sub> as a significant impurity from the decomposition of **2** under vacuum. Nevertheless, upon drying under vacuum, the <sup>19</sup>F NMR spectrum revealed primarily a single fluorine-containing product.



Crystalline **6** was isolated in modest yields by cooling a pentane solution of the product mixture to -40 °C. An ORTEP depiction of the solid-state molecular structure is shown in Figure 3. The structure features two molecules in the asymmetric unit. In the molecule shown in Figure 3, a disorder of the fluorine locations is omitted. The disorder model involves the identical isomer predicted by DFT calculations, but with the fluorine atoms bound to C(6), C(5), C(4), and C(3). This minor disorder was fitted as occurring with a site occupancy of 0.155(4) in the molecule associated with Ni(1) and Ni(2). In the second molecule in the asymmetric unit an identical disorder was observed, but with equal occupancies. Further details are provided in the Supporting Information. Bond lengths are provided from the

molecule featuring the least disorder. Similar to the previously reported adducts of  $C_6F_6$  and  $C_6F_5H$ , this complex exhibits signs of extensive back-bonding, with a short C-(1)-C(6) distance of 1.325(5) Å indicative of a localized double bond, with the remaining bonds of the  $C_6F_4H_2$  moiety significantly longer than an aromatic C-C bond and ranging from 1.420(4) to 1.461(4) Å.

The low-temperature 282.4 MHz  $^{19}F{^1H}$  NMR spectrum of dinuclear adduct 6 in pentane or toluene- $d_8$  is consistent with the isomer observed in the solid state by X-ray crystallography. In pentane at 163 K, four <sup>19</sup>F resonances are observed at  $\delta$  -132.8, -141.5, -158.2, and -189.2. These peaks broaden upon warming, with the peaks at  $\delta$  -132.8 and -141.5 coalescing between 183 and 193 K and the peaks at  $\delta$  -158.2 and -189.2 coalescing between 193 and 203 K. Of the two resonances observed above 203 K, the peak at  $\delta$  -136 sharpens into a well-defined second-order multiplet at 254 K, which resembles a doublet of pentets that becomes unresolved at room temperature. The resonance at  $\delta$  –171.3 continues to sharpen until 298 K, where the second-order coupling displays seven barely resolved lines, giving the appearance of a septet. Fitting the line widths of these fluorine spectra from 183 to 233 K provides an Arrhenius activation energy for the exchange process of 8.0 kcal  $mol^{-1}$ .

The low-temperature 121.5 MHz<sup>31</sup>P{<sup>1</sup>H} NMR spectra of the dinuclear adduct **6** are also consistent with the predicted isomer. At 163 K, four environments are observed at  $\delta$  25.3, 21.3, 16.3, and 12.6. At this temperature the resolution is



Figure 3. ORTEP depiction of the solid-state molecular structure of  $[(PEt_3)_2Ni]_2(\mu-\eta^2;\eta^2-1,2,3,4-C_6F_4H_2)$  (6). One of the two molecules in the asymmetric unit is shown. Hydrogen atoms and an 85:15 disorder of the fluorine locations are omitted for clarity, and 30% probability thermal ellipsoids are shown. Selected bond lengths (Å): Ni(1)-C(2), 1.924(3); Ni(1)-C(3), 1.954(3); Ni(2)-C(4), 1.971(3); Ni(2)-C(5), 1.958(3); C(1)-C-(6), 1.325(5); C(1)-C(2), 1.450(4); C(2)-C(3), 1.430(4); C-(3)-C(4), 1.461(4); C(4)-C(5), 1.420(4); C(5)-C(6), 1.449(5).

insufficient to observe coupling. The middle pair of resonances coalesce between 173 and 183 K, whereas the outer pair of resonances sharpens to reveal apparent doublets of triplets of triplets, with a  ${}^{2}J_{\rm PP}$  value of 47.5 Hz. At 213 K, all three resonances are sharp multiplets, with the central multiplet at  $\delta$  18.9 appearing as a triplet with a  $J_{\rm PF}$  value of 19.9 Hz. The outer multiplets were observed at  $\delta$  25.2 and 13.3 and are half the intensity of the central multiplet. Modeling the line shapes for the coalescence of the middle peaks from 173 to 193 K provides an Arrhenius activation energy of 8.1 kcal mol<sup>-1</sup> for this exchange, which indicates that this is the same exchange process observed in the fluorine NMR spectra.

We have previously observed fluxional behavior in the dinuclear Ni(PEt<sub>3</sub>)<sub>2</sub> adducts of  $C_6F_6$  and  $C_6F_5H$ .<sup>17</sup> Consistent with our previous observations, the 1,3-shift of a Ni-(PEt<sub>3</sub>)<sub>2</sub> moiety in the dinuclear adduct provides a simple mechanism for the observation of two <sup>19</sup>F environments at room temperature, without requiring the intermediacy of any higher energy isomers. This process is shown in Scheme 7. However, for only two phosphorus environments to be exchanged by this process, as observed in the low-temperature <sup>31</sup>P{<sup>1</sup>H} NMR spectrum, the locations of the phosphines labeled  $L_c$  and  $L_d$  must change, contrary to what we had observed previously. This process only exchanges the environments of  $L_a$  and  $L_b$ , but not  $L_c$  and  $L_d$ .

Above 213 K, all three resonances in the 121.5 MHz  $^{31}P{^{1}H}$  NMR spectrum of **6** begin to broaden. Coalescence of all three peaks occurs between 163 and 173 K, and the room-temperature <sup>31</sup>P{<sup>1</sup>H} NMR spectrum features a broad resonance at  $\delta$  19.2 with a peak width at half-height of 140 Hz. This exchange process is difficult to model with certainty, as multiple processes may exchange the environments of La, Lb, Lc, and Ld. Using a simple model where the rate of exchange between La and Lb is rapid and the exchanges between the remaining pairs of nuclei are equally as likely, the line widths from the  $253-273 \text{ K}^{31}\text{P}{}^{1}\text{H}$  NMR data were used to estimate an Arrhenius activation energy of 14 kcal mol for this process. This activation energy is consistent with the intermediacy of the higher energy 6-1645 isomer shown in Scheme 7. The <sup>1</sup>H resonance associated with the coordinated 1.2.3.4-tetrafluorobenzene moiety in the dinuclear adduct was observed as a second-order multiplet that resembled a doublet with a 19.5 Hz coupling constant at  $\delta$  3.62. Below 226 K this multiplet broadens significantly, indicative of fluxional behavior. At 183 K, this resonance has a peak width at half-height of approximately 250 Hz. The proposed structure should exhibit two <sup>1</sup>H environments for the aromatic ring; however, the signals for these environments were too broad to be observed at 173 or 163 K.

Spectroscopic Characterization of a Mononuclear Adduct of 1,2,3,4-C<sub>6</sub>F<sub>4</sub>H<sub>2</sub>. There are four possible isomers for the mononuclear adduct of 1,2,3,4-tetrafluorobenzene (PEt<sub>3</sub>)<sub>2</sub>Ni-( $\eta^2$ -1,2,3,4-C<sub>6</sub>F<sub>4</sub>H<sub>2</sub>) (7). DFT calculations were performed







using the model complexes  $(PMe_3)_2Ni(\eta^2-1,2,3,4-C_6F_4H_2)$  $(7^{Me})$ , where the four potential isomers are labeled 7-12, 7-23, 7-45, and 7-56, as shown in Scheme 8. The 7-23 isomer was found to have the lowest energy, with a  $\Delta G_{298 \text{ K}}$  value of  $2.0 \text{ kcal mol}^{-1}$  for conversion to the next lowest energy isomer, the 7-56 isomer. This suggests that the equilibrium concentration of the other isomers should account for less than 3.5% of the mononuclear adducts at room temperature, and the NMR spectrum of the mononuclear adduct should be predominantly that of the 7-23 isomer. The calculated <sup>19</sup>F NMR shifts for the 7-23 isomer of  $(PMe_3)_2Ni(\eta^2-1,2,3,4 C_6F_4H_2$ ) for  $F_{1,4}$  and  $F_{2,3}$  are  $\delta$  -133 and -170, respectively. The equilibrium reaction of the dinuclear adduct with 1,2,3,4-C<sub>6</sub>F<sub>4</sub>H<sub>2</sub> to form 2 equiv of the mononuclear adduct is predicted to have a  $\Delta G_{298 \text{ K}}$  value of 1.9 kcal mol<sup>-1</sup>, which suggests that the mononuclear adduct should be observable using suitable concentrations of the dinuclear adduct and 1,2,3,4-C<sub>6</sub>F<sub>4</sub>H<sub>2</sub>. This isomer is different than the lowest energy isomer predicted for the adduct of CpRe(CO)<sub>2</sub>,<sup>29</sup> where the adduct with the Re bound to the 5- and 6-sites was calculated to have the lowest energy.

The addition of 1,2,3,4-tetrafluorobenzene to a benzene solution containing the dinuclear adduct allowed for the observation of an equilibrium amount of the mononuclear adduct (PEt<sub>3</sub>)<sub>2</sub>Ni( $\eta^2$ -1,2,3,4-C<sub>6</sub>F<sub>4</sub>H<sub>2</sub>) (7), as assigned by <sup>19</sup>F, <sup>31</sup>P{<sup>1</sup>H}, and <sup>1</sup>H NMR spectroscopy. With relatively low concentrations of 1,2,3,4-C<sub>6</sub>F<sub>4</sub>H<sub>2</sub>, the equilibrium constant for the reaction of the dinuclear complex with 1,2,3,4-tetra-fluorobenzene to form 2 equiv of the mononuclear adduct was measured as 0.038(1), which corresponds to a  $\Delta G_{298 \text{ K}}$  value of 1.9 kcal mol<sup>-1</sup> for this reaction.

Sharp resonances were observed in the <sup>19</sup>F{<sup>1</sup>H}, <sup>31</sup>P{<sup>1</sup>H}, and <sup>1</sup>H NMR spectra of an equilibrium mixture of mononuclear adduct 7 in pentane obtained at 253 K obtained on a spectrometer operating at 300 MHz with respect to <sup>1</sup>H. The <sup>19</sup>F{<sup>1</sup>H} NMR spectrum of 7 featured sharp second-order multiplets at  $\delta$  –128.1 and –173.8. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum featured a triplet with a <sup>3</sup>J<sub>PF</sub> value of 23.3 Hz at  $\delta$  16.5. The <sup>1</sup>H NMR spectrum displayed a second-order multiplet resembling a triplet at  $\delta$  5.27 with a 6.5 Hz coupling constant. The features of these spectra did not change upon cooling to as low as 213 K. When the solution was warmed to room temperature, the <sup>31</sup>P{<sup>1</sup>H} and <sup>19</sup>F NMR spectra both broadened slightly. More profoundly affected was the <sup>1</sup>H resonance associated with the  $\eta^2$ -bound 1,2,3,4-C<sub>6</sub>F<sub>4</sub>H<sub>2</sub> moiety, which had a line width at half-height of 120 Hz. The fluxional process associated with the line broadening appears to involve exchange with the free 1,2,3,4-C<sub>6</sub>F<sub>4</sub>H<sub>2</sub> in solution, because the <sup>19</sup>F and <sup>1</sup>H resonances associated with the tetrafluorobenzene are also broadened at room temperature. The spectra are all consistent with the  $C_s$ -symmetric 7-23 isomer predicted by DFT calculations.

Activation of the C–H Bond in 1,2,3,4-C<sub>6</sub>F<sub>4</sub>H<sub>2</sub>. Calculations on the model complex (PMe<sub>3</sub>)<sub>2</sub>NiH-2,3,4,5-F<sub>4</sub>C<sub>6</sub>H (8<sup>Me</sup>) suggest that the hydride obtained by C–H activation in the mononuclear adduct 7 is most likely kinetically accessible, as 8<sup>Me</sup> is thermodynamically uphill from 7<sup>Me</sup> by only a modest  $\Delta G_{298 \text{ K}}$  value of 2.6 kcal mol<sup>-1</sup>. Regardless, the hydride should not be present in large enough quantities to be observed by standard NMR spectroscopy. The DFT calculations on 8<sup>Me</sup> provided the predicted <sup>19</sup>F NMR shifts of  $\delta$  –125, –162, –168, and –147 for F<sub>2</sub>, F<sub>3</sub>, F<sub>4</sub>, and F<sub>5</sub>, respectively. Experimentally, no peaks were observed in the <sup>19</sup>F or <sup>1</sup>H NMR spectra that could be assigned as an equilibrium amount of the hydride.

Characterization of a Dinuclear Ni(PEt<sub>3</sub>)<sub>2</sub> Adduct of 1,2,3,5-C<sub>6</sub>F<sub>4</sub>H<sub>2</sub>. There are three possible isomers for the dinuclear adduct of 1,2,3,5-tetrafluorobenzene [(PEt<sub>3</sub>)<sub>2</sub>Ni]<sub>2</sub>- $(\mu - \eta^2 : \eta^2 - 1, 2, 3, 5 - C_6 F_4 H_2)$  (9). DFT calculations were performed using the model complexes  $[(PMe_3)_2Ni]_2(\mu-\eta^2:\eta^2-1,2)$ , 3.5-C<sub>6</sub>F<sub>4</sub>H<sub>2</sub>) (9<sup>Me</sup>) to predict which isomer is favored, where the three potential isomers are labeled 9-1234, 9-3456, and 9-1256, as shown in Scheme 9. The 9<sup>Me</sup>-1234 isomer was found to have the lowest energy, with a  $\Delta G_{298 \text{ K}}$  value of 1.6 kcal mol<sup>-1</sup> for conversion to the next lowest energy isomer, the 9<sup>Me</sup>-3456 isomer. This value suggests that the equilibrium concentration of the 9-3456 isomer at room temperature should be 6% of the sample, and although the NMR spectra of the dinuclear adduct should be dominated by the 9-1234 isomer, it may be possible to observe line broadening due to the 9-3456 isomer. At 193 K, the equilibrium concentration of the 9-3456 isomer is predicted to be 1.5%, which could be difficult to assign. The highest energy isomer is predicted to be the  $9^{Me}$ -1256 isomer, which has a  $\Delta G_{298 \text{ K}}$  value of 3.0 kcal mol<sup>-</sup> from the 9<sup>Me</sup>-1234 isomer. The calculated <sup>19</sup>F NMR shifts for the lowest energy isomer  $9^{Me}$ -1234 are  $\delta$  -169, -161, -135, and -123 for F<sub>1</sub>, F<sub>2</sub>, F<sub>3</sub>, and F<sub>5</sub>, respectively. In a rapidly fluxional molecule the shifts for  $F_1$  and  $F_3$  could be in exchange, and their <sup>19</sup>F NMR shifts would be predicted to be observed at  $\delta$  -152.

Attempts to isolate the dinuclear adduct of 1,2,3,5-tetrafluorobenzene have thus far failed. This species appears to undergo C-F bond activation significantly more quickly than either 1,2,4,5- or 1,2,3,4-tetrafluorobenzene under identical

<sup>(29)</sup> Clot, E.; Oelckers, B.; Klahn, A. H.; Eisenstein, O.; Perutz, R. N. *Dalton Trans.* 2003, 4065–4074.

conditions. Heating a solution of 2 and  $1,2,3,5-C_6F_4H_2$  to reflux in pentane, analogous to the procedure used to generate the dinuclear adduct of 1, 2, 4, 5-C<sub>6</sub>F<sub>4</sub>H<sub>2</sub>(3), produced mainly the product of C-F activation. The application of vacuum to a hexamethyldisiloxane solution of 2 and  $1,2,3,5-C_6F_4H_2$ provided the best route to solutions containing the dinuclear adduct [(PEt<sub>3</sub>)<sub>2</sub>Ni]<sub>2</sub>( $\mu$ - $\eta^2$ : $\eta^2$ -1,2,3,5-C<sub>6</sub>F<sub>4</sub>H<sub>2</sub>) (9), which were readily characterized by NMR spectroscopy. The solution contained significant impurities in the <sup>19</sup>F NMR spectrum, which included the C-F activation product<sup>19</sup> (PEt<sub>3</sub>)<sub>2</sub>NiF- $(2,3,5-C_6F_3H_2)$  and the unexpected aryne complex  $[(PEt_3)_2Ni]_2$ - $(\mu - \eta^2 : \eta^2 - 3, 4, 6 - C_6 F_3 H)$  (12; vide infra), as shown in Scheme 10. The aryne complex is significantly less soluble than 9; thus, attempts at recrystallization of 9 from pentane and hexamethyldisiloxane failed. Complex 9 has significantly less thermal stability in solution than the related dinuclear adducts of 1,2,4,5- and 1,2,3,4-C<sub>6</sub>F<sub>4</sub>H<sub>2</sub>. Solutions of 9 thermally convert at 25 °C over the course of hours to the C-F activation product (PEt<sub>3</sub>)<sub>2</sub>NiF(2,3,5-C<sub>6</sub>F<sub>3</sub>H<sub>2</sub>), even in the absence of 1 equiv of 1,2,3,5- $C_6F_4H_2$  to trap the excess Ni(PEt<sub>3</sub>)<sub>2</sub>.

Despite the difficulties in isolating pure crystalline samples of dinuclear complex **9**, it still proved possible to obtain solutions of sufficient concentration to be amenable to characterization by multinuclear NMR spectroscopy. The low-temperature 282.4 MHz  ${}^{19}F{}^{1}H{}$  NMR spectra of the dinuclear adduct in pentane or toluene- $d_8$  are consistent with the isomer **9-1234**. In pentane at 193 K, four  ${}^{19}F{}$  resonances are observed at  $\delta - 113.7, -137.1, -162.2,$  and -175.7. When





the temperature is raised, the peaks at -137.1 and -175.7 broaden significantly, and at 293 K they have line widths at half-height of ~1500 Hz, which makes them hard to discern in spectra of dilute solutions of **9**. This exchange broadening, along with the predicted shifts obtained using DFT, allows the assignment of the low-temperature <sup>19</sup>F NMR shifts as arising from F<sub>5</sub>, F<sub>3</sub>, F<sub>2</sub>, and F<sub>1</sub>, respectively. The broadening due to the exchange of F<sub>1</sub> and F<sub>3</sub> can be modeled from 273 to 293 K and provides an Arrhenius activation energy of 12 kcal mol<sup>-1</sup> for this process.

The process that exchanges environments  $F_1$  and  $F_3$  should also exchange the two hydrogen environments of the 1,2,3,5- $C_6F_4H_2$  moiety in **9**. At 233 K, the <sup>1</sup>H NMR spectrum displays two doublets of multiplets at  $\delta$  4.81 and 2.75 with doublet coupling constants of 11.5 and 23 Hz, respectively. These signals broaden on warming and coalesce at 283 K. At 293 K, a very broad resonance is observed at  $\delta$  3.8. The rate of exchange of the <sup>1</sup>H environments can be modeled from 253 to 293 K and provides an Arrhenius activation energy of 11 kcal mol<sup>-1</sup> for this process, similar to the barrier ascertained from the variable-temperature <sup>19</sup>F NMR spectra.

This exchange process is different from those observed previously in the dinuclear complexes of pentafluorobenzene and 1,2,4,5- and 1,2,3,4-tetrafluorobenzene. In all previous cases the lowest exchange fluxional processes occurred without a change in the formal positions of the double bonds; that is, the aromatic ring is stuck in one of two possible resonance structures, with the Ni(PEt<sub>3</sub>)<sub>2</sub> moieties undergoing 1,3-shifts. It is not clear what exact mechanism operates in this exchange process. It can be conjectured that the mechanism could involve one of the Ni(PEt<sub>3</sub>)<sub>2</sub> moieties escaping the  $\pi$  system and  $\sigma$  bonding to a C-F bond, as in the proposed intermediate to C-F activation. Such a mechanism for exchange is consistent with the unexpected fluxionality and the relatively rapid rate at which **9** undergoes C-F activation relative to adducts of the other tetrafluorobenzenes.

Fluxionality is also evident in the variable-temperature 121.5 MHz  ${}^{31}P{}^{1}H{}$  NMR spectra. At 193 K, four environments are observed at  $\delta$  25.8, 21.1, 15.6, and 13.4. All the resonances coalesce on warming. At 298 K, a single resonance was observed at  $\delta$  19.0 with a line width at half-height 130 Hz. A model of the line shapes where all four  ${}^{31}P$  environments are assumed to exchange at the same rate fits the observed data



Scheme 10

 $\begin{array}{cccc} \textbf{10-34, L=PEt_3} & \textbf{10-45, L=PEt_3} & \textbf{10-12, L=PEt_3} \\ \textbf{10^{Me}-34, L=PMe_3} & \textbf{10^{Me}-45, L=PMe_3} & \textbf{10^{Me}-12, L=PMe_3} \\ \textbf{L=PMe_3} & \textbf{L=PMe_3} & \textbf{L=PMe_3} \\ \hline \textbf{Calculated } \Delta H_{298 \ K} & +3.7 \ \text{kcal mol}^{-1} & +2.9 \ \text{kcal mol}^{-1} \\ \textbf{Calculated } \Delta G_{298 \ K} & +3.1 \ \text{kcal mol}^{-1} & +1.9 \ \text{kcal mol}^{-1} \end{array}$ 

well from 233 to 293 K and provides an Arrhenius activation energy of 2.5 kcal mol<sup>-1</sup> for this exchange. Although it is conceivable that this exchange could simply involve the **9**-**3456** and **9-1256** isomers as intermediates, with 1,3-shifts of the Ni(PEt<sub>3</sub>)<sub>2</sub> moieties as we have observed previously, the low energy barrier is not consistent with this.

Spectroscopic Characterization of the Mononuclear Adduct of 1,2,3,5-C<sub>6</sub>F<sub>4</sub>H<sub>2</sub>. There are three possible isomers for the mononuclear adduct of 1,2,3,5-tetrafluorobenzene (PEt<sub>3</sub>)<sub>2</sub>Ni- $(\eta^2-1,2,3,5-C_6F_4H_2)$  (10). DFT calculations were performed using the model complexes  $(PMe_3)_2Ni(\eta^2-1,2,3,5-C_6F_4H_2)$  $(10^{Me})$ , where the three potential isomers are labeled 10-12, 10-34, and 10-45, as shown in Scheme 11. The 10-34 isomer was found to have the lowest energy, with a  $\Delta G_{298 \text{ K}}$  value of 1.9 kcal  $mol^{-1}$  for conversion to the next lowest energy isomer, the 10-12 isomer. This suggests that the equilibrium concentration of the other isomers should account for less than 4% of the mononuclear adducts at room temperature, and the NMR spectra of the mononuclear adduct should be predominantly that of the **10-34** isomer. The calculated <sup>19</sup>F NMR shifts for the 10-34 isomer of  $(PMe_3)_2Ni(\eta^2-1,2,3,$ 5-C<sub>6</sub>F<sub>4</sub>H<sub>2</sub>) for F<sub>1</sub>, F<sub>2</sub>, F<sub>3</sub>, and F<sub>5</sub> are  $\delta$  -152, -166, -141, and -113, respectively. For a fluxional complex, with the Ni moiety whizzing around the ring, the resonances for  $F_1$  and  $F_3$  would be expected to give a signal at  $\delta$  -146 of double intensity. The equilibrium reaction of the dinuclear adduct 9 with 1,2,3,5-C<sub>6</sub>F<sub>4</sub>H<sub>2</sub> to form 2 equiv of the mononuclear adduct 10 is estimated to have a  $\Delta G_{298 \text{ K}}$  value of 1.3 kcal mol<sup>-1</sup> and should be observable by the addition using suitable concentrations of the dinuclear adduct and  $1,2,3,5-C_6F_4H_2$ .

The addition of 1,2,3,5-tetrafluorobenzene to a toluene- $d_8$ solution containing the dinuclear adduct allowed for the observation of an equilibrium amount of the mononuclear adduct (PEt<sub>3</sub>)<sub>2</sub>Ni( $\eta^2$ -1,2,3,5-C<sub>6</sub>F<sub>4</sub>H<sub>2</sub>), as assigned by <sup>19</sup>F, <sup>31</sup>P{<sup>1</sup>H}, and <sup>1</sup>H NMR spectroscopy. The mononuclear adduct 10 exhibits three resonances in the room-temperature 282 MHz <sup>19</sup>F{<sup>1</sup>H} NMR spectrum at  $\delta$  -106.0, -149.9, and -161.5, as anticipated for a fluxional complex. The resonances at  $\delta$  – 106.0 and – 161.5 can be assigned to F<sub>5</sub> and  $F_2$  by comparison to the calculated values. The resonance at  $\delta$  –149.9 integrates to two fluorine environments and can be assigned as F1 and F3. This resonance broadens below 213 K and finally decoalesces into two peaks at  $\delta$  -143 and -146 at 173 K. The energy barrier for this process can be estimated as 2.3 kcal mol<sup>-1</sup>, by modeling the <sup>19</sup>F NMR line shapes from 173 to 203 K. This value is consistent with the intermediacy of the 10-12 isomer and is in good agreement with the energy barrier estimated from DFT calculation. The 300 MHz <sup>1</sup>H

NMR spectrum of **10** reveals a single sharp multiplet for the aromatic hydrogens at  $\delta$  4.90 at 255 K, which broadens significantly below 213 K but does not decoalesce at temperatures as low as 173 K.

The room-temperature <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **10** exhibits a broad resonance spanning from  $\delta$  10 to 20 with a peak width at half-height of ~600 Hz. A slow-exchange spectrum was obtained at 213 K and features two unresolved multiplets at  $\delta$  15.4 and 20.9. Modeling the line shapes of the <sup>31</sup>P{<sup>1</sup>H} NMR spectra from 233 to 253 K allows for an estimation of the Arrhenius activation energy for the exchange environments as 2.4 kcal mol<sup>-1</sup>. It is unexpected that this is the same energy observed for exchange of the F<sub>1</sub> and F<sub>3</sub> environments in the <sup>19</sup>F NMR spectra, because the anticipated mechanism of exchange, where the Ni(PEt<sub>3</sub>)<sub>2</sub> moiety spins as it adopts an  $\eta^3$  bonding mode to whiz around the ring, would not be expected to exchange <sup>31</sup>P environments.<sup>28</sup>

Spectroscopic Characterization of (PEt<sub>3</sub>)<sub>2</sub>NiH(2,3,4,6-C<sub>6</sub>F<sub>4</sub>H). The aromatic hydrogen in 1,2,3,5-tetrafluorobenzene has two o-F substituents, and thus the C-H activation product 11 was expected to be in equilibrium with the mononuclear adduct, as shown in Scheme 10. DFT calculations on the model complex (PMe<sub>3</sub>)<sub>2</sub>NiH(2,3,4,6-C<sub>6</sub>F<sub>4</sub>H) (11<sup>Me</sup>) provided predicted <sup>19</sup>F NMR shifts of  $\delta$  –116, –172, –146, and –100 for F<sub>2</sub>, F<sub>3</sub>, F<sub>4</sub>, and F<sub>6</sub>, respectively. The hydride model complex is predicted by DFT to be 0.3 kcal mol<sup>-1</sup> less favorable than the mononuclear adduct; however, an equilibrium amount should be observed. Experimentally, signals for hydride 11 are observed in the <sup>19</sup>F NMR spectrum at  $\delta$  -90.5 -110.0, -144.6, and -170.2, which can be tentatively assigned as arising from  $F_6$ ,  $F_2$ ,  $F_4$ , and  $F_3$ , respectively, by comparison to the values obtained by DFT calculation. The room-temperature <sup>1</sup>H NMR spectrum features a hydridic signal at  $\delta$  -14.6 that is a broad triplet. When the temperature is lowered to 223 K, the hydridic proton at  $\delta$  -14.56 sharpens and can be resolved as a triplet with a  ${}^{2}J_{\rm PH}$  value of 69 Hz but coupling to the fluorines is poorly resolved in the <sup>1</sup>H NMR. The coupling between the <sup>1</sup>H and <sup>19</sup>F nuclei was well-resolved in the 293 K <sup>19</sup>F NMR spectrum and was modeled to obtain accurate coupling constants (see the Supporting Information). Three of the <sup>19</sup>F environments couple to both the aromatic hydrogen and the Ni-H. The 298 K <sup>31</sup>P{<sup>1</sup>H} NMR spectrum displays a slightly broad resonance at  $\delta$  23.5, which sharpens slightly on cooling. This minor resonance was assignable because it split into a doublet in the <sup>31</sup>P NMR spectrum, with a  ${}^{2}J_{PH}$  coupling of 70 Hz.

Thermodynamic Considerations with 1,2,3,5-C<sub>6</sub>F<sub>4</sub>H<sub>2</sub>. Different concentrations of 1,2,3,5-tetrafluorobenzene were reacted with dinuclear complex 9, to determine equilibrium constants for its conversion to the mononuclear adduct 10 and hydride 11. The equilibrium constant for the conversion of the mononuclear complex to the hydride can be estimated from the ratio of integrals to be 0.18(1); carbon-hydrogen bond activation of 1,2,3,5-tetrafluorobenzene by Ni(PEt<sub>3</sub>)<sub>2</sub> is just slightly less thermodynamically favorable than mononuclear adduct formation with a  $\Delta G_{298}$  value of 1.0 kcal mol<sup>-1</sup> for the conversion of the mononuclear adduct to the hydride. The equilibrium constant for the reaction of the dinuclear adduct with 1,2,3,5-tetrafluorobenzene to provide 2 equiv of the mononuclear adduct was determined to be 0.056(1), which corresponds to a  $\Delta G_{298}$  value of 1.7 kcal mol<sup>-1</sup>. The equilibrium constant for the conversion of the dinuclear adduct to the hydride is 0.0019(1), which corresponds to a  $\Delta G_{298}$  value of 3.7 kcal mol<sup>-1</sup>. The hydride from C–H activation of 1,2,3,5-C<sub>6</sub>F<sub>4</sub>H<sub>2</sub> is less favored than that of 1,2,4,5-tetrafluorobenzene. This can be attributed to the fact that the fluorine substituent para to the C–H bond has a significantly stronger influence of the C–H bond strength than a meta fluorine, whereas both meta and para fluorine substituents strengthen the Ni–C bond in the C–H activation product, with a slightly stronger bond observed with meta substitution. The C–H bond dissociation energy of 1,2,3,5-C<sub>6</sub>F<sub>4</sub>H<sub>2</sub> has been calculated to be 0.55 kcal mol<sup>-1</sup> greater than that of 1,2,4,5-C<sub>6</sub>F<sub>4</sub>H<sub>2</sub>, and nearly identical with that of C<sub>6</sub>F<sub>5</sub>H.<sup>29</sup>

Synthesis of the Aryne Complex  $[(PEt_3)_2Ni]_2(\mu-\eta^2:\eta^2-3,4,6 C_6F_3H$ ). As previously noted, the aryne complex [(PEt<sub>3</sub>)<sub>2</sub>-Ni]<sub>2</sub> $(\mu - \eta^2 : \eta^2 - 3, 4, 6 - C_6 F_3 H)$  (12) proved to be a significant byproduct in the reaction of isobutene adduct 3 with 1,2,3, 5-tetrafluorobenzene. Even though it is present in a mixture, this compound was readily isolated as orange-brown crystals from pentane or hexamethyldisiloxane at -40 °C, because it is less soluble than the other products. The solid-state molecular structure was determined using X-ray crystallography, which conclusively identified the product as the dinuclear aryne  $[(\text{PEt}_3)_2\text{Ni}]_2(\mu-\eta^2:\eta^2-3,4,6-\text{C}_6\text{F}_3\text{H})$  (12). An ORTEP depiction is shown in Figure 4. There are two molecules in the asymmetric unit, both of which display disorder of the fluorine attached to the 4-position of the ring. The second molecule also displays extensive disorder of the PEt<sub>3</sub> donor. Further details are provided in the Experimental Section and Supporting Information.

The product formally involves the dehydrohalogenation of an ortho-disposed hydrogen and fluorine from 1,2,3,5tetrafluorobenzene. Dinuclear complexes with bridging aryne ligands are uncommon, but a similar structure has been previously reported for the closely related complex [(PEt<sub>3</sub>)<sub>2</sub>-Ni]<sub>2</sub>( $\mu$ - $\eta$ <sup>2</sup>: $\eta$ <sup>2</sup>-4,5-C<sub>6</sub>F<sub>2</sub>H<sub>2</sub>).<sup>30</sup> There is considerable back-bonding from the Ni moieties to the aryne moieties aromatic  $\pi$ bonds as evident in the C(1)–C(2) bond length of 1.389(2) Å as well as the short C(3)–C(4) and C(5)–C(6) bond lengths of 1.357(3) and 1.345(3) Å, respectively. The Ni(1)–Ni(2) distance of 2.8276(6) Å suggests there is no significant bonding interaction between the Ni centers.

The <sup>19</sup>F, <sup>31</sup>P{<sup>1</sup>H}, and <sup>1</sup>H NMR spectra of **12** are all consistent with the solid-state structure. The <sup>19</sup>F NMR spectrum displays three resonances at  $\delta$  –102.4, –137.0, and –152.6, which are a doublet with  $J_{FF}$  = 49.3 Hz, a doublet of doublets with  $J_{FF}$  = 49.3 and 31.1 Hz, and a doublet with  $J_{FF}$  = 31.1 Hz, respectively. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum features a pair of second-order AA'BB' doublets at  $\delta$  15.6 and 15.3. The <sup>1</sup>H NMR spectrum reveals a single aromatic resonance at  $\delta$  6.12. There is no evidence of fluxional behavior at room temperature.

Several possible mechanisms could lead to the formation of **12**, which was also observed in much smaller amounts in the synthesis of the dinuclear complex of 1,2,4,5-tetrafluorobenzene (**3**). Spectra of the reaction of 1,2,4,5-C<sub>6</sub>F<sub>4</sub>H<sub>2</sub> with the phenanthrene and anthracene adducts (PEt<sub>3</sub>)<sub>2</sub>Ni( $\eta^2$ -C<sub>14</sub>H<sub>10</sub>) were also found to display very minor resonances in the <sup>19</sup>F NMR spectra that could be attributed to **12**. In the synthesis of **12** during the attempted isolation of **9**, it is conceivable that hydride **11** could undergo  $\beta$ -fluorine elimination and ultimately lose HF. Evidence against this mechanism is that the formation of **12** was always observed to occur



Figure 4. ORTEP depiction of the solid-state molecular structure of 12 as determined by X-ray crystallography. Hydrogen atoms and an occupational disorder of the F(2) fluorine atom are omitted for clarity, and 30% probability thermal ellipsoids are shown. Selected bond lengths (Å): Ni(1)–C(2), 1.930(2); Ni(1)–C(1), 1.952(2); Ni(1)–Ni(2), 2.8276(6); Ni(2)–C(1), 1.922(2); Ni(2)–C(2), 1.948(2); Ni(2)–P(3), 2.1721(7); Ni-(2)–P(4), 2.1757(7); C(1)–C(2), 1.389(2); C(1)–C(6), 1.404(3); C(2)–C(3), 1.414(3); C(3)–C(4), 1.357(3); C(4)–C(5), 1.394(3); C(5)–C(6), 1.345(3).

after the initial C–F activation product  $(PEt_3)_2NiF(2,3, 5-C_6F_3H_2)$  (13)<sup>19</sup> was observed. The reaction of 2 with the monodeuterated species 1,2,4,5-C\_6F\_4HD produced 12-*d* and 12 in a 1.5:1 ratio, which is slightly less than the equilibrium ratio of  $(PEt_3)_2NiH-2,3,5,6-F_4C_6D$  to  $(PEt_3)_2NiD-2,3,5,6-F_4C_6H$  of 2.1:1 observed in this reaction.<sup>19</sup> This provides further evidence that C–H activation does not precede C–F activation in the formation of 12, because a nearly identical ratio would be expected, although there is some error in the measurement due to the formation of some 1,2,4,5-C\_6F\_4H\_2 and 1,2,4,5-C\_6F\_4D\_2 under the reaction conditions.

Several mechanisms for the formation of 12 are conceivable from C-F activation product 13. The deprotonation of the  $\beta$ -hydrogen in related complexes to form arynes has precedent,<sup>31</sup> though it is not clear what species could act as a strong base under the conditions used here. Furthermore, the ratio of 12-d and 12 formed in the reaction of 2 with the monodeuterated species 1,2,4,5-C<sub>6</sub>F<sub>4</sub>HD is significantly smaller than that anticipated for a direct deprotonation. The cleavage of the aromatic C-H bond is more likely to occur with the assistance of the Ni center. Complex 12 was observed in the reaction of (PEt<sub>3</sub>)<sub>2</sub>NiMe<sub>2</sub> with 1,2,4,5- and 1,2,3,5-tetrafluorobenzene, as previously noted, and could arise from C-F activation by a  $Ni(PEt_3)_2$  moiety obtained by reductive elimination of ethane, followed by ligand redistribution between (PEt<sub>3</sub>)<sub>2</sub>NiMe<sub>2</sub> and the C-F activation products. A final  $\beta$ -abstraction of the hydrogen would provide 12 with the elimination of methane. However, the direct reaction of the C-F activation product (PEt<sub>3</sub>)<sub>2</sub>NiF(2,3,5- $C_6F_3H_2$ ) with (PEt<sub>3</sub>)<sub>2</sub>NiMe<sub>2</sub> (1) failed to provide any 12. A similar mechanism could explain the formation of 12 in the reaction of  $1,2,3,5-C_6F_4H_2$  with 2. The hydride ligand of 11 could exchange with the fluoride ligand of the C-F activation product 13 to produce  $(PEt_3)_2NiH(2,3,5-C_6F_3H_2)$ , which could undergo a  $\beta$ -abstraction to eliminate H<sub>2</sub> and provide 12. However, the expected byproduct  $(PEt_3)_2$ - $NiF(2,3,5,6-C_6F_4H)^{17}$  was not observed in the  ${}^{19}F{}^{1}H{}$ NMR spectrum. The reaction of either  $Ni(PEt_3)_4$  or 2 with

<sup>(30)</sup> Keen, A. L.; Doster, M.; Johnson, S. A. J. Am. Chem. Soc. 2007, 129, 810–819.

<sup>(31)</sup> Bennett, M. A.; Kopp, M. R.; Wenger, E.; Willis, A. C. J. Organomet. Chem. 2003, 667, 8–15.

 $(PEt_3)_2NiF(2,3,5-C_6F_3H_2)$  failed to produce any **12**. This provides strong evidence that the C-F activation product  $(PEt_3)_2NiF(2,3,5-C_6F_3H_2)$  is not an intermediate in the formation of **12** in the reaction of the isobutene adduct **2** with  $1,2,3,5-C_6F_4H_2$ .

Without an identifiable byproduct, it has proven difficult to ascertain the mechanism by which **12** forms in the synthesis of **9**. A hypothesis from this mechanistic investigation is that complex **12** is formed as a byproduct in the formation of  $(PEt_3)_2NiF(2,3,5-C_6F_3H_2)$ . This is supported by the observation that, in the reaction of **2** and 1,2,3,5-tetrafluorobenzene, aryne **12** is observed as soon as the C-F activation product is present. It is not clear whether this mechanistic pathway involves a radical intermediate, occurs by a phosphine-assisted mechanism<sup>32</sup> that produces (PEt<sub>3</sub>)Ni-(PFEt<sub>3</sub>)(2,3,5-C<sub>6</sub>F<sub>3</sub>H<sub>2</sub>), which could lose HF to lead to **12**, or via an alternate mechanism.

It should be noted that related transformations that produce aryne complexes have recently been reported to play an important role in the chemistry of many fluorinated aryl complexes.<sup>33</sup> The mechanism by which these aryne products form is not always clear. Aryne **12** may act as an intermediate for some of the previously reported unusual products of C-F activation observed in the reaction of the phenanthrene adduct (PEt<sub>3</sub>)<sub>2</sub>Ni( $\eta^2$ -C<sub>14</sub>H<sub>10</sub>) and 1,2,3,5- and 1,2,4,5-tetra-fluorobenzene.<sup>19</sup>

Thermodynamic Comparison of the Tetrafluorobenzene Adducts. The addition of the dinuclear adduct 3 to a solution containing a mixture of all three tetrafluorobenzenes, followed by about 3 h to allow the mixture to reach equilibrium, provided an experimental method for obtaining thermodynamic parameters for the interconversion of the adducts. Integration of the <sup>19</sup>F NMR signal intensities were used to determine the equilibrium concentrations of each observable species. It has been noted that the equilibria between these species in benzene is sensitive to the concentration of the tetrafluorobenzenes used, and thus the equilibria were also measured in pentane and THF using similar conditions to determine the effect of solvent polarity. The data are summarized in Table 3, with complex 3 arbitrarily chosen as zero. For dinuclear complexes 6 and 9 the values provided are the Gibbs free energy for the reaction of 3 with  $1,2,3,4-C_6F_4H_2$ and 1,2,3,5-C<sub>6</sub>F<sub>4</sub>H<sub>2</sub>, respectively, with the production of  $1,2,4,5-C_6F_4H_2$ . For the mononuclear complexes and hydrides the Gibbs free energy is for the production of 2 equiv of these species from 3; thus, the energy differences between 1 equiv of these species is half the difference of values in Table 3.

Remarkably, all of these compounds, whether dinuclear adducts, mononuclear adducts, or C-H activation products, vary in their thermodynamic stability by modest amounts, and resonances for all the compounds can be observed in a

 Table 3. Experimentally Determined Thermodynamic Data for

 the Interconversion of the Tetrafluorobenzene Adducts and C-H

 Activation Products via Reaction with 1 or 2 Equiv of the

 Appropriate Tetrafluorobenzene

|       | $\Delta G_{298\mathrm{K}}\mathrm{(kcal\ mol^{-1})}^a$ |         |      |  |
|-------|---|---------|------|--|
| compd | pentane   | benzene | THF  |  |
| 3     | 0   | 0       | 0    |  |
| 4     | 2.8   | 2.4     | 1.9  |  |
| 5     | 1.2   | 0.3     | 0.6  |  |
| 6     | 0.1   | -0.2    | -0.2 |  |
| 7     | 2.9   | 1.9     | 1.2  |  |
| 9     | 0.6   | 0.3     | 0.3  |  |
| 10    | 2.4   | 1.5     | 0.9  |  |
| 11    | 4.2   | 3.7     | 3.6  |  |
|       |   |         |      |  |

<sup>*a*</sup> Relative  $\Delta G_{298 \text{ K}}$  values are given for the reactions starting from **3**, and for reactions that produce hydrides or mononuclear adducts these values are with respect to 2 equiv of product.

single <sup>19</sup>F NMR spectrum. The highest energy observable species, hydride **11**, is only 4.2 kcal mol<sup>-1</sup> higher in energy than **3** in pentane. The range of energies for the dinuclear adducts **3**, **6**, and **9** is 0.6 kcal mol<sup>-1</sup> in pentane and is even less in benzene and THF. In pentane, the mononuclear adducts lie significantly higher in energy than the dinuclear adducts but once again cover a very small range, from 2.4 to 2.8 kcal mol<sup>-1</sup>. As anticipated, hydride **5** was found to be significantly more thermodynamically favorable than hydride **11** with a 3.0 kcal mol<sup>-1</sup> Gibbs free energy difference in the production of 2 equiv of each from **3**. Hydride **5** was also lower energy than any of the mononuclear adducts.

The relative energies of the dinuclear adducts with respect to each other are only mildly affected by solvent, with a maximum change relative to **3** of only 0.3 kcal  $mol^{-1}$ . In contrast, the choice of solvent dramatically affects the equilibria between the dinuclear and mononuclear species. The mononuclear adducts are stabilized considerably relative to 3 upon going from pentane to THF as a solvent, with changes ranging from 0.9 kcal mol<sup>-1</sup> for **4** to 1.7 kcal mol<sup>-</sup> for 7. Although solvent-molecule interactions are complex, it is interesting to note that for the model complexes  $3^{Me}-11^{Me}$  it was found that the dinuclear adducts had relatively low calculated dipole moments, ranging from 0.9 to 1.5 D, whereas the mononuclear adducts had dipole moments in the range of 6.4-6.7 D. This dipole moment difference may partially explain the effect of solvent on the equilibrium concentrations. The hydride model complexes 5<sup>the</sup> and 11<sup>Me</sup> have intermediate dipole moments of 4.9 and 5.8 D, respectively, and both were found to be 0.6 kcal  $mol^{-1}$ more stable with respect to 3 in THF than pentane. In general the Gibbs free energy values found in benzene are intermediate between those in pentane and THF, with the exception of the hydrides 5 and 11, where the Gibbs free energies are much closer to the values determined in THF.

Although the large energy difference between the C<sub>6</sub>F<sub>5</sub>H and C<sub>6</sub>F<sub>6</sub> adducts, in comparison with the tetranuclear adducts, prevents the determination of equilibrium constants by NMR spectroscopy, comparison with previous DFT calculations on the dinuclear C<sub>6</sub>F<sub>5</sub>H and C<sub>6</sub>F<sub>6</sub> model complexes [(PMe<sub>3</sub>)<sub>2</sub>Ni]<sub>2</sub>( $\mu$ - $\eta$ <sup>2</sup>: $\eta$ <sup>2</sup>-C<sub>6</sub>F<sub>5</sub>H) and [(PMe<sub>3</sub>)<sub>2</sub>Ni]<sub>2</sub>-( $\mu$ - $\eta$ <sup>2</sup>: $\eta$ <sup>2</sup>-C<sub>6</sub>F<sub>6</sub>) provides some insight. The reactions of **3**<sup>Me</sup>, **6**<sup>Me</sup>, and **9**<sup>Me</sup> with C<sub>6</sub>F<sub>5</sub>H to provide [(PMe<sub>3</sub>)<sub>2</sub>Ni]<sub>2</sub>( $\mu$ - $\eta$ <sup>2</sup>: $\eta$ <sup>2</sup>-C<sub>6</sub>F<sub>5</sub>H) and 1 equiv of the appropriate tetrafluorobenzene are predicted to have Gibbs free energy changes of -4.0 to -6.6 kcal mol<sup>-1</sup> The analogous reactions with C<sub>6</sub>F<sub>6</sub> in

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<sup>(33)</sup> Werkema, E. L.; Andersen, R. A. J. Am. Chem. Soc. 2008, 130, 7153–7165. Maron, L.; Werkema, E. L.; Perrin, L.; Eisenstein, O.; Andersen, R. A. J. Am. Chem. Soc. 2005, 127, 279–292. Fout, A. R.; Scott, J.; Miller, D. L.; Bailey, B. C.; Pink, M.; Mindiola, D. J. Organometallics 2009, 28, 331–347. Reade, S. P.; Mahon, M. F.; Whittlesey, M. K. J. Am. Chem. Soc. 2009, 131, 1847–1861. Hughes, R. P.; Laritchev, R. B.; Williamson, A.; Incarvito, C. D.; Zakharov, L. N.; Rheingold, A. L. Organometallics 2002, 21, 4873–4885. Edelbach, B. L.; Kraft, B. M.; Jones, W. D. J. Am. Chem. Soc. 1999, 121, 10327–10331. Kraft, B. M.; Lachicotte, R. J.; Jones, W. D. Organometallics 2002, 21, 727–731. Zheng, T.; Sun, H.; Chen, Y.; Li, X.; Durr, S.; Radius, U.; Harms, K. Organometallics 2009, 28, 5771–5776.

lieu of  $C_6F_5H$  are predicted to have Gibbs free energy changes in the range of -9.5 to -12.1 kcal mol<sup>-1</sup>. The adducts of the more electron-deficient arenes are strongly favored; however, irrespective of degree of fluorination, observable equilibria exist between dinuclear adducts and mononuclear complexes.

# Conclusions

We have previously reported the importance of equilibria between C-H activation, mononuclear adducts, and unexpected dinuclear adducts in the chemistry of the  $Ni(PEt_3)_2$ moiety with pentafluorobenzene. The tetrafluoroarene adducts studied here are considerably more difficult synthetic targets and required the use of the highly reactive isobutene adduct (PEt<sub>3</sub>)<sub>2</sub>Ni( $\eta^2$ -H<sub>2</sub>C=CMe<sub>2</sub>) (2) for their synthesis. All three isomers of tetrafluorobenzene formed dinuclear adducts that were in equilibrium with mononuclear adducts in the presence of added tetrafluoroarene. Only 1.2.4.5- and 1,2,3,5-C<sub>6</sub>F<sub>4</sub>H<sub>2</sub> had C–H activation products that were observable by <sup>19</sup>F NMR spectroscopy. Calculations suggest that the C-H activation product of 1,2,3,4-C<sub>6</sub>F<sub>4</sub>H<sub>2</sub> should be kinetically accessible at room temperature, though it proved too thermodynamically unfavorable to be observed by NMR spectroscopy. For the majority of these adducts, the spectroscopic data obtained positively identified which isomer is favored in solution for both the dinuclear and mononuclear adducts. DFT calculations provided supporting evidence for the predicted lowest energy isomers and also provided reasonable predictions of <sup>19</sup>F NMR shifts. A full summary of predicted and experimental <sup>19</sup>F NMR chemical shifts is provided in Table 1.

For the adducts, the lowest energy dinuclear complexes 3, 6, and 9 were found to always have one Ni bound to the same position as the lowest energy isomer of the mononuclear adduct of the same arene. The preferred isomers of the mononuclear complexes are not all the same as those observed for other metal complexes, which indicates that perhaps different selectivity may be possible in these systems by the appropriate choice of metal and ligand fragment.<sup>29</sup> Indeed, we have already observed that the Ni(PEt<sub>3</sub>)<sub>2</sub> fragment activates pentafluorobenzene at the o-F. The observation of dinuclear adducts as precursors to C-F activation is unique for these  $Ni(PEt_3)_2$  moieties; however, it is still unclear if C-F bond activation from the dinuclear adducts rather than mononuclear adducts is responsible for the unusual selectivity observed in the C-F activation of pentafluorobenzene with the Ni(PEt<sub>3</sub>)<sub>2</sub> moiety. It is notable that 1,2,3,5-tetrafluorobenzene undergoes the most rapid C-F activation in these systems and that that its dinuclear complex 9 also exhibits unexpectedly rapid fluxionality in comparison to the other known dinuclear complexes. Further studies are underway to better understand the mechanism of the subsequent C-F activation step in these species.

#### **Experimental Section**

General Procedures. Unless otherwise stated, all manipulations were performed under an inert atmosphere of nitrogen using either standard Schlenk techniques or an Innovative Technology glovebox. Dry, oxygen-free solvents were employed throughout. Anhydrous pentane was purchased from Aldrich, sparged with dinitrogen, and passed through activated alumina under a positive pressure of nitrogen gas and further deoxygenated using Ridox catalyst columns.<sup>34</sup> Deuterated benzene was dried by heating at reflux with sodium/potassium alloy in a sealed vessel under partial pressure and then trap-to-trap distilled and freezepump-thaw degassed three times. Deuterated toluene was purified in an analogous manner by heating at reflux over Na. NMR spectra were recorded on a Bruker AMX (300 MHz) or Bruker AMX (500 MHz) spectrometer. All chemical shifts are reported in ppm, and all coupling constants are in Hz. For  $^{19}F{}^{1}H$  NMR spectra, CFCl<sub>3</sub> in CDCl<sub>3</sub> was used as the external reference at  $\delta$  0.00. It should be noted that <sup>19</sup>F NMR shifts can be very sensitive to the concentration of the solute, solvent choice, and temperature; in multiple spectra under different conditions it is not unusual to see shifts vary as much as 1 ppm for a given species. <sup>1</sup>H NMR spectra were referenced to residual protons (C<sub>6</sub>D<sub>5</sub>H,  $\delta$  7.15; C<sub>7</sub>D<sub>7</sub>H,  $\delta$  2.09) with respect to tetramethylsilane at  $\delta 0.00$ . <sup>31</sup>P{<sup>1</sup>H} NMR spectra were referenced to external 85% H<sub>3</sub>PO<sub>4</sub> at  $\delta$  0.0. <sup>13</sup>C{<sup>1</sup>H} spectra were referenced relative to solvent resonances (C<sub>6</sub>D<sub>6</sub>,  $\delta$  128.0; C<sub>7</sub>D<sub>8</sub>,  $\delta$  20.4). Elemental analyses were performed by the Centre for Catalysis and Materials Research (CCMR), Windsor, Ontario, Canada. The compounds (PEt<sub>3</sub>)<sub>2</sub>NiCl<sub>2</sub>,<sup>35</sup> the anthracene adduct (PEt<sub>3</sub>)<sub>2</sub>Ni- $(\eta^2$ -C<sub>14</sub>H<sub>10</sub>),<sup>35</sup> Ni(PEt<sub>3</sub>)<sub>4</sub>,<sup>27</sup> (PEt<sub>3</sub>)<sub>2</sub>NiF(2,3,5-C<sub>6</sub>F<sub>3</sub>H<sub>2</sub>),<sup>19</sup> and 1,2,4, 5-C<sub>6</sub>F<sub>4</sub>HD<sup>19</sup> were prepared by literature procedures. The three isomers of tetrafluorobenzene, isobutene, and MeMgBr were purchased from Aldrich. The tetrafluorobenzenes were degassed and dried over molecular sieves prior to use.

Synthesis and Characterization of (PEt<sub>3</sub>)<sub>2</sub>NiMe<sub>2</sub>(1). The synthesis of (PEt<sub>3</sub>)<sub>2</sub>NiMe<sub>2</sub> has been described before, but both the stability of the compound and the room-temperature NMR spectra vary from those previously reported; therefore, the procedure used here, which reproducibly provided an isolable crystalline solid with sharp resonances in both the  $^{31}P\{^{1}H\}$  and  $^{1}H$  NMR spectra, is described. Solid (PEt<sub>3</sub>)<sub>2</sub>NiCl<sub>2</sub> (4.0 g, 0.01105 mol) was added to a roundbottom flask equipped with a stir bar, and 250 mL of Et<sub>2</sub>O was added. The round-bottom flask was cooled to -78 °C, and 3.0 M MeMgBr in ether (7.3 mL, 2 equiv) was added dropwise. The solution was warmed to 10 °C and then evaporated to dryness. The remaining solid was extracted into pentane and the extract filtered through Celite. Crystalline (PEt<sub>3</sub>)<sub>2</sub>NiMe<sub>2</sub> was obtained by concentrating the solution and cooling to -40 °C. The resultant large yellow crystals were isolated by filtration and dried under vacuum. A second crop was obtained by concentrating the solution (total yield 2.644 g, 75%). Crystals of suitable quality for X-ray diffraction were obtained directly from the recrystallized product. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz, 298 K):  $\delta - 0.70$  (t, <sup>3</sup>*J*<sub>PH</sub> = 8.5 Hz, 6H, NiC*H*<sub>3</sub>), 1.04 (m, 18H, PCH<sub>2</sub>CH<sub>3</sub>), 1.52 (m, 12H, PCH<sub>2</sub>CH<sub>3</sub>), <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 121.5 MHz, 298 K): δ 23.0 (s). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 75.4 MHz, 298 K):  $\delta - 10.8$  (t,  ${}^{2}J_{PC} = 23.5$  Hz, NiCH<sub>3</sub>), 8.9 (s, PCH<sub>2</sub>CH<sub>3</sub>), 14.8 (vt,  $J_{PC} = 10.4$  Hz, PCH<sub>2</sub>), Anal. Calcd for  $C_{14}H_{36}NiP_2$  (mol wt 325.08): C, 51.73; H, 11.16. Found: C, 51.55; H, 10.94.

Synthesis and Characterization of  $(PEt_3)_2Ni(\eta^2-H_2C=CMe_2)$ (2). A solution of  $(PEt_3)_2NiMe_2$  (1.0 g, 3.08 mmol) in 10 mL of pentane was transferred into a reaction vessel equipped with a Teflon valve. The solution was degassed and then stirred vigorously under an atmosphere of isobutene to generate a saturated solution. The vessel was then sealed and heated in a 60 °C oil bath for 3 h. The vessel was cooled to room temperature and then briefly opened to an N<sub>2</sub> atmosphere to remove the majority of ethane and isobutene. <sup>1</sup>H, <sup>31</sup>P{<sup>1</sup>H}, and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy on the crude reaction mixture all indicated that the reaction had gone to completion with nearly quantitative conversion. Attempts to isolate the product by removing the solvent under vacuum all resulted in decomposition into Ni(0) complexes of PEt<sub>3</sub>. Characterization by <sup>1</sup>H, <sup>31</sup>P{<sup>1</sup>H}, and <sup>13</sup>C{<sup>1</sup>H}

<sup>(34)</sup> Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.

<sup>(35)</sup> Stanger, A.; Vollhardt, K. P. C. Organometallics 1992, 11, 317–320.

NMR was done under similar conditions in  $C_6D_6$  in an NMR tube equipped with a Teflon valve.

An alternate synthesis was performed in neat isobutene at room temperature. A solution of  $(PEt_3)_2NiMe_2$  (1.0 g, 3.08 mmol) was dissolved in 10 mL of isobutene. After 2 weeks the solution was slowly evaporated at  $-35 \,^{\circ}$ C to provide a thermally sensitive yellow oil that was identified as  $(PEt_3)_2Ni(\eta^2-H_2C=CMe_2)$  by <sup>1</sup>H, <sup>31</sup>P{<sup>1</sup>H}, and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz, 298 K): 0.96 (overlapping m, 18H total, PCH<sub>2</sub>CH<sub>3</sub>), 1.43 (overlapping m, 12H total, PCH<sub>2</sub>CH<sub>3</sub>), 1.67 (d, 6H,  $J = 7.3 \,$ Hz, C=CMe<sub>2</sub>), 1.78 (m, 2H, C=CH<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 121.5 MHz, 298 K):  $\delta$  16.0 and 17.2 (AB doublets, <sup>2</sup>J<sub>PP</sub> = 53 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 75.4 MHz, 298 K):  $\delta$  8.77 (s, PCH<sub>2</sub>CH<sub>3</sub>), 9.02 (s, PCH<sub>2</sub>CH<sub>3</sub>), 19.0 (dd, J<sub>PC</sub> = 16.4, 4.0 Hz, PCH<sub>2</sub>), 19.5 (dd, J<sub>PC</sub> = 15.0, 3.0 Hz, PCH<sub>2</sub>), 27.7 (d, J<sub>PC</sub>=4.0 Hz, C=CMe<sub>2</sub>), 46.7 (dd, J<sub>PC</sub> = 18.0, 4.0 Hz, C=CH<sub>2</sub>), 56.0 (dd, J<sub>PC</sub> = 24, 4 Hz, Me<sub>2</sub>C=C).

Synthesis of  $[(PEt_3)_2Ni]_2(\mu-\eta^2:\eta^2-1,2,4,5-C_6F_4H_2)$  (3). To a pentane solution of 2 generated from 1 (1.0 g, 3.08 mmol) was added 1,2,4,5-tetrafluorobenzene (1.0 g, 6.66 mmol, 2.2 equiv). The solution was heated to the boiling point of pentane with rapid stirring for 1.5 h; the progress of the reaction was monitored by <sup>31</sup>P{<sup>1</sup>H} NMR using aliquots of the solution. The solution was then dried, and the remaining solid was recrystallized from pentane, which provided the product as yellow crystals (0.30 g, 13%) of sufficient quality for structure determination by X-ray diffraction. <sup>1</sup>H NMR (toluene- $d_8$ , 300 MHz, 298 K):  $\delta$  1.05 (m, 36H, PCH<sub>2</sub>CH<sub>3</sub>), 1.64 (br, 24H, PC-H<sub>2</sub>CH<sub>3</sub>), 3.02 (m, 2H, C<sub>6</sub>F<sub>4</sub>H<sub>2</sub>). <sup>19</sup>F NMR (C<sub>6</sub>D<sub>6</sub>, 282.4 MHz, 298 K): δ -136.0 (m, 2F, F<sub>1</sub> and F<sub>2</sub>), -146.7 (br m, 2F, F<sub>4</sub> and F<sub>5</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (toluene- $d_8$ , 121.5 MHz, 298 K):  $\delta$  19.0 (br,  $W_{1/2} = 325$  Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (toluene- $d_8$ , 121.5 MHz, 233 K): δ 15.0 (m, <sup>2</sup>J<sub>PP</sub> = 42 Hz, d of apparent t, <sup>2</sup>J<sub>PP</sub> = 42 Hz, J<sub>PF</sub> = 27 Hz, 2P), 22.8 (m, <sup>2</sup>J<sub>PP</sub> = 42 Hz, 2P). Anal. Calcd for C<sub>30</sub>H<sub>62</sub>-F<sub>4</sub>Ni<sub>2</sub>P<sub>4</sub> (mol wt 740.09): C, 48.69; H, 8.44. Found: C, 48.90; H, 8.73.

**Characterization of** (**PEt**<sub>3</sub>)<sub>2</sub>**Ni**( $\eta^2$ -1,2,4,5-C<sub>6</sub>F<sub>4</sub>**H**<sub>2</sub>) (4). Complex 4 was prepared in equilibrium amounts by the addition of 1,2,4,5-C<sub>6</sub>F<sub>4</sub>H<sub>2</sub> to 3 in toluene-*d*<sub>8</sub> and characterized by variable-temperature <sup>1</sup>H, <sup>31</sup>P{<sup>1</sup>H}, and <sup>19</sup>F NMR spectroscopy. <sup>1</sup>H NMR (toluene-*d*<sub>8</sub>, 300 MHz, 298 K, select resonances):  $\delta$  4.87 (virtual pentet, *J* = 9.0 Hz, 2H, C<sub>6</sub>F<sub>4</sub>H<sub>2</sub>). <sup>19</sup>F{<sup>1</sup>H} (toluene-*d*<sub>8</sub>, 282.4 MHz, 298 K):  $\delta$  –143.4 (m, 4F). <sup>31</sup>P{<sup>1</sup>H} NMR (toluene-*d*<sub>8</sub>, 300 MHz, 183 K, select resonances):  $\delta$  3.9 and 5.8 (br, C<sub>6</sub>F<sub>4</sub>H<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (toluene-*d*<sub>8</sub>, 121.5 MHz, 298 K):  $\delta$  –12.5 MHz, 263 K):  $\delta$  17.5 (pentet, *J*<sub>PF</sub> = 12.5 Hz).

**Characterization of (PEt<sub>3</sub>)<sub>2</sub>NiH-2,3,5,6-F<sub>4</sub>C<sub>6</sub>H (5).** Complex **5** was prepared in equilibrium amounts by the addition of 1,2, 4,5-C<sub>6</sub>F<sub>4</sub>H<sub>2</sub> to **4** in toluene- $d_8$  and characterized by variable-temperature <sup>1</sup>H, <sup>31</sup>P, <sup>31</sup>P{<sup>1</sup>H}, and <sup>19</sup>F NMR spectroscopy. <sup>1</sup>H NMR (toluene- $d_8$ , 300 MHz, 233 K, selected resonances):  $\delta$ -14.30 (ttt, <sup>2</sup> $J_{PH}$  = 67.7 Hz, <sup>4</sup> $J_{FH}$  = 9.5 Hz, <sup>5</sup> $J_{FH}$  = 4.2 Hz, Ni-*H*), 6.48 (m, Ar-*H*). <sup>19</sup>F{<sup>1</sup>H} NMR (toluene- $d_8$ , 282.4 MHz, 298 K, complex **2** only):  $\delta$  -117.8 (AA'MM' multiplet, *o*-F), -143.7 (AA'MM' multiplet, *m*-F). <sup>31</sup>P{<sup>1</sup>H</sup> NMR (toluene- $d_8$ , 121.5 MHz, 233 K):  $\delta$  23.5 (s). <sup>31</sup>P NMR (C<sub>7</sub>D<sub>8</sub>, 121.5 MHz, 233 K):  $\delta$  23.5 (br d, <sup>2</sup> $J_{PH}$  = 68 Hz).

Synthesis of  $[(PEt_3)_2Ni]_2(\mu - \eta^2 \cdot \eta^2 - 1, 2, 3, 4 - C_6F_4H_2)$  (6). To a pentane solution of 2 generated from 1 (1.0 g, 3.08 mmol) was added 1,2,3,4-tetrafluorobenzene (1.0 g, 6.6 mmol, 2.1 equiv). The solution was heated to the boiling point of pentane with rapid stirring for 1 h; the progress of the reaction was monitored by <sup>31</sup>P{<sup>1</sup>H} NMR using aliquots of the solution. The solution was then dried, and the remaining solid was recrystallized from hexamethyldisiloxane, which provided the product as yellow crystals (0.23 g, 10%) of sufficient quality for structure determination by X-ray diffraction. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz, 298 K):  $\delta$  1.01 (m, 36H, PCH<sub>2</sub>CH<sub>3</sub>), 1.60 (br, 24H, PCH<sub>2</sub>CH<sub>3</sub>), 3.62 (m, 1H, C<sub>6</sub>F<sub>4</sub>H<sub>2</sub>). <sup>19</sup>F NMR (C<sub>6</sub>D<sub>6</sub>, 282.4 MHz, 298 K):

 $\delta$  – 135.8 (m, 2F, F<sub>1</sub> and F<sub>4</sub>), –171.3 (m, 2F, F<sub>2</sub> and F<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 121.5 MHz, 298 K):  $\delta$  19.2 (br,  $W_{1/2}$  = 140 Hz). <sup>19</sup>F NMR (pentane, 282.4 MHz, 163 K):  $\delta$  –132.8 (m, 1F, F<sub>1</sub> or F<sub>4</sub>), –141.5 (m, 2F, F<sub>1</sub> or F<sub>4</sub>)  $\delta$  –158.2 (m, 1F, F<sub>3</sub>), –189.2 (m, 1F, F<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (pentane, 121.5 MHz, 163 K):  $\delta$  12.6, 16.3, 21.3, and 25.3 (m). Anal. Calcd for C<sub>30</sub>H<sub>62</sub>F<sub>4</sub>Ni<sub>2</sub>P<sub>4</sub> (mol wt 740.09): C, 48.69; H, 8.44. Found: C, 48.91; H, 8.69.

**Characterization of (PEt<sub>3</sub>)<sub>2</sub>Ni(\eta^2-1,2,3,4-C<sub>6</sub>F<sub>4</sub>H<sub>2</sub>) (7).** Complex 7 was prepared in equilibrium amounts by the addition of 1,2,3,4-C<sub>6</sub>F<sub>4</sub>H<sub>2</sub> to **6** in toluene-*d*<sub>8</sub> and characterized by variable-temperature <sup>1</sup>H, <sup>31</sup>P{<sup>1</sup>H}, and <sup>19</sup>F NMR spectroscopy. <sup>1</sup>H NMR (*d*<sub>8</sub>-toluene, 300 MHz, 298 K, aromatic resonance):  $\delta$  5.27 (br, 2H, *W*<sub>1/2</sub> = 120 Hz, C<sub>6</sub>F<sub>4</sub>H<sub>2</sub>, peak associated with free 1,2,3, 4-C<sub>6</sub>F<sub>4</sub>H<sub>2</sub> is also broad). <sup>19</sup>F (toluene-*d*<sub>8</sub>, 282.4 MHz, 298 K):  $\delta$  -128.9 (br apparent d, 2F, *W*<sub>1/2</sub> = 60 Hz), -173.2 (br, 2F, *W*<sub>1/2</sub> = 70 Hz), <sup>31</sup>P{<sup>1</sup>H} NMR (toluene-*d*<sub>8</sub>, 121.5 MHz, 298 K):  $\delta$  16.3 (br, *W*<sub>1/2</sub> = 70 Hz). <sup>1</sup>H NMR (toluene-*d*<sub>8</sub>, 300 MHz, 253 K, aromatic resonance):  $\delta$  5.27 (apparent t, *J* = 6.5 Hz, 2H). <sup>19</sup>F NMR (toluene-*d*<sub>8</sub>, 282.4 MHz, 213 K):  $\delta$  -127.7 (br, second-order multiplet), -174.5 (sharp second-order multiplet, 2F). <sup>31</sup>P{<sup>1</sup>H} NMR (toluene-*d*<sub>8</sub>, 121.5 MHz, 213 K):  $\delta$  16.5 (sharp t, *J*<sub>FP</sub> = 23.3 Hz).

Characterization of  $[(PEt_3)_2Ni]_2(\mu - \eta^2: \eta^2 - 1, 2, 3, 5 - C_6F_4H_2)$  (9). To a solution of 2 in hexamethyldisiloxane generated from 1(1.0 g, 3.08 mmol) was added 1,2,3,5-tetrafluorobenzene (0.5 g, 3.3 mmol, 1.1 equiv). The mixture was placed under reduced pressure and rapidly stirred. The vacuum was stopped occasionally to allow the solution to remain near room temperature. This procedure was continued for 30 min. An aliquot was analyzed by NMR spectroscopy, and 9 was found to be the major fluorine-containing product, but it could not be isolated by recrystallization. <sup>1</sup>H NMR (toluene-d<sub>8</sub>, 300 MHz, 293 K, arene resonances):  $\delta 3.8$  (br, 2H,  $W_{1/2} = 70$  Hz C<sub>6</sub>F<sub>4</sub>H<sub>2</sub>). <sup>19</sup>F{<sup>1</sup>H} NMR (toluene-d<sub>8</sub>, 282.4 MHz, 293 K): δ -113.7 (m, F<sub>5</sub>), -137 (br,  $W_{1/2}$ =1500 Hz, F<sub>3</sub>), -162.2 (m, F<sub>2</sub>), -176 (br,  $W_{1/2}$ =1500 Hz, F<sub>1</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (toluene- $d_8$ , 121.5 MHz, 298 K):  $\delta$  19.0 (br,  $W_{1/2} = 130$  Hz). <sup>1</sup>H NMR (toluene- $d_8$ , 300 MHz, 233 K, arene resonances):  $\delta$  2.75 (dm, J = 23 Hz, 1H, C<sub>6</sub>F<sub>4</sub>H<sub>2</sub>), 4.81 (dm, J =11.5 Hz, 1H,  $C_6F_4H_2$ ). <sup>19</sup>F{<sup>1</sup>H} NMR (pentane, 282.4 MHz, 193 K):  $\delta -113.7$  (br m, 1F, F<sub>5</sub>), -137.1 (br m, apparent 36 Hz quartet, F<sub>3</sub>), -162.2 (br m, F<sub>2</sub>), -175.7 (br m, apparent 36 Hz quartet, F<sub>1</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (pentane, 121.5 MHz, 193 K):  $\delta$  13.4 (br dddd, J = 8,26,38 and 82 Hz), 15.6 (br m), 21.1 (br ddd J = 5, 36, and 42 Hz), 25.8 (br ddd, *J* = 8, 29, and 40 Hz).

**Characterization of (PEt<sub>3</sub>)<sub>2</sub>Ni(\eta^2-1,2,3,5-C<sub>6</sub>F<sub>4</sub>H<sub>2</sub>) (10).** Complex 10 was prepared in equilibrium amounts by the addition of 1,2,3,5-C<sub>6</sub>F<sub>4</sub>H<sub>2</sub> to a solution of 9 in toluene- $d_8$  and characterized by variable-temperature <sup>1</sup>H, <sup>31</sup>P{<sup>1</sup>H}, and <sup>19</sup>F NMR spectroscopy. <sup>1</sup>H NMR ( $d_8$ -toluene, 300 MHz, 253 K, aromatic resonance):  $\delta$  4.90 (m, 2H). <sup>19</sup>F{<sup>1</sup>H} NMR ( $d_8$ -toluene, 282.4 MHz, 298 K):  $\delta$  -106.0 (br m, 1F, F<sub>5</sub>), -149.9 (br m, 2F, F<sub>1</sub> and F<sub>3</sub>), -161.5 (br m, 1F, F<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (toluene- $d_8$ , 121.5 MHz, 298 K):  $\delta$  15 (br,  $W_{1/2}$  = 600 Hz). <sup>1</sup>H NMR ( $d_8$ -toluene, 300 MHz, 185 K, aromatic resonance):  $\delta$  4.9 (br,  $W_{1/2}$  = 100 Hz, 2H). <sup>19</sup>F NMR (toluene- $d_8$ , 282.4 MHz, 173 K):  $\delta$  -106.0 (br m, 1F, F<sub>5</sub>), -143 (br m, 1F, F<sub>1</sub> or F<sub>3</sub>), -146 (br m, 1F, F<sub>1</sub> or F<sub>3</sub>), -161.5 (br m, F<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (toluene- $d_8$ , 121.5 MHz, 213 K):  $\delta$  15.4 and 20.9 (m).

**Characterization of (PEt<sub>3</sub>)<sub>2</sub>NiH-2,3,4,6-F<sub>4</sub>C<sub>6</sub>H (11).** Complex **11** was prepared in equilibrium amounts by the addition of 1,2,3,5-C<sub>6</sub>F<sub>4</sub>H<sub>2</sub> to a solution of **9** in toluene-*d*<sub>8</sub> and characterized by variable-temperature <sup>1</sup>H, <sup>31</sup>P, <sup>31</sup>P{<sup>1</sup>H}, and <sup>19</sup>F NMR spectroscopy. <sup>1</sup>H NMR (hydride region) (toluene-*d*<sub>8</sub>, 300 MHz, 223 K):  $\delta$  -14.56 (t, <sup>2</sup>*J*<sub>PH</sub> = 69 Hz, Ni-*H*). <sup>19</sup>F{<sup>1</sup>H} NMR (toluene-*d*<sub>8</sub>, 282.4 MHz, 293 K):  $\delta$  -90.5 (dd, *J*<sub>FF</sub> = 13.7, 2.8 Hz, F<sub>6</sub>), -110.0 (dt, *J*<sub>FF</sub> = 33.3 Hz, *J*<sub>PF</sub> = 2.8 Hz, F<sub>2</sub>), -144.6 (dd, *J*<sub>FF</sub> = 19.0, 2.8 Hz, F<sub>4</sub>), -170.2 (ddd, *J*<sub>FF</sub> = 33.3, 19.0, and 13.7 Hz, F<sub>3</sub>). <sup>19</sup>F NMR (toluene-*d*<sub>8</sub>, 282.4 MHz, 293 K):  $\delta$  -90.5 (dddd, *J*<sub>FF</sub> = 13.7, 2.8 Hz, *J*<sub>FH</sub> = 7.8, 4.5 Hz, F<sub>6</sub>), -110.0 (dddt, *J*<sub>FF</sub> = 33.3 Hz, *J*<sub>FH</sub> = 7.8, 4.5 Hz, F<sub>6</sub>), -110.0 (dddt, *J*<sub>FF</sub> = 33.3 Hz, *J*<sub>FH</sub> = 10.0, 2.5 Hz, *J*<sub>PF</sub> = 2.8 Hz, F<sub>2</sub>), -144.6 (ddd,

 $J_{\rm FF} = 19.0, 2.8 \text{ Hz}, J_{\rm FH} = 10.3 \text{ Hz}, F_4), -170.2 (ddddd, J_{\rm FF} = 33.3, 19.0, and 13.7 \text{ Hz}, J_{\rm FH} = 4.7, 3.5 \text{ Hz}, F_3). {}^{31}P{}^{1}H} \text{ NMR}$  (toluene- $d_8, 121.5 \text{ MHz}, 298 \text{ K}$ ):  $\delta 23.5 \text{ (br)}. {}^{31}P \text{ NMR}$  (toluene- $d_8, 121.5 \text{ MHz}, 223 \text{ K}$ ):  $\delta 23.5 \text{ (br)}. {}^{31}P \text{ Hz}$ ).

Synthesis of the Dinuclear Aryne Complex  $[(PEt_3)_2Ni]_2(\mu-\eta^2)$ :  $\eta^2$ -3,4,6-C<sub>6</sub>F<sub>3</sub>H) (12). To a solution of 2 in pentane generated from 1 (1.0 g, 3.08 mmol) was added 1,2,3,5-tetrafluorobenzene (1.0 g, 6.6 mmol, 2.1 equiv). The mixture was stirred rapidly for 8 h, at which point minimal 2 remained, as ascertained by  ${}^{31}P{}^{1}H$ NMR spectroscopy on an aliquot of the complex, and the solution consisted primarily of 12 and the C-F activation product  $(PEt_3)_2NiF(2,3,5-C_6F_3H_2)$ . The volume of the brown solution was reduced under vacuum, and pure crystalline 12 was obtained by cooling to -40 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz, 298 K):  $\delta$  0.97 (overlapping m, 36H, both PCH<sub>2</sub>CH<sub>3</sub>), 1.64 and 1.54 (overlapping m, 24H, PCH<sub>2</sub>CH<sub>3</sub>), 6.12 (ddd, 1H, J<sub>FH</sub> = 8.5, 2.5, 2.5, Ar-H). <sup>19</sup>F{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 282.4 MHz, 298 K): δ -102.4 (d, 1F,  $J_{FF}$ =49.3), -137.0 (ddm, 1F,  $J_{FF}$ =49.3, 31.1 Hz) -152.6 (dm, 1F,  $J_{FF}$ =31.1 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 121.5 MHz, 298 K):  $\delta$  15.6 and 15.3 (second-order AA'BB' m). Anal. Calcd for C<sub>30</sub>H<sub>61</sub>F<sub>3</sub>Ni<sub>2</sub>P<sub>4</sub> (mol wt 720.24): C, 50.04; H, 8.54. Found: C, 50.11; H, 8.52.

X-ray Crystallography. The X-ray structures were obtained at low temperature, with the crystals covered in Paratone and placed rapidly into the cold N<sub>2</sub> stream of the Kryo-Flex lowtemperature device. The data were collected using SMART<sup>36</sup> software on a Bruker APEX CCD diffractometer with a graphite monochromator and Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). A hemisphere of data was collected using a counting time of 10– 30 s per frame. Details of crystal data, data collection, and structure refinement are given in Table 2. Data reductions were performed using SAINT<sup>37</sup> software, and the data were corrected for absorption using SADABS or TWINABS.<sup>38</sup> The structures were solved by direct methods using SIR97<sup>39</sup> and refined by full-matrix least squares on  $F^2$  with anisotropic displacement parameters for the non-H atoms using SHELXL-97<sup>40</sup> and the WinGX<sup>41</sup> software package, and thermal ellipsoid plots were produced using ORTEP32.<sup>42</sup>

Crystalline 3 was obtained as large blocks, but repeated attempts at crystallization provided nonmerohedral twins. The crystals were monoclinic, but with a second nonmerohedral twin domain associated with a 180° rotation about the reciprocal axis 1, 0, -0.954 axis and the real axis 1, 0, 0, which gave the twin law

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ -1.9 & 0 & -1 \end{bmatrix}$$

A high-quality solution was obtained using the twinned data; however, ultimately an untwinned crystal was obtained that confirmed the proposed model. The data were of sufficient quality to locate and refine the positions of the two hydrogen atoms associated with the tetrafluorobenzene moiety without any restraints. The isotropic thermal parameters for these two hydrogens were also refined.

The solid-state structure of 6 contained two molecules in the asymmetric unit. Both molecules displayed a disorder of the tetrafluoroarene moiety consistent with the fact that there are two orientations by which the 1,2,3,4-tetrafluorobenzene can bind to the pair of nickel moieties in these dinuclear compounds and still provide the same isomer. This disorder is not surprising, considering the similar sizes of hydrogen and fluorine. The molecule containing Ni(1) and Ni(2) displayed only a partial disorder of the 1,2,3,4-tetrafluoroarene moiety, with refined 0.845(4) and 0.155(4) site occupancies of the two possible arrangements. The second molecule displayed equal contributions from both possible arrangements of the tetrafluoroarene ring. The PEt<sub>3</sub> group associated with P(5) also exhibited 2-fold disorder of the Et groups, which was fully modeled, and is likely associated with the disorder of the tetrafluoroarene ring. Further details are provided in the Supporting Information.

Multiple attempts to obtain untwinned crystals of aryne complex **12** failed. Crystals of **12** exhibited an apparent monoclinic unit cell (a=26.77 Å, b=32.45 Å, c=19.93 Å,  $\beta=122.24^{\circ}$ ) with statistics consistent with the space group C 2/c. The solution of the structure in this space group failed and exhibited an unrealistic 2-fold disorder of all atoms. The correct unit cell was determined to be triclinic, with the unit cell data given in Table 2. The correct space group was determined to be PI, with a nonmerohedral twin domain associated with a 180° rotation about the reciprocal axis -1, 1, 1 and the real axis 1, -0.5, -0.5, which gave the twin law

$$\begin{bmatrix} 0 & -0.5 & -0.5 \\ -1 & -0.5 & 0.5 \\ -1.9 & 0.5 & -0.5 \end{bmatrix}$$

The solution was refined successfully with excellent statistics using the data from both twin domains. The structure of **12** featured two molecules in the asymmetric unit and disorder in some of the PEt<sub>3</sub> group orientations and the fluorine atom locations. Further details are provided in the Supporting Information.

**Calculations.** Ab initio DFT calculations were performed using the hybrid functional B3LYP<sup>43</sup> method with the Gaussian 03 package.<sup>44</sup> The basis functions used were the TZVP set, provided in the Gaussian 03 program. Calculated <sup>19</sup>F NMR shielding tensors were predicted using the gauge-independent atomic orbital method that is the default of the Gaussian 03 program. The isotropic shielding values were converted to chemical shifts using a linear fit to the experimental chemical shifts, given in parentheses, for a set of molecules: CFCl<sub>3</sub> ( $\delta$  0.0), hexafluorobenzene ( $\delta$  –164.9), pentafluorobenzene ( $\delta$  –162.3, –154.0, –139.0), SiF<sub>4</sub> ( $\delta$  –163.3), CF<sub>4</sub> ( $\delta$  –62.3), CFH<sub>3</sub> ( $\delta$  –271.9), and

<sup>(36)</sup> SMART, Molecular analysis research tool; Bruker AXS Inc., Madison, WI,:2001.

<sup>(37)</sup> SAINTPlus, Data reduction and correction program; Bruker AXS Inc., Madison, WI, 2001.

<sup>(38)</sup> SADABS, An empirical absorption correction program; Bruker AXS Inc., Madison, WI, 2001.

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fluorobenzene ( $\delta$  -113.5). A plot of the calculated isotropic shielding values versus experimental shift was fit by a linear model with a slope of -1.11 and an intercept of -158.7; full details are provided elsewhere.<sup>17</sup>

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Supporting Information Available: CIF files giving crystallographic information for 1, 3, 6, and 5 and text, figures, and tables giving select experimental NMR spectra and optimized coordinates and energies for DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.