ORGANOMETALLICS

Carbon–Fluorine Bond Activation of Tetrafluoroethylene on Palladium(0) and Nickel(0): Heat or Lewis Acidic Additive Promoted Oxidative Addition

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Supporting Information

ABSTRACT: The C–F bond cleavage reaction of tetrafluoroethylene (TFE; $CF_2=CF_2$) with an M(0) complex (M = Pd, Ni) was investigated. The treatment of an M(0) precursor with TFE in the presence of the appropriate monodentate phosphine ligand led to a clean formation of the corresponding η^2 -TFE adduct (η^2 -TFE)M(PR₃)₂. In the case of the Ni(0) species, in particular, the choice of phosphine ligands is crucial



for the preparation of the desired η^2 -TFE complex: the use of either PCy₃ or PⁱPr₃ resulted in the target adduct, while less sterically hindered phosphines such as PPh₃ and PⁿBu₃ gave the known octafluoronickelacyclopentane as a result of the oxidative cyclization of two TFE molecules. Thermolysis of both palladium and nickel η^2 -TFE adducts bearing PCy₃ as the ligand resulted in a C–F bond activation reaction and gave the corresponding (trifluorovinyl)metal fluorides, *trans*-(PCy₃)₂M(F)(CF=CF₂). The reaction of (η^2 -TFE)Pd(PPh₃)₂ with LiI as an additive allowed cleavage of the C–F bond in THF, even at room temperature, and gave *trans*-(PPh₃)₂Pd(I)(CF=CF₂) with a concomitant formation of lithium fluoride. Other metal halides, such as MgBr₂ and AlCl₃, also promoted the C–F bond cleavage of TFE. In addition, the use of either BF₃·Et₂O or B(C₆F₅)₃ exerted a similar accelerative effect on the C–F bond activation of TFE on either nickel or palladium. The molecular structures of a series of η^2 -TFE and trifluorovinyl complexes were unambiguously determined by means of X-ray crystallography. The resultant (trifluorovinyl)palladium or -nickel species have shown the potential to utilize a key intermediate in cross-coupling reactions with organometallic reagents to prepare a variety of trifluorovinyl compounds.

INTRODUCTION

The activation of C-F bonds by homogeneous transition-metal complexes has been a fascinating subject in the field of organometallic and organic chemistry, since it provides not only new routes to metal-fluoride complexes under mild conditions but also novel potential synthetic routes to fluorinated organics that are difficult to access by conventional reactions.¹ Although striking developments have been made in recent years on the intermolecular C-F bond activation of fluorinated olefins,² the alkenyl $C(sp^2)$ -F bond cleavage of perfluoroalkenes remains a great challenge. In fact, among the perfluoroalkenes, only hexafluoropropylene, $CF_3CF=CF_2$, has been used as a substrate in transition-metal-catalyzed C-F bond activation reactions.^{2j,o-q} In contrast, until 2010, no homogeneous catalytic reactions that involve C-F bond cleavage of the simplest perfluoroalkene, tetrafluoroethylene (1; TFE, CF_2 = CF_2), had been reported, and C-F bond cleavage of TFE by a transition metal had only been achieved in a few stoichiometric reactions.³ In 1973, Kemmitt and co-workers reported that treatment of an η^2 -TFE platinum complex with lithium iodide at 95 °C gave a (trifluorovinyl)platinum complex in quantitative yield (Scheme 1a).^{3b} Similar C-F bond cleavage reactions using either a dinuclear iridium or a mononuclear rhodium complex were developed by Cowie and Booth,

respectively (Scheme 1b,c).3c,d In these reactions, either the use of additives such as lithium iodide and silvl triflate or the existence of a trimethylstannyl group bound to the rhodium center could play an important role in the C-F bond activation of TFE; the formation of thermodynamically favored Li-F, Si-F, and Sn-F bonds might be a driving force behind these reactions. Inspired by such groundbreaking studies, we have developed the first coupling reaction of TFE with aryl zinc compounds to yield $(\alpha,\beta,\beta$ -trifluoro)styrene derivatives, in which efficient C-F bond cleavage on palladium was achieved by using lithium iodide as a coadditive.⁴ Moreover, we have recently demonstrated the Pd⁰/PR₃-catalyzed cross-coupling reaction of fluoroalkenes with arylboronates, which required neither an extraneous base to enhance the reactivity of organoboronates nor a Lewis acid to promote the oxidative addition of a C-F bond.⁵

Our next concern was to investigate how efficiently the $C(sp^2)-F$ bond of TFE is cleaved under mild conditions. We, therefore, started evaluating the effect of additives to the C–F bond activation reaction. Among a variety of candidates with Lewis acidity, boron Lewis acids in particular, such as BF₃ and

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Scheme 1. Stoichiometric C-F Bond Cleavage on Transition-Metal Complexes



 $B(C_6F_5)_{3}$, are well-known to show fluorophilicity, as evidenced by the fact that in 1964 Olah et al. demonstrated the first Friedel–Craft alkylation reaction of alkyl fluoride by employing BF_3 .⁶ Furthermore, C–F bond activation promoted by the addition of commercially available $B(C_6F_5)_3$ has also been developed in the past decade.⁷ It is assumed that the fluorophilicity of the boron atom is the driving force behind these reactions.

In addition, zerovalent nickel complexes are assumed to be promising candidates to accomplish the C-F bond cleavage of TFE, since some of them are known to promote the oxidative addition of the aromatic $C(sp^2)$ -F bond.^{8,9} However, the traditional approach using $Ni^0 \hat{L}_2$ precursors had mostly been unsuccessful because the expected η^2 -CF₂=CF₂ intermediate overreacted with further TFE molecules to give octafluoronickelacyclopentanes as a result of oxidative cyclization with Ni(0).¹⁰ To overcome this circumstance, we started preparing a novel η^2 -TFE nickel complex with bulkier supporting ligands, since such a ligand is most certainly believed to circumvent the overreaction. This concept was supported by the fact that η^2 - $CF_2 = CF_2 Ni(0)$ complexes coordinated by a tridentate ligand, such as $(tdt)Ni(\eta^2-CF_2=CF_2)$ (tdt = trans,trans,trans-cyclododeca-1,5,9-triene) and (triphos)Ni(η^2 -CF₂=CF₂) (triphos = $CH_3C(CH_2PPh_2)_3)$, were unreactive toward the second TFE molecule. 10b,d,11 In addition, the use of ligands with strong σ donor abilities was anticipated to often allow the oxidative addition of substrates that are otherwise unreactive. We thus investigated the reaction of $Ni(cod)_2$ with TFE in the presence of PCy₃ and IPr (1,3-bis(2,6-diisopropylphenyl)imidazol-2ylidene), with combined bulkiness and strong σ -donor abilities. Herein, we give a detailed account of the C-F bond cleavage reactions of TFE for both Pd(0) and Ni(0) species. These reactions were found to be promoted by the addition of Lewis acids to give a series of (trifluorovinyl)palladium or -nickel complexes. In addition, isolation and molecular structures of these trifluorovinyl complexes as well as η^2 -TFE palladium and nickel adducts were also discussed.

RESULTS AND DISCUSSION

Synthesis of η^2 -TFE Palladium Complexes Bearing Phosphine Ligands. Formation of $(\eta^2$ -CF₂=CF₂)Pd(PCy₃)₂ (2a) was accomplished by treating either Pd(PCy₃)₂¹² with TFE $(1)^{13}$ or a mixture of $Pd_2(dba)_3$ and PCy_3 with 1 (Scheme 2a). Both reactions proceeded almost quantitatively, and



complex **2a** was isolated in 92% yield. In contrast, the reaction of $Pd_2(dba)_3$ with **1** in the presence of PPh_3 (2 equiv, relative to Pd atom) gave an equilibrium mixture of the corresponding η^2 -TFE complexes supported by two triphenylphosphine ligands, $(\eta^2-CF_2=CF_2)Pd(PPh_3)_2$ (**2b**) and $(\eta^2-dba)Pd(PPh_3)_2$,¹⁴ which hampered the isolation of the desired product **2b**. Thus, the isolation of **2b** was accomplished by the substitution of a TFE molecule for the coordinated ethylene in $(\eta^2-CH_2=CH_2)Pd(PPh_3)_2$ (Scheme 2a).¹⁵ On the other hand, treatment of $Pd(P^tBu_3)_2^{-12c}$ with **1** gave no products, probably due to the greater bulkiness of P^tBu_3 .

Some bidentate phosphine ligands were found to allow the formation of the corresponding η^2 -TFE complex. For example, in the presence of either bis(dicyclohexylphosphino)ethane (DCPE) or bis(dicyclohexylphosphino)butane (DCPB), CpPd- $(\eta^3$ -allyl)¹⁶ reacted with 1 in toluene to give the desired product (**3a** or **3b**, respectively) in quantitative yield (Scheme 3a). In

Scheme 3. Formation of $(\eta^2$ -TFE)Pd(P-P) (3: P-P = Bidentate Phosphine Ligand)



contrast, a higher reaction temperature was required to generate the corresponding η^2 -TFE complex (η^2 -TFE)Pd(*rac*-BINAP) (**3c**) when *rac*-BINAP was used as the bidentate ligand (Scheme 3b).

Synthesis of η^2 -TFE Nickel Complexes Bearing Phosphine Ligands. Exposing a toluene solution of a mixture of Ni(cod)₂ and 2 equiv of PCy₃ to an atmosphere of TFE at room temperature led to the clean formation of an η^2 -TFE complex, (η^2 -CF₂=CF₂)Ni(PCy₃)₂ (4a), and it was isolated in 64% yield (Scheme 4a). In contrast, as already reported by Stone et al.,^{10b} the use of PPh₃ instead of PCy₃ as a ligand exclusively gave the octafluoronickelacyclopentane complex **5a** as a result of the oxidative cyclization of two molecules of TFE with nickel (Scheme 4b). Systematic investigation into the Scheme 4. Formation of η^2 -TFE Nickel Complexes (4 and 6) and an Octafluoronickelacyclopentane Complex (5a)



reaction of Ni(cod)₂ with TFE in the presence of a variety of monodentate phosphines revealed that the reaction product depends primarily on the bulkiness of phosphine ligands. That is, a similar η^2 -TFE nickel complex (4b) was generated when bulkier phosphines with a wider cone angle¹⁷ than ca. 160°, such as isopropylphosphine, were employed as ligands (Scheme 4a). In contrast, reactions with the narrower phosphines such as PPh₃, PEt₃, PBu₃, and P(OMe)₃ yielded the known octafluoronickelacyclopentanes,¹⁰ regardless of the basicity of the phosphine (Scheme 4b). Furthermore, neither *tert*-butyl phosphine nor *o*-tolylphosphine gave any TFE-containing products, probably due to their bulkiness.

The formation of an η^2 -TFE nickel complex could be achieved by using bidentate phosphine ligands; for example, treating Ni(cod)₂ with an equimolar amount of DCPE under a TFE gas atmosphere led to the formation of the η^2 -TFE analogue (η^2 -TFE)Ni(dcpe) (**6a**) in quantitative yield (Scheme 4c). DCPB could also be applied to the same reaction conditions to afford the corresponding complex (η^2 -TFE)Ni-(dcpb) (**6b**). In contrast, reactions with both Ph₂PCH₂PPh₂ and 2,2'-bipyridyl are known to give the corresponding octafluoronickelacyclepentanes.^{10b}

The attempt to employ IPr as a ligand in the preparation of a η^2 -TFE nickel complex failed. When a mixture of Ni(cod)₂ and 2 equiv of IPr was treated with TFE, no generation of a putative

product, $(\eta^2$ -TFE)Ni(IPr)₂, was observed. Instead, IPr itself was found to smoothly react with TFE to give the undesired 1,3-bis(2,6-diisopropylphenyl)-2-(perfluoroethylidene)-1*H*-imidazole.⁵

Molecular Structures of η^2 -TFE Palladium and Nickel **Complexes.** The molecular structures of a series of n^2 -TFE complexes, 2a,b, 3c, and 4a, were definitively determined by means of X-ray crystallography (Figures 1 and 2). In these complexes, the coordination geometry of the metal center is regarded as a Y-shaped trigonal plane in which the midpoint of the carbon-carbon double bond is assumed to be a coordination center. The C1-C2 bond lengths of 1.419(4) Å for 2a, 1.425(4) Å for 2b, 1.430(4) Å for 3c, and 1.4257(15) Å for 4a fell within the range of previously reported C=C bond lengths of a coordinated TFE molecule (1.37(3)-1.45(2))Å) $^{\hat{H},18}$ but were significantly longer than that of a free TFE molecule (1.311(3) Å).¹⁹ In addition, the normal angles between the F1-C1-F2 and F3-C2-F4 planes, which is used by Ibers to define how far the olefin substituents bend backward,²⁰ are 97.90(24)° for 2a, 103.35(21)° for 2b, $103.45(20)^{\circ}$ for 3c, and $99.62(10)^{\circ}$ for 4a. These values are beyond the corresponding maximum that has been previously observed in related η^2 -TFE complexes (70.4-84°), ^{11,18c-f,k,1} indicating that the contribution of the back-donation from palladium to the π^* antibonding orbital of TFE must be very large. Therefore, these complexes make some kind of contribution to metallacyclopropane.

The Ni–P bond distances (2.2453(3) and 2.2429(3) Å) in 4a are almost similar to the average of those observed in the structurally characterized Ni–PCy₃ complexes (2.211 Å).²¹ The average Ni–C bond distance of 1.905(1) Å is slightly longer than those found in (triphos)Ni(η^2 -CF₂=CF₂) (1.86(2) Å)¹¹ and (tmeda)Ni(η^2 -CF₂=CF₂) (1.838(3) Å),^{18h} which is probably due to the steric repulsion between the TFE and PCy₃ molecules. In addition, unlike the case for the palladium analogue 2a, the ligated C=C bond in 4a is twisted by 23.5° (cf. 1.4° in 2a) with respect to the P–Ni–P plane, which is probably due to an avoidance of steric hindrance that is caused by the smaller ionic radius of nickel.

Dynamic Behavior in Solution of an η^2 -TFE Nickel Complex. As mentioned above, an X-ray diffraction study revealed that 4a has a pseudorotationally symmetrical structure in the solid state and should be an AA'BB'XX spin system, where A and B represent ¹⁹F nuclei and X represents ³¹P. The ¹⁹F NMR spectrum measured in toluene- d_8 at -80 °C, although it did not reach the slow-limit temperature, was



Figure 1. ORTEP drawings of 2a with thermal ellipsoids at the 30% probability level. H atoms are omitted for clarity.



Figure 2. ORTEP drawing of 4a with thermal ellipsoids at the 30% probability level. H atoms and solvent molecules (benzene) are omitted for clarity.

consistent with the structure; two broadened signals with the same intensity were observed at δ –112.8 and –140.0 (see also the Supporting Information). These signals, however, broadened and flattened with elevating temperature as they coalesced into one signal at –20 °C, which implied that a fluxional process involving either rotation or a twisting motion of the coordinated TFE ligand had occurred (Figure 3). The ¹⁹F



Figure 3. Fluxional behavior of 4a in solution.

NMR spectrum of **4a** at room temperature exhibited a single but broadened resonance at δ –131.7 assignable to the coordinated TFE. At that temperature, the ³¹P signal of **4a** appeared at δ 32.6 with a complicated coupling pattern, which indicated that the ¹⁹F atoms A and B become chemically equivalent but are still magnetically inequivalent, resulting in an AAA'A'XX' spin system.

Molecular Structure of Octafluoronickelacyclopentane 5a and Its Fluxional Behavior in Solution. Figure 4



Figure 4. ORTEP drawing of **5a** with thermal ellipsoids at the 30% probability level. H atoms are omitted for clarity.

gives an ORTEP drawing of the octafluoronickelacyclopentane 5a, showing a coordination geometry of the nickel center that is slightly distorted in the square plane, as indicated by the sum of the angles around nickel (369.1°) as well as by a twist between the C1-Ni-C4 and P1-Ni-P2 planes (32.1°). The complex 5a essentially has the same stereochemical arrangement as the PEt_3 analogue $(PEt_3)_2Ni(C_4F_8)$, which was previously fully characterized by Burch et al. 22 The ^{19}F and ^{31}P NMR spectra of 5a measured in C_6D_6 at room temperature displayed resonances at $\delta_{\rm F}$ -101 (t, $J_{\rm PF}$ = 24.2 Hz) and $\delta_{\rm P}$ 25.8 ppm with the same coupling constant as the ¹⁹F nuclei (quin, J_{PF} = 24.2 Hz), which is attributable to α -CF₂ and PPh₃, respectively. In addition, the β -CF₂ signal was observed at -138 ppm as a singlet signal. The observation of the apparent quintet of ³¹P nuclei as well as the apparently equivalent chemical shifts of ¹⁹F nuclei of both the α - and β -CF₂ groups clearly indicated the existence of rapid ring flipping of the nickelacyclopentane via a transition state with a planar five-membered ring on the NMR time scale.

Thermally Promoted C–F Bond Activation of TFE on Palladium(0) or Nickel(0). Before the effect of additives on the C–F bond cleavage of TFE was evaluated, control experiments were carried out in the absence of any additive.²³ Although complex 2a remained intact in a THF solution at room temperature, heating the THF solution at 100 °C under a N₂ atmosphere initiated a C–F bond activation of TFE to yield the expected (trifluorovinyl)palladium(II) fluoride 7 in 45% yield (Scheme 5). NMR observation revealed the concomitant

Scheme 5. Generation of Trifluorovinylpalladium(II) and Trifluorovinylnickel(II) Fluorides via Direct Oxidative Addition of TFE



formation of a palladium 2-perfluorobutenyl species (8).²⁴ The recovery of $Pd(PCy_3)_2$ (26%) indicated the existence of a coordination–dissociation equilibrium of TFE to palladium under the reaction conditions. Thus, this reaction was conducted under a TFE atmosphere (1 atm), resulting in an improvement in the yield of 7. In contrast, thermolysis of the palladium triphenylphosphine complex **2b** under the same conditions resulted in its rapid decomposition to give palladium black and a free TFE molecule; the C–F bond activation did not proceed at all.⁴

In addition, the nickel analogue 4a was found to cleave the C-F bond of TFE at 100 °C under a nitrogen atmosphere. giving the corresponding (trifluorovinyl)nickel fluoride 9 in 70% vield (Scheme 5). However, conducting this reaction under a TFE atmosphere (1.0 atm) resulted in the formation of the difluorophosphorane F_2PCy_3 (δ_F -64.2 (d), δ_P -23.4 (t), $J_{\rm PF}$ = 650 Hz); complex 9 was not obtained at all. The characteristic upfield-shifted resonances attributable to a fluorine adjacent to a group 10 metal appeared at δ -317.9 (br s) and -385.7 (t, $J_{PF} = 41.4$ Hz) in the ¹⁹F NMR spectra of 7 and 9, respectively. In the ¹⁹F NMR spectrum of 9, three resonances assignable to the trifluorovinyl moiety were detected at δ -92.4, -133.3, and -159.1. Attempts to carry out the corresponding C-F bond activation on nickel or palladium supported by a dcpe ligand failed; neither 3a nor 6a gave any trifluorovinyl complex even at 100 °C.

Lil-Promoted C–F Bond Activation of TFE on Palladium(0) or Nickel(0). As reported in a previous communication,⁴ the addition of lithium iodide to a THF solution of **2b** at room temperature resulted in the very smooth oxidative addition of a C–F bond, within a few minutes, to afford *trans*-(PPh₃)₂Pd(I)(CF=CF₂) (**10b**) with the concomitant formation of lithium fluoride (Scheme 6). The rate of the



C-F bond activation on palladium in the presence of lithium iodide was found to depend on the ligand that coordinates to the palladium. When the reaction of 2a with lithium iodide was conducted, it took more than 4 days to consume 2a while a similar trifluorovinyl complex, trans-(PCy₃)₂Pd(I)(CF=CF₂) (10a), was also generated. Furthermore, oxidative addition to nickel was also accelerated by the addition of an equimolar amount of LiI to afford *trans*-(PCy_3)₂Ni(I)($CF=CF_2$) (11a). In these reactions, lithium iodide would act as a Lewis acid to enhance the elimination ability of fluorine. This is supported by the fact that both MgBr₂ and AlCl₃ can accelerate the C-F bond activation of TFE (vide infra), although another possibility of basic iodide attacking the M-F center (M = Pd, Ni) cannot be completely ruled out. The high lattice enthalpy of LiF(s) might also be important for the occurrence of the oxidative addition at room temperature.

As anticipated by the fact that a thermally promoted C–F bond activation of TFE did not occur at all, treating the η^2 -TFE dcpe complexes **3a** and **6a** with lithium iodide in THF even at a

higher temperature $(100 \ ^{\circ}C)$ did not give the expected oxidative addition products (Scheme 7).



Metal Halide Promoted C–F Bond Activation of TFE on M(0) (M = Pd, Ni). We next investigated which additives can effectively cleave the C–F bond of TFE on η^2 -TFE complexes. The C–F bond activation of TFE can be achieved through treatment with other metal halides. The reaction of 2a with a half equimolar amount of magnesium bromide afforded the corresponding trifluorovinyl complex *trans*-(PCy₃)₂Pd(Br)-(CF=CF₂) (12) in quantitative yield (Scheme 8). In contrast,

Scheme 8. Metal Halide Promoted C-F Bond Activation of TFE



the reaction with aluminum chloride required a prolonged reaction time, and after 120 h, the starting material 2a was quantitatively converted into $trans-(PCy_3)_2Pd(Cl)(CF=CF_2)$ (13). On the other hand, the nickel complex 4a indeed reacted with MgBr₂ or AlCl₃ more smoothly than the palladium analogue 2a, to give the corresponding (trifluorovinyl)nickel halides trans- $(PCy_3)_2Ni(X)(CF=CF_2)$ (14, X = Br; 15, X = Cl) in excellent yield. Thus, the nature of group 10 metals apparently influenced the reactivity in cleaving the C-F bond of TFE. In addition, the factor determining the reactivity, of course, depended on not only the nature of the group 10 metals but also the metal halides employed. For example, in the transformation of 4a into 15, the reaction with magnesium chloride was very slow (room temperature, 24 h), and the use of lithium chloride gave a complicated mixture, including the desired complex 15. A series of trifluorovinyl complexes were identified on the basis of the characteristic ¹⁹F resonances of the trifluorovinyl group. It should be mentioned that a related (trifluorovinyl)palladium chloride complex, trans-(PPh₃)₂Pd- $(Cl)(CF=CF_2)$, has recently been isolated and structurally defined by Lu, Shen, and co-workers.²⁵

Molecular Structures of Trifluorovinyl Metal Halides. The occurrence of the C–F bond cleavage of TFE was unambiguously confirmed by X-ray crystallography of 7 and 9, the results of which were previously reported in our recent communication (Figure 5).⁵ Each group 10 metal center in 7 and 9 possessed an approximate square-planar geometry with a *trans* alignment of the PCy₃ ligands in the solid state. The fluoride and trifluorovinyl ligands were also situated in mutually *trans* positions, and the trifluorovinyl and either palladium or nickel coordination planes are almost orthogonal (dihedral



Figure 5. ORTEP drawing of 9 with thermal ellipsoids at the 30% probability level. H atoms are omitted for clarity.

angle: $87.73(13)^{\circ}$ for 7; $88.93(21)^{\circ}$ for 9). The Pd–F bond length of 2.139(5) Å in 7 and the Ni–F bond length of 1.833(4) Å in 9 lie within the ranges of the corresponding metal-fluoride bonds (1.947(4)–2.1024(17) Å for palladium and 1.836(3)–1.916(3) Å for nickel, respectively).^{2,26,27}

The ORTEP drawing of **10b** shows that palladium adopts a square-planar coordination geometry and is coordinated with two PPh₃ ligands in a *trans* manner (Figure 6). Similar to the



Figure 6. ORTEP drawing of 10b with thermal ellipsoids at the 30% probability level. H atoms are omitted for clarity.

case for 7, the trifluorovinyl group was almost orthogonal to the coordination plane (dihedral angle: $87.12(19)^{\circ}$). We also carried out an X-ray diffraction study of the (trifluorovinyl) nickel iodide **11a**. Whereas the structure refinement was not sufficient due to a deterioration in the quality of the crystal analyzed, two PCy₃ ligands in **11a** coordinated to the nickel center in a trans manner, and the trifluorovinyl and iodide ligands were bound to the nickel center to form a square-planar geometry.

Boron Derivative Promoted C–F Bond Activation of TFE. We found that the C–F bond cleavage of TFE was also promoted by the addition of boron derivatives with Lewis acidity. The addition of an equimolar amount of $BF_3 \cdot Et_2O$ to a C_6D_6 solution of **2a** allowed the oxidative addition of the C–F bond to the palladium to give *trans*-(PCy₃)₂Pd(BF₄)(CF= CF₂) (**16**) in quantitative yield (Scheme 9). The (trifluorovinyl)palladium complex **16** was isolated in 58% yield, and its molecular structure was determined by X-ray crystallography.

Scheme 9. BF₃*Et₂O-Promoted C-F Bond Activation of TFE



One of the most significant structural features of 16 was that one of the fluorine atoms in the tetrafluoroborate bridges between the palladium and boron atoms (Figure 7). Thus,



Figure 7. ORTEP drawing of 16 with thermal ellipsoids at the 30% probability level. H atoms are omitted for clarity.

BF₂·Et₂O served as a Lewis acid to promote the C-F bond cleavage, and in addition, the resultant tetrafluoroborate served as a Lewis base in order to stabilize the square-planar geometry of the palladium(II) center in 16 by coordination of the fluorine atom to the palladium. The same coordination mode of the tetrafluoroborate anion in the Pd(II) complex has been reported in three different citations in the literature.²⁸ The Pd-F4 bond distance of 2.161(3) Å in 16 is quite a bit shorter than those observed in the other reported Pd^{II}-F-BF₃ complexes (2.241(2)-2.355(5) Å), while the Pd-F4-B bond angle of 141.9(5)° was almost equal to the upper range of the observed values $(123.5(7)-141.9(4)^\circ)$.²⁸ The B–F4 bond distance of 1.446(7) Å in 16 was found to be slightly longer than the average of the other three nonbridged B-F bonds (1.377(7)) Å). We found the C=C bond distance of the coordinated trifluorovinyl group (1.297(8) Å for 16) to be equal within the margin of error to those observed in Hg(CF=CF₂)₂, $(\eta^{5} C_5Me_4Et)_2Ti(OH)(CF=CF_2)$, (PPh₃)Au(CF=CF₂), [Ir₂(η^{1-} $CF=CF_2$ (CH₃)(CO)₂(μ -Cl)(dppm)₂](CF₃SO₃), and Ph₃Ge- $(CF=CF_2)$ (1.312(6), 1.331(4), 1.297(14), 1.298(9), and 1.30(8) Å, respectively)²⁹ as well as that in *trans*-(PPh₃)₂Pd-(Cl)(CF=CF₂) (1.270(4) Å).²⁵

The NMR spectra of 16 revealed that its molecular structure in solution is consistent with that observed in the solid state, in which the tetrafluoroborate anion interacted with the palladium center. The variable-temperature ¹⁹F NMR spectra of **16** demonstrated the fluxionality of the tetrafluoroborate. The ¹⁹F signal assignable to the tetrafluoroborate anion, measured in toluene- d_8 at room temperature, was observed as a broad signal at δ –172, and there was an obvious chemical shift to upper magnetic field from that of the free tetrafluoroborate anion (NaBF₄; ca. δ –150 to –153).³⁰ With a decrease in the temperature, the peak broadened and decoalesced at –40 °C, and then it split into two signals with an intensity ratio of 3:1 at –90 °C, while the spectrum measured at that temperature did not reach the slow-limit spectrum. This temperature dependence of the spectra strongly indicates the site-exchange process of the fluorine atoms on the tetrafluoroborate between the bridging Pd–F–B site and the terminal B–F sites.

A similar procedure could be applied to the nickel analogue 4a, giving trans-(PCy₃)₂Ni(BF₄)(CF=CF₂) (17), which was characterized on the basis of the observation of a similar fluxional behavior of the tetrafluoroborate anion in variable-temperature ¹⁹F NMR spectra (Scheme 9).

The (trifluorovinyl)palladium tetrafluoroborate complex 16 was found to be stable in either toluene or benzene solution even when the temperature was elevated to 100 °C. However, it showed reactivity toward a Lewis base that contains a nitrogen atom, and the nature of the Lewis base was apparently influenced by the choice of the two different types of reactions. That is, the formation of the Lewis acid—base adduct took place by the addition of a half equimolar amount of 1,4-diazabicyclo[2.2.2]octane (DABCO) to a benzene solution of 16, giving 7 in quantitative yield with a concomitant generation of (DABCO) \cdot (BF₃)₂ (Scheme 10). The use of NEt₃, instead of

Scheme 10. Reactivity of 16 toward DABCO and Pyridine



DABCO, led to a decrease in the yield of 7 to 30% even after a prolonged reaction time (23 h). As already mentioned above, (trifluorovinyl)palladium fluoride 7 could be obtained by the thermally promoted oxidative addition of a C–F bond of TFE on palladium (Scheme 5), whereas an undesired side reaction inevitably took place to give 8 and hamper the isolation of 7. In contrast, this reaction enabled the selective formation of 7, as depicted in Scheme 10.

On the other hand, treatment of **16** with an equimolar amount of pyridine in benzene resulted in the rapid substitution of pyridine for tetrafluoroborate on palladium to give a cationic trifluorovinyl complex, $[trans-(PCy_3)_2Pd(py)(CF=CF_2)]$ - $[BF_4]$ (**18-BF**₄) (Scheme 10). In the ¹⁹F NMR spectrum of **18-BF**₄, a resonance assignable to the tetrafluoroborate anion at δ -154.2 (s) appeared at almost the same region as the signal for NaBF₄, clearly indicating that it lies out of the coordination sphere of palladium. The difference in the product between DABCO and pyridine is probably caused by the difference in the pK_a values of their conjugate acids ([DABCO-H]⁺, 8.82; [pyridine-H]⁺, 5.17);^{31,32} the stronger Lewis base DABCO is more amenable to complexation with BF₃. The treatment of **18-BF₄** with DABCO, however, did not give a transformation to 7.

As for the reaction with $BF_3 \cdot Et_2O$, the addition of an equimolar amount of $B(C_6F_5)_3$ to a C_6D_6 solution of **2a** promoted a C–F bond cleavage, and this reaction proceeded within a few minutes. Monitoring of the initial stage of the reaction by means of ¹⁹F NMR spectroscopy indicated the generation of $[FB(C_6F_5)_3]^-$ anion as a result of the abstraction of a fluorine atom, suggesting the formation of a cationic trifluorovinylpalladium complex (**19**; Scheme 11). The





observation of a set of ¹⁹F resonances with characteristic I_{FF} coupling constants attributable to a trifluorovinyl group also supported the formation of 19. Complex 19 was unstable in solution and decomposed gradually at room temperature. This instability may stem from either a vacancy in the coordination site of the square-planar geometry on palladium as a result of the formation of the $[FB(C_6F_5)_3]^-$ anion³³ with a much weaker coordinating ability, or it may be the result of the insufficient occupancy of the resultant vacant site in 19 by a ligand, such as benzene, used as a solvent, or the result of a perfluorophenyl ring in the counteranion that could not sufficiently stabilize the metal center. Thus, we conducted successive treatments of 2a with $B(C_6F_5)_3$ followed by pyridine, giving the stable cationic complex 18-FB(C_6F_5)₃. Unlike 19, 18-FB(C_6F_5)₃ was stable enough to be isolated, and indeed, a benzene or toluene solution of 18-FB(C₆F₅)₃ remained intact at room temperature for 1 day.

The molecular structure of $18\text{-FB}(C_6F_5)_3$ was unambiguously determined by means of X-ray crystallography, and an ORTEP drawing of the cationic part of $18\text{-FB}(C_6F_5)_3$ is shown in Figure 8. The drawing clearly demonstrates that the palladium center possesses a square-planar geometry with a *trans* alignment of the trifluorovinyl and pyridine ligands, and the Pd–N bond distance was 2.103(2) Å. In the crystal lattice, the $[FB(C_6F_5)_3]^-$ anion lies out of the coordination sphere of the palladium. In the ¹H NMR spectrum of $18\text{-FB}(C_6F_5)_3$ measured in C_6D_6 , the five signals assignable to the coordinating pyridine molecule were observed to be inequivalent, indicating that neither rapid coordination–dissociation equilibrium nor rotation of the coordinating pyridine about the Pd–N bond took place in solution.



Figure 8. ORTEP drawing of the cationic part of 18-FB(C₆F₅)₃ with thermal ellipsoids at the 30% probability level. H atoms and solvated molecules (toluene) are omitted for clarity.

The reaction of the η^2 -TFE nickel complex 4a with B(C₆F₅)₃ occurred in a manner similar to that for 2b, and the initial unstable product (20) was treated with pyridine to give the corresponding cationic complex [trans-(PCy₃)₂Ni(py)(CF= CF_2][FB(C₆F₅)₃] (21) in quantitative yield (Scheme 11).

CONCLUSIONS

In conclusion, we demonstrated the preparation of a series of η^2 -TFE palladium and nickel complexes, $(\eta^2$ -TFE)M(PR₃)₂ (M = Ni, Pd). Heating both palladium and nickel η^2 -TFE complexes supported by PCy3 ligands allowed C-F bond activation to take place in order to generate the corresponding (trifluorovinyl)metal fluorides trans-(PCy₃)₂M(F)(CF=CF₂). The C-F bond cleavage of TFE on a group 10 metal was found to be accelerated even at room temperature by the addition of metal halides such as LiI, MgBr2, and AlCl3, giving the corresponding (trifluorovinyl)metal halides. Furthermore, the C-F bond activation reaction was also promoted by boron Lewis acids, such as BF_3 and $B(C_6F_5)_3$. We unambiguously determined the molecular structures of not only the η^2 -TFE complexes but also the (trifluorovinyl)metal(II) complexes by X-ray diffraction studies. As reported in our previous communications, the trifluorovinyl complexes generated as a result of the cleavage of a C-F bond in TFE acted as key intermediates in the cross-coupling reaction with organometallic reagents to prepare a variety of trifluorovinyl compounds. Further theoretical studies on the reaction mechanism are ongoing in our laboratory.

ASSOCIATED CONTENT

Supporting Information

Text, figures, tables, and CIF files giving detailed experimental procedures, analytical and spectral data for all new compounds, and crystallographic data for 2a,b, 3c, 4a, 5a, 9, 10b, 16, and 18-FB $(C_6F_5)_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) For reviews on C-F activation see: (a) Doherty, N. M.; Hoffmann, N. W. Chem. Rev. 1991, 91, 553-573. (b) Kiplinger, J. L.; Richmond, T. G.; Osterberg, C. E. Chem. Rev. 1994, 94, 373-431. (c) Murphy, C. E.; Murugavel, R.; Roesky, H. W. Chem. Rev. 1997, 97, 3425-3468. (d) Burdeniuc, J.; Jedlicka, B.; Crabtree, R. H. Chem. Ber. 1997, 130, 145-154. (e) Richmond, T. G. Angew. Chem., Int. Ed. 2000, 39, 3241-3244. (f) Braun, T.; Perutz, R. N. Chem. Commun. 2002, 38, 2749-2757. (g) Jones, W. D. Dalton Trans. 2003, 3991-3995. (h) Torrens, H. Coord. Chem. Rev. 2005, 249, 1957-1985. (i) Meier, G.; Braun, T. Angew. Chem., Int. Ed. 2009, 48, 1546-1548. (j) Amii, H.; Uneyama, K. Chem. Rev. 2009, 109, 2119-2183. (k) Sun, A. D.; Love, J. A. Dalton Trans. 2010, 39, 10362-10374. (1) Braun, T.; Wehmeier, F. Eur. J. Inorg. Chem. 2011, 613-625. (m) Clot, E.; Eisenstein, O.; Jasim, N.; Macgregor, S. A.; McGrady, J. E.; Perutz, R. N. Acc. Chem. Res. 2011, 44, 333-348. (n) Kuehnel, M. F.; Lentz, D.; Braun, T. Angew. Chem., Int. Ed. 2013, 52, 3328-3348.

(2) For examples on olefinic C-F bond activation, see: (a) Watson, P. L.; Tulip, T. H.; Williams, I. Organometallics 1990, 9, 1999-2009. (b) Peterson, T. H.; Golden, J. T.; Bergman, R. G. Organometallics 1999, 18, 2005-2020. (c) Kraft, B. M.; Lachicotte, R. J.; Jones, W. D. J. Am. Chem. Soc. 2000, 122, 8559-8560. (d) Huang, D.; Bollinger, J. C.; Streib, W. E.; Folting, K.; Young, V., Jr.; Eisenstein, O.; Caulton, K. G. Organometallics 2000, 19, 2281-2290. (e) Kirkham, M. S.; Mahon, M. F.; Whittlesey, M. K. Chem. Commun. 2001, 813-814. (f) Kraft, B. M.; Jones, W. D. J. Am. Chem. Soc. 2002, 124, 8681-8689. (g) Ferrando-Miguel, G.; Gérard, H.; Eisenstein, O.; Caulton, K. G. Inorg. Chem. 2002, 41, 6440-6449. (h) Clot, E.; Mégret, C.; Kraft, B. M.; Eisenstein, O.; Jones, W. D. J. Am. Chem. Soc. 2004, 126, 5647-5653. (i) Renkema, K. B.; Werner-Zwanziger, U.; Pagel, M. D.; Caulton, K. G. J. Mol. Catal. A 2004, 224, 125-131. (j) Saeki, T.; Takashima, Y.; Tamao, K. Synlett 2005, 1771-1774. (k) Vela, J.; Smith, J. M.; Yu, Y.; Ketterer, N. A.; Flaschenriem, C. J.; Lachicotte, R. J.; Holland, P. L. J. Am. Chem. Soc. 2005, 127, 7857-7870. (1) Huang, D.; Renkema, K. B.; Caulton, K. G. Polyhedron 2006, 25, 459-468. (m) Peterson, A. A.; McNeill, K. Organometallics 2006, 25, 4938-4940. (n) Yamada, S.; Noma, M.; Konno, T.; Ishihara, T. Org. Lett. 2006, 8, 843-845. (o) Rieth, R. D; Brennessel, W. W.; Jones, W. D. Eur. J. Inorg. Chem. 2007, 2839-2847. (p) Yamada, S.; Takahashi, T.; Konno, T.; Ishihara, T. Chem. Commun. 2007, 3679-3681. (q) Braun, T.; Wehmeier, F.; Altenhöner, K. Angew. Chem., Int. Ed. 2007, 46, 5321-5324. (r) Engman, M.; Diesen, J. S.; Paptchikhine, A.; Andersson, P. G. J. Am. Chem. Soc. 2007, 129, 4536-4537. (s) Narumi, T.; Tomita, K.; Inokuchi, E.; Kobayashi, K.; Oishi, S.; Ohno, H.; Fujii, N. Org. Lett. 2007, 9, 3465-3468. (t) Braun, T.; Salomon, M. A.; Altenhöner, K.; Hinze, S. Angew. Chem., Int. Ed. 2009, 48, 1818-1822. (u) Peterson, A. A.; Thoreson, K. A.; McNeill, K. Organometallics 2009, 28, 5982-5991. (v) Künnel, M. F.; Lentz, D. Angew. Chem., Int. Ed. 2010, 49, 2933-2936. (w) Kuehnel, M. F.; Schloeder, T.; Riedel, S.; Nieto-Ortega, B.; Ramirez, F. J.; Lopez Navarrete, J. T.; Casado, J.; Lentz, D. Angew. Chem., Int. Ed. 2012, 51, 2218-2220. (x) Kuehnel, M. F.; Holstein, P.; Kliche, M.; Krueger, J.; Matthies, S.; Nitsch, D.; Schutt, J.; Sparenberg, M.; Lentz, D. Chem. Eur. J. 2012, 18, 10701-10714.

(3) (a) Clark, H. C.; Tsang, W. S. J. Am. Chem. Soc. 1967, 89, 529-533. (b) Hacker, M. J.; Littlecott, G. W.; Kemmitt, R. D. W. J. Am. Chem. Soc. 1973, 47, 189-193. (c) Howard, J. A. K.; Knox, S. A.R.;

н

Terrill, N. J.; Yates, M. I. J. Chem. Soc., Chem. Commun. **1989**, 640–642. (d) Anderson, D. J.; McDonald, R.; Cowie, M. Angew. Chem., Int. Ed. **2007**, 46, 3741–3744.

(4) Ohashi, M.; Kambara, T.; Hatanaka, T.; Saijo, H.; Doi, R.; Ogoshi, S. J. Am. Chem. Soc. 2011, 133, 3256–3259.

(5) Ohashi, M.; Saijo, H.; Shibata, M.; Ogoshi, S. *Eur. J. Org. Chem.* 2013, 443–447.

(6) Olah, G. A.; Kuhn, S. J. Org. Chem. 1964, 29, 2317-2320.

(7) (a) Chen, M.-C.; Roberts, J. A. S.; Marks, T. J. Organometallics 2004, 23, 932–935. (b) Frohn, H.-J.; Giesen, M.; Welting, D.; Bardin, V. V. J. Fluorine Chem. 2010, 131, 922–932. (c) Alcarazo, M.; Gomez, C.; Holle, S.; Goddaed, R. Angew. Chem., Int. Ed. 2010, 49, 5788– 5791. (d) Caputo, C. B.; Stephan, D. W. Organometallics 2012, 31, 27–30.

(8) For examples of structurally characterized Ni(II)-F complexes as a result of C-F bond activation on Ni(0), see: (a) Cronin, L.; Higgitt, C. L.; Karch, R.; Perutz, R. N. Organometallics 1997, 16, 4920-4928.
(b) Sladek, M. I.; Braun, T.; Neumann, B.; Stammler, H.-G. Dalton Trans. 2002, 297-299. (c) Burling, S.; Elliott, P. I.; Jasim, N. A.; Lindup, R. J.; McKenna, J.; Perutz, R. N.; Archibald, S. J.; Whitwood, A. C. Dalton Trans. 2005, 3686-3695. (d) Schaub, T.; Backes, M.; Radius, U. J. Am. Chem. Soc. 2006, 128, 15964-15965. (e) Schaub, T.; Fischer, P.; Steffen, A.; Braun, T.; Radius, U.; Mix, A. J. Am. Chem. Soc. 2008, 130, 9304-9317. (f) Johnson, S. A.; Taylor, E. T.; Cruise, S. J. Organometallics 2009, 28, 3842-3855. (g) Doster, M. E.; Johnson, S. A. Angew. Chem., Int. Ed. 2009, 48, 2185-2187.

(9) For other examples of C-F bond activation on Ni(0), see:
(a) Fahey, D. R.; Mahan, J. E. J. Am. Chem. Soc. 1977, 99, 2501-2508.
(b) Bach, I.; Pörschke, K.-R.; Goddard, R.; Kopiske, C.; Krüger, C.; Rufinska, A.; Seevogel, K. Organometallics 1996, 15, 4959-4966.
(c) Yamamoto, T.; Abla, M. J. Organomet. Chem. 1997, 535, 209-211.
(d) Braun, T.; Foxon, S. P.; Perutz, R. N.; Walton, P. H. Angew. Chem, Int. Ed. 1999, 38, 3326-3329. (e) Braun, T.; Cronin, L.; Higgitt, C. L.; McGrady, J. E.; Perutz, R. N.; Reinhold, M. New J. Chem. 2001, 25, 19-21. (f) Schaub, T.; Radius, U. Chem. Eur. J. 2005, 11, 5024-5030.
(g) Johnson, S. A.; Huff, C. W.; Mustafa, F.; Saliba, M. J. Am. Chem. Soc. 2008, 130, 17278-17280.

(10) (a) Greco, A.; Green, M.; Shakshooki, S. K.; Stone, F. G. A. Chem. Commun. 1970, 1374–1375. (b) Cundy, C. S.; Green, M.; Stone, F. G. A. J. Chem. Soc. A 1970, 1647–1653. (c) Green, M.; Shakshooki, S. K.; Stone, F. G. A. J. Chem. Soc. A 1971, 2828–2834. (d) Mapies, P. K.; Green, M.; Stone, F. G. A. J. Chem. Soc., Dalton Trans. 1973, 388–392. (e) Davies, C. H.; Game, C. H.; Green, M.; Stone, F. G. A. J. Chem. Soc., Dalton Trans. 1974, 357–363. (f) Tolman, C. A.; Seidel, W. C. J. Am. Chem. Soc. 1974, 96, 2774–2780. (g) Tolman, C. A. J. Am. Chem. Soc. 1974, 96, 2780–2789.

(11) Browning, J.; Penfold, B. R. J. Chem. Soc., Chem. Commun. 1973, 198-199.

(12) (a) Van Der Linde, R.; De Jongh, R. O. Chem. Commun. 1971, 563-564. (b) Musco, A.; Kuran, W.; Silvani, A.; Anker, M. W. J. Chem. Soc., Chem. Commun. 1973, 938-939. (c) Otsuka, S.; Yoshida, T.; Matsumoto, M.; Nakatsu, K. J. Am. Chem. Soc. 1976, 98, 5850-5858. (13) Caution! Tetrafluoroethylene is suspected to be carcinogenic. The reaction mixture must be handled in a well-ventilated fume hood. (14) Herrmann, W. A.; Thiel, W. R.; Brossmer, C.; Oefele, K.;

Priermeier, T.; Scherer, W. J. Organomet. Chem. **1993**, 461, 51–60. (15) Visser, A.; van der Linde, R.; de Jongh, R. O. Inorg. Synth. **1976**,

(15) Vissel, K.; van der Ende, K.; de Jongh, K. O. *Inorg. Synth.* **19**/0, 16, 127.

(16) Tatsuno, Y.; Yoshida, T.; Otsuka, S. Inorg. Synth. 1979, 19, 220–223.

(17) Tolman, C. A. Chem. Rev. 1977, 77, 313-348.

(18) (a) Hitchcock, P. B.; McPartlin, M.; Mason, R. Chem. Commun.
1969, 1367–1368. (b) Evans, J. A.; Russell, D. R. Chem. Commun.
1971, 197–198. (c) Guggenberger, L. J.; Cramer, R. J. Am. Chem. Soc.
1972, 94, 3779–3786. (d) Green, M.; Howard, J. A. K.; Spencer, J. L.;
Stone, F. G. A. J. Chem. Soc., Chem. Commun. 1975, 449–451.
(e) Russell, D. R.; Tucker, P. A. J. Chem. Soc., Dalton Trans. 1975, 1752–1757. (f) Howard, J. A. K.; Mitrprachachon, P.; Roy, A. J. Organomet. Chem. 1982, 235, 375–381. (g) Burch, R. R.; Harlow, R.

L.; Ittel, S. D. Organometallics **1987**, *6*, 982–987. (h) Kaschube, W.; Schröder, W.; Pörschke, K. R.; Angermund, K.; Krüger, C. J. Organomet. Chem. **1990**, 389, 399–408. (i) Burrell, A. K.; Clark, G. R.; Rickard, C. E. F.; Roper, W. R.; Ware, D. C. J. Organomet. Chem. **1990**, 398, 133–158. (j) Burrell, A. K.; Clark, G. R.; Rickard, C. E. F.; Roper, W. R. J. Chem. Soc., Dalton Trans. **1991**, 609–614. (k) Curnow, O. J.; Hughes, R. P.; Rheingold, A. L. J. Am. Chem. Soc. **1992**, 114, 3153–3155. (l) Curnow, O. J.; Hughes, R. P.; Mairs, E. N.; Rheingold, A. L. Organometallics **1993**, *12*, 3102–3108.

(19) (a) Lentz, D.; Bach, A.; Buschmann, J.; Luger, P.; Messerschmidt, M. Chem. Eur. J. 2004, 10, 5059–5066. (b) Carlos, J. L., Jr.; Karl, R. R., Jr.; Bauer, S. H. J. Chem. Soc., Faraday Trans. 2 1974, 70, 177–187.

(20) Stalick, J. K.; Ibers, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 5333–5338. (21) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson,

D. G.; Taylor, R. J. Chem. Soc., Dalton Trans. **1989**, S1–S83. (22) Burch, R. R.; Calabrese, J. C.; Ittel, S. D. Organometallics **1988**, 7, 1642–1648.

(23) Most of the results have already reported in a previous communication.⁵

(24) Complex **8** was identified on the basis of the similarity of its 19 F NMR pattern to that observed for the perfluoro-2-butenyl zinc species CF₃(ZnX)C=CFCF₃: Burton, D. J. *J. Fluorine Chem.* **1994**, *66*, 81–85.

(25) Xu, C.; Chen, S.; Lu, L.; Shen, Q. J. Org. Chem. 2012, 77, 10314-10320.

(26) For examples of structurally characterized Pd(II)–F complexes as a result of C–F bond activation on Pd(0), see: (a) Jasim, N. A.; Perutz, R. N.; Whitwood, A. C.; Braun, T.; Izundu, J.; Neumann, B.; Rothfeld, S.; Stammler, H.-G. *Organometallics* **2004**, *23*, 6140–6149. (b) Macgregor, S. A.; Roe, D. C.; Marshall, W. J.; Bloch, K. M.; Bakhmutov, V. I.; Grushin, V. V. *J. Am. Chem. Soc.* **2005**, *127*, 15304– 15321. (c) Braun, T.; Steffen, A.; Schorlemer, V.; Neumann, B.; Stammler, H.-G. *Dalton Trans.* **2005**, 3331–3336. (d) Cargill, M. R.; Sandford, G.; Tadeusiak, A. J.; Yufit, D. S.; Howard, J. A. K.; Kilickiran, P.; Nelles, G. *J. Org. Chem.* **2010**, *75*, 5860–5866.

(27) Some Pd(II)-F bond lengths have been summarized in the literature; see: (a) Ball, N. D.; Kampf, J. W.; Sanford, M. S. Dalton Trans. **2010**, 39, 632–640. (b) Grushin, V. V.; Marshall, W. J. J. Am. Chem. Soc. **2009**, 131, 918–919.

(28) (a) Rheingold, A. L.; Wu, G.; Heck, R. F. Inorg. Chim. Acta 1987, 131, 147–150. (b) Chernyshova, E. S.; Goddard, R.; Pörschke, K.-R. Organometallics 2007, 26, 3236–3251. (c) Babbini, D. C.; Schulhauser, H. R.; Kramer, F. R.; Nichol, G. S.; Hurst, S. K. J. Organomet. Chem. 2011, 696, 3143–3149.

(29) (a) Banger, K. K.; Brisdon, A. K.; Brain, P. T.; Parsons, S.; Rankin, D. W. H.; Robertson, H. E.; Smart, B. A.; Bühl, M. Inorg. Chem. 1999, 38, 5894–5900. (b) Kickbusch, R.; Lentz, D. Chem. Commun. 2010, 46, 2118–2120. (c) Barnes, N. A.; Brisdon, A. K.; Cross, W. I.; Fay, J. G.; Greenall, J. A.; Pritchard, R. G.; Sherrington, J. J. Organomet. Chem. 2000, 616, 96–105. (d) Ristic-Petrovic, D.; Wang, M.; McDonald, R.; Cowie, M. Organometallics 2002, 21, 5172–5181. (e) Brisdon, A. K.; Crossley, I. R.; Pritchard, R. G.; Warren, J. E. Inorg. Chem. 2002, 41, 4748–4755.

(30) Finze, M.; Bernhardt, E.; Zalhres, M.; Willner, H. Inorg. Chem. 2004, 43, 490-505.

(31) Staley, R. H.; Beauchamp, J. L. J. Am. Chem. Soc. 1974, 96, 1604–1606.

(32) Brown, H. C.; Mihm, X. R. J. Am. Chem. Soc. 1955, 77, 1723–1726.

(33) Taube, R.; Wache, S. J. Organomet. Chem. 1993, 459, 335-347.