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Nickel(0)-Catalyzed Isomerization of an Aryne Complex: Formation of a Dinuclear Ni(I) Complex via C−H Rather than C−F Bond Activation

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There has been great interest lately in the ability of transition metal complexes to activate C−H and C−F bonds, both stoichiometrically and catalytically.[1] These bonds are typically inert, and the products of activation provide synthetic avenues inaccessible by conventional procedures. It has been shown that precursors to nickel bisphosphine fragments, such as (COD)Ni(PEt_3)$_2$, are highly selective in the activation of C−F over C−H bonds in their reaction with a variety of fluorinated aryl and azaheterocycles.[2,3] Calculational studies have demonstrated that the chemoselectivity is due to the fact that the activation of an aromatic C−F bond by Ni(PEt_3)$_2$ is thermodynamically favorable, whereas C−H bond activation is not.[4] A few examples of C−H bond activation by Ni are known, where additional factors render the products thermodynamically viable,[5] but never in the presence of C−F bonds. The mechanistic details of C−F bond activation are uncertain; however, η^2-bound arene intermediates have been isolated and characterized,[3] and calculations suggest a concerted C−F bond cleavage step.[4] The selectivity of Ni(0) complexes toward C−F bonds engenders synthetic utility; however, if Ni complexes could be tuned to yield C−H bond activation products, the resultant methodology would be economically attractive compared to the current alternatives which require more expensive 2nd and 3rd row metals.

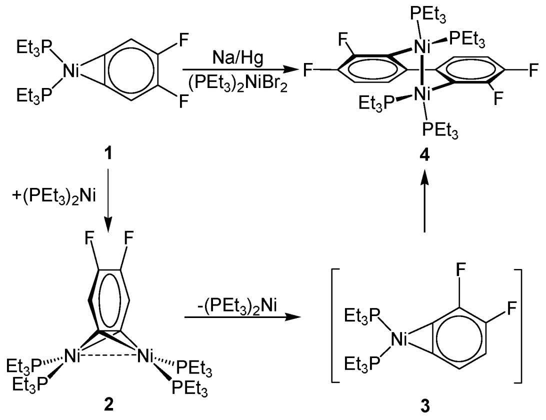
The reaction of the known aryne complex (PEt_3)$_2$Ni(η^2-C_6H_2-4,5-F_2)[6] (**1**) with a catalytic amount of $Br_2Ni(PEt_3)_2$ over Na/Hg was found to cleanly produce the dark brown dinuclear Ni(I) complex **4**, as shown in Scheme 1. Crystals of **4** were obtained in 60% isolated yield by crystallization from pentane at −40 °C.

The reduction of $Br_2Ni(PEt)_3$ presumably produces transient Ni(PEt_3)$_2$, which appears to catalyze this reaction; no reaction is observed in the absence of a Ni(PEt_3)$_2$ precursor, and other sources of Ni(0), such as Ni(PEt_3)$_4$, do not result in the formation of **4**. At first glance, **4** appears to result from the coupling of two aryne moieties of complex **1**; however, due to the ortho disposed hydrogen substituents, it is *not* the product anticipated from the coupling of **2**, but rather of the putative intermediate (PEt_3)$_2$Ni(η^2-C_6H_2-5,6-F_2) (**3**), an isomer of **1** which could be formed by aromatic C−H bond activation followed by the formation of an alternate aromatic C−H bond.

The solid-state molecular structure of **4** was determined by X-ray crystallography, and a simplified ORTEP depiction is shown in Figure 1. The molecule has approximate C_2 symmetry, but no crystallographic symmetry. The two Ni(PEt_3)$_2$ fragments are asymmetrically bridged by a ($C_6F_2H_2$)$_2$ biarylyl fragment, with a Ni−Ni bond distance of 2.3710(5) Å. The Ni(1)−C(1) and Ni(2)−C(8) distances of 1.965(3) and 1.952(3) Å are shorter than the Ni(1)−C(8) and Ni(2)−C(1) contacts of 2.317(3) and 2.308(3) Å.

Solution NMR spectroscopy demonstrates that the approximate C_2 symmetry observed for the solid-state structure of **4** is maintained in solution at low temperature. In the 213 K $^{31}P\{^1H\}$ NMR spectrum, two environments are observed, a virtual triplet at δ −5.2 (J_{PP} = 10 Hz) and a complex multiplet at δ 9.0, which can be modeled as a virtual triplet of doublets of doublets (J_{PP} = 10 Hz, J_{PF} = 6.0 Hz, J_{PF} = 11.4 Hz). The observation of virtual coupling indicates that a Ni−Ni bond must be present. Moreover, the observed coupling constants between the hydrogen and fluorine substituents on the aromatic ring verify that the connectivity observed in the solid-state structure is correct, and no other isomers are observed.

Scheme 1



The conversion of aryne complex **1** to the dinuclear nickel complex **4** occurs over the course of 24 h with $Br_2Ni(PEt_3)_2$ and Na/Hg, and a long-lived intermediate is observed by NMR spectroscopy. The intermediate is symmetric, with a single aromatic hydrogen environment at δ 7.33 (vt), a single fluorine environment at δ −74.03 (m), and a single phosphorus environment at δ 14.8 in the ^1H, ^{19}F, and $^{31}P\{^1H\}$ NMR spectra, respectively. This intermediate could be isolated by the addition of 1 equiv of $Br_2Ni(PEt_3)_2$ to a pentane solution of **1** stirred over Na/Hg over the course of 1 h. The solution was cooled to −40 °C, and complex **2** was isolated as a crystalline orange solid. The solid-state structure of **2** was determined by X-ray crystallography and is shown in Figure 2.

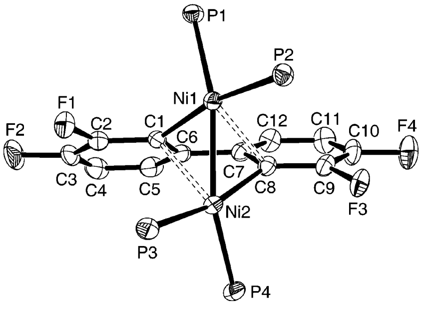


Figure 1. Solid-state molecular structure of **4** as determined by X-ray crystallography. Ethyl substituents on the phosphine ligands and hydrogen atoms are omitted for clarity.

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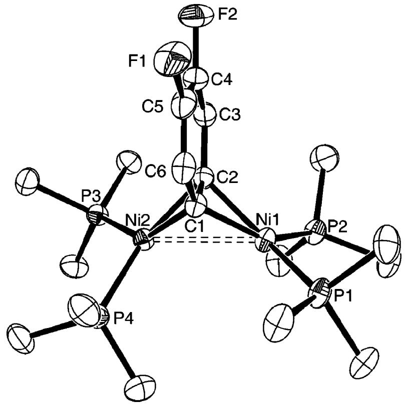
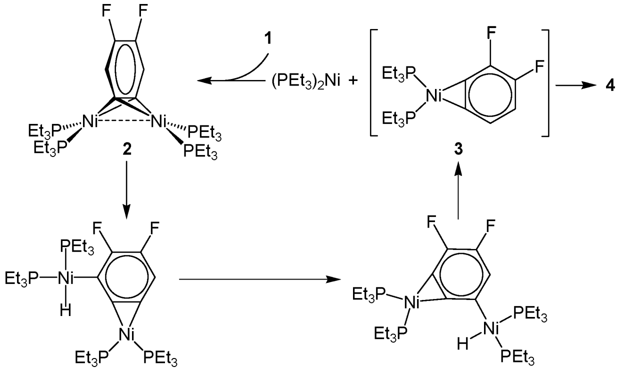


Figure 2. Solid-state molecular structure of **2** as determined by X-ray crystallography. The methyl group of the ethyl substituents on the phosphine ligands and hydrogen atoms are omitted for clarity.

Scheme 2



Related μ-η^2: η^2-alkyne complexes are known;[7] however, this bonding mode is unprecedented for aryne complexes, whose orthogonal π-orbitals are vastly different in energy; all related aryne complexes are best described as 1,2-disubstituted phenylenes and bind the aryne in a μ-η^1:η^1-manner.[8] The Ni(1)−Ni(2) distance of 2.7242(3) Å observed for **2** is much longer than the Ni−Ni bond length in **4** of 2.3710(5) Å. The presence or absence of a Ni−Ni bonding interaction in **2** is not readily ascertained from the structural data alone. The C−C bond lengths of the aryne fragment indicate a slight disruption of aromaticity. The C(3)−C(4) and C(5)−C(6) bond lengths of 1.3529(35) and 1.3560(36) Å are slightly shorter than typical aromatic C−C bonds, whereas the C(1)−C(6) and C(2)−C(3) distances of 1.4203(34) and 1.4272(32) Å are slightly longer. These structural features verify that the coordination of Ni(PEt_3)$_2$ to complex **1** does require back-donation into both π-systems of the aryne, and that **2** can be viewed as an analogue of the arene π-adducts that have been observed as intermediates for C−F bond cleavage.[2,3] However, in **2**, the distance between the C−F bonds and the Ni(PEt_3)$_2$ moieties appears to preclude C−F bond activation.

Complex **2** was found to cleanly catalyze the slow conversion of solutions of **1** to **4** in the absence of Na/Hg. No other fluorine-containing products are observed by ^{19}F NMR after 24 h. The mechanism shown in Scheme 2 may be operative, where C−H bond activation occurs in preference to C−F bond activation due to the proximity of the C−H bond.[9] This is followed by a transfer of the hydride from one metal to another.[10] Reductive elimination and loss of Ni(PEt_3)$_2$ forms **3**, which can dimerize to form **4**. The reaction of (PEt_3)$_2$Ni(η^2-C_6D_2-4,5-F_2), (**1-*d*₂**) with 9% $Br_2Ni(PEt_3)_2$ and Na/Hg in pentane produced only the deuterated product **4-*d*₄**. Further investigations are underway to distinguish this mechanism from another plausible mechanism, where C−C bond formation precedes C−H bond rearrangement.[11]

The rearrangement of aryne **1** to its isomer **3** is reminiscent of the chain walking of alkenes in their reaction with metal hydride complexes. The driving force for the reaction appears to be the formation of a more stable isomer of **1**; hydrocarbyl complexes bearing proximal fluoro substituents have stronger M−C bonds, and DFT calculations on the model complexes (PMe_3)$_2$Ni(η^2-C_6H_2-4,5-F_2) and (PMe_3)$_2$Ni(η^2-C_6H_2-3,4-F_2) demonstrate that the latter is more stable by 9 kcal/mol. Although aromatic C−H bond activations by Ni bisphosphine complexes are typically thermodynamically unfavorable, clearly these reactions are kinetically accessible and, under suitable conditions, can provide products resulting from C−H bond activation, even in the presence of C−F bonds. The development of methods to trap the transitory C−H bond activation products could render Ni(0) bisphosphine complexes as useful reagents for synthetic methods which utilize C−H bond activation.

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Supporting Information Available: Full experimental details; crystal data collection and refinement parameters; coordinates and energies from DFT calculations; CIF files for **2** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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