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PAPER

A mechanistic investigation of carbon-hydrogen bond stannylation: synthesis and characterization of nickel catalysts[†]

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The complex (ⁱPr₃P)Ni(η^2 -Bu₃SnCH=CH₂)₂ (**1a**) was characterized by NMR spectroscopy and was identified as the active species for catalytic C–H bond stannylation of partially fluorinated aromatics, for example in the reaction between pentafluorobenzene and Bu₃SnCH=CH₂, which generates C₆F₅SnBu₃ and ethylene. The crystalline complex (ⁱPr₃P)Ni(η^2 -Ph₃SnCH=CH₂)₂ (**1b**) provides a more easily handled analogue, and is also capable of catalytic stannylation with added Ph₃SnCH=CH₂ and C₆F₅H. Mechanistic studies on **1b** show that the catalytically active species remains mononuclear. The rate of catalytic stannylation is proportional to [C₆F₅H] and inversely proportional to [Ph₃SnCH=CH₂]. This is consistent with a mechanism where reversible Ph₃SnCH=CH₂ dissociation provides (ⁱPr₃P)Ni(η^2 -Ph₃SnCH=CH₂), followed by a rate-determining reaction with C₆F₅H to generate the stannylation products. Kinetic competition reactions between the fluorinated aromatics pentafluorobenzene, 1,2,4,5-tetrafluorobenzene, 1,2,3,5-tetrafluorobenzene, 1,2,4-trifluorobenzene, 1,3,5-trifluorobenzene and 1,3-difluorobenzene all suggest significant Ni–aryl bond formation in the rate-determining step under catalytic conditions. Labelling studies are consistent with an insertion of the hydrogen of the arene into the vinyl group, followed by β-elimination or β-abstraction of the SnPh₃ moiety.

Introduction

Over the past decades, catalytic C-H bond functionalization has undergone significant developments as a practical, economical and green synthetic approach.1 Our research has targeted methods to utilize available and cost effective Ni complexes for C-H activation in place of more expensive noble metal complexes (e.g. Pt, Ir, Rh, Au) that are commonly used in catalytic C-H functionalization reactions. Although Ni complexes have been suggested as better suited for selective C-F activation² for thermodynamic reasons,³ Ni complexes are finding increasing use in the catalytic transformation of C-H bonds.⁴ We have found that partially fluorinated arenes and pyridines can undergo oxidative addition of their C-H bonds to Ni(0) phosphine complexes, which suggests that these complexes should be capable of catalytic C-H bond functionalization.⁵ Previously, we communicated that the reaction of partially fluorinated arenes with Bu₃SnCH=CH₂ resulted in catalytic C-H bond stannylation with the loss of ethylene gas, as shown in Scheme 1.6 The reaction was catalysed by a combination of Ni(COD)₂ and either the nitrogen donor MeNC₅H₄NⁱPr^{2a} or a phosphine donor.

This catalytic functionalization is of interest for several reasons. The products provide useful reagents for Stille coupling reactions.⁷ Although the catalytic borylation of C-H bonds have seen extensive development over the past two decades,^{8,9} and these C-B bond containing compounds are of utility to synthetic chemists due to their use in Suzuki coupling reactions,¹⁰ similar reactions to form other important carbon-heteroatom bonds are lacking. To the best of our knowledge this is the first example of catalytic C-H bond stannylation. Equally intriguing is the mechanism of the conversion. Typical C-H borylation reactions occur with reagents that contain B-H or B-B bonds. The transformation of the Sn-C bond in Scheme 1 to form a new Sn-C in the product with the loss of an ethylene bond provides a unique mechanism of C-H bond functionalization. Although this reaction is currently limited to activated aromatics, for example fluorobenzene has been found to react but not benzene, insight into



Scheme 1

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the mechanism may allow for the design of catalysts capable of the stannylation of a broader scope of substrates. Similarly, knowledge of the reaction mechanism may allow for the design of catalysts capable of converting C–H bonds to other carbon– heteroatom bonds, such as C–Si bonds. In our previously published work, no catalytically active species were identified. In this work, we describe isolable species that perform catalytic C–H bond stannylation, and investigate the mechanism of this reaction.

Results and discussion

The resting state of nickel C-H bond stannylation catalysts

The reaction of Ni(COD)₂ with one equivalent of triisopropylphosphine and two equivalents of Bu₃SnCH=CH₂ provided the species (ⁱPr₃P)Ni(η^2 -Bu₃SnCH=CH₂)₂ (1a), as shown in Scheme 2. The ³¹P{¹H} NMR spectrum displays a resonance at δ 50.2 with ¹¹⁹Sn/¹¹⁷Sn satellite peaks (³J_{SnP} = 29.7 Hz) of appropriate intensities for two coordinated Bu₃SnCH=CH₂ moieties (¹¹⁷Sn, 7.7%, and ¹¹⁹Sn, 8.6% abundant, both *I* = 1/2). The different couplings to ¹¹⁷Sn and ¹¹⁹Sn were not resolved owing to the line-widths and modest difference in gyromagnetic ratios between these isotopes. The ¹¹⁹Sn{¹H} NMR spectrum displayed the expected doublet from coupling to a single phosphorus nucleus. The intensities in the ¹H NMR spectrum were consistent with the proposed formulation, and featured the chemical shifts for the coordinated vinyl moieties shifted several ppm upfield relative to free Bu₃SnCH=CH₂.

Although 1a was an isolable air-sensitive oil, it proved impossible to crystallize, so characterization was limited to multinuclear NMR spectroscopy. We chose to investigate Ph₃SnCH=CH₂ as a reagent that could provide a crystalline and easily handled stannylation catalyst that was more amenable to mechanistic studies. The reaction of Ni(COD)₂ with one equivalent of ¹Pr₃P and two equivalents of Ph₃SnCH=CH₂ provided the complex, $({}^{1}Pr_{3}P)Ni(\eta^{2}-Ph_{3}SnCH=CH_{2})_{2}$ (1b), which was crystallized from toluene at -40 °C. An ORTEP of the solidstate molecular structure as determined by X-ray crystallography is shown in Fig. 1. The structure is as expected, with η^2 -coordinated Ph₃SnCH=CH₂ groups. The two Ph₃Sn substituents arrange themselves so that they are far away from the bulky PⁱPr₃ donor, and on opposite sides of the Ni coordination plane to best avoid each other, which gives a complex with pseudo- C_2 symmetry.

The NMR spectra of **1b** in C_6D_6 displayed resonances consistent with the solid-state structure. The ${}^{31}P{}^{1}H{}$ NMR spectrum



Fig. 1 ORTEP of complex **1b**, shown with 50% thermal ellipsoid parameters. Hydrogen atoms are omitted, and only the *ipso* carbons of the aromatic rings are shown for clarity. Selected bond distances (Å) and angles (°): Ni(1)–C(2), 1.984(7); Ni(1)–C(4), 1.986(7); Ni(1)–C(1), 1.989(7); Ni(1)–C(3), 1.998(8); Ni(1)–P(1), 2.203(2); C(1)–C(2), 1.387 (11); C(3)–C(4), 1.369(12); C(2)–Ni(1)–C(4), 171.0(4); C(2)–Ni(1)–C (3), 131.4(4); C(2)–Ni(1)–P(1), 94.7(2); C(4)–Ni(1)–P(1), 94.0(3); C (1)–Ni(1)–P(1), 135.2(2); C(3)–Ni(1)–P(1), 133.8(3).



displayed a signal at δ 49.8 with satellites separated by 32.3 Hz due to coupling to two equivalent Sn nuclei, and the ¹¹⁹Sn NMR spectrum displayed a doublet at δ –122.0 with the same coupling constant. The ¹H NMR spectrum displayed diastereotopic methyl groups on the ⁱPr₃P donor, consistent with the lack of a mirror plane of symmetry in **1b**, and featured coordinated vinyl moiety environments at δ 3.00, 3.09 and 4.11. The NMR parameters are all comparable to those for **1a**.

Stoichiometric stannylation using 1b

The addition of C_6F_5H to solutions of **1b** in C_6D_6 , shown in Scheme 3, provided conversion to the C-H activation product C₆F₅SnPh₃, as monitored by ¹⁹F and ¹¹⁹Sn{¹H} NMR spectroscopy. The reaction proceeds slowly at room temperature under the conditions used. Two additional nickel-containing products were readily identified from a combination of ${}^{31}P{}^{1}H$, ${}^{1}H$ and ¹¹⁹Sn^{{1}H} NMR spectroscopy. Early in the reaction, a product assigned as $(P^iPr_3)Ni(\eta^2-Bu_3SnCH=CH_2)(\eta^2-C_2H_4)$ (2) was observed, with a ${}^{31}P{}^{1}H$ shift of δ 50.9 and satellites with a 25.2 Hz separation and intensities consistent with coupling to a single Sn environment. The ¹¹⁹Sn{¹H} NMR spectrum of 2 features a doublet at -109.2, with a J_{PSn} of 25.2 Hz, which confirms a single phosphine is coordinated to the metal centre. The ¹H NMR spectrum features diastereotopic Me groups from the ⁱPr₃P moiety and three distinctive multiplets from the coordinated vinyl moiety at δ 3.22, 3.03 and 2.78 that integrate to 1H each. A pair of second-order multiplets at δ 2.94 and 2.66

assigned as the coordinated ethylene moiety integrate to 2H environments each, consistent with rapid rotation about the Ni– $(n^2-C_2H_4)$ bond at room temperature, which exchanges only the trans-disposed hydrogen environments. Before 1b is fully consumed to form 2, the reaction of 1b with C₆F₅H also generates $(P^{i}Pr_{3})Ni(\eta^{2}-C_{2}H_{4})_{2}$ (3), presumably either by reaction of 2 with C₆F₅H or from ligand redistribution between two equivalents of **2**. This known¹¹ complex was identified by its distinctive ¹H NMR spectrum, which features a single ⁱPr₃P methyl environment, a singlet at δ 2.73 for the coordinated C₂H₄ moiety, and a singlet in the ${}^{31}P{}^{1}H{}$ NMR spectrum at δ 52.5. Unfortunately, no further intermediates were observed, to provide insight into the mechanism of C-Sn bond formation. The compositions of 2 and 3, which could not be isolated from these reaction mixtures, were further confirmed by an alternate synthesis. Ethylene was added to a C₆D₆ solution of 1b in an NMR tube, followed by warming the sealed tube to 50 °C in an NMR probe, as shown on the bottom of Scheme 3. This reaction provided equilibrium amounts of 2 and 3, as analysed by multinuclear NMR spectroscopy. The reverse reaction, the replacement of coordinated ethylene in 2 and 3 by Ph₃SnCH=CH₂, regenerated 1b from 2 and 3, and thus allows the catalytic stannylation of C-H bonds with vinyltin reagents.

Rate law and mechanism of catalytic stannylation

The failure to observe any additional intermediates in the stoichiometric reaction of **1b** with C_6F_5H provides little additional insight into the mechanism of this unusual C–H functionalization reaction. The effect of the concentration of nickel catalyst, C_6F_5H , and $Ph_3SnCH=CH_2$ was examined in an attempt to determine the rate law. The determination of exact rate constants in these systems was complicated by small amounts of Ni metal precipitate over the course of reactions, and the multiple components sometimes observed in solution (*e.g.* **1b** and **2**); however, experimentally it proved possible to generate reproducible and informative rate data.

Given the fact that Ni complexes sometimes undergo reactions to form dinuclear complexes that perform transformations involving both C-C bond formation¹² and C-H activation,^{5f,13} we chose to initially verify that the active catalyst remains mononuclear during the rate determining steps of the reaction. By using a stock solution of 0.172 M Ph₃SnCH=CH₂ and 0.177 M C₆F₅H with both a ¹⁹F and ¹H NMR internal standard, different masses of the catalyst (${}^{i}Pr_{3}P$)Ni(η^{2} -Ph₃SnCH=CH₂) **1b** were added to 0.6 mL aliquots to give approximate catalyst concentrations of 0.005 M, 0.01 M, 0.02 M, 0.04 M and 0.08 M, respectively. These solutions do not react appreciably at room temperature, and transferring to an NMR probe preheated to 338 K provided a convenient means to monitor the initial reaction rates, which remained constant for several minutes under these conditions. The results clearly show a linear correlation between reaction rate and catalyst concentration, as shown in Fig. 2. This supports a mononuclear nickel complex as the active species during the rate determining steps of catalytic stannylation. This data also suggests that metallic nickel or nickel nanoparticles are not the active species.

Similar experiments were performed to determine the effect C_6F_5H and $Ph_3SnCH=CH_2$ concentration have on reaction rate.



Fig. 2 Rate of formation of $C_6F_5SnPh_3$ versus the concentration of the catalyst (ⁱPr₃P)Ni(η^2 -Ph₃SnCH=CH₂)₂ (**1b**) in the catalytic stannylation of C_6F_5H with Ph₃SnCH=CH₂.



A stock solution in toluene with concentrations of 0.0052 M of catalyst 1b and 0.212 M Ph₃SnCH=CH₂ was used to make five solutions with concentrations of C₆F₅H ranging from 0.123 to 1.97 M. These were transferred to an NMR probe preheated to 338 K and the initial catalytic reaction rates were monitored. The reaction rate was found to be linearly proportional to the C₆F₅H concentration. A similar experiment where a stock solution with constant catalyst 1b concentration (0.0052 M) and C₆F₅H concentration (0.476 M) was used to make five solutions with different Ph₃SnCH=CH₂ concentrations (0.053, 0.094, 0.218, 0.507, and 1.13 M) showed that reaction rate is inversely proportional to the concentration of Ph₃SnCH=CH₂. With the lowest concentration of Ph₃SnCH=CH₂ used (0.053 M) the initial reaction rate did not remain constant over the course of minutes, but instead slowed rapidly until the reaction was complete after only 20 min. The precipitation of a visibly large amount of nickel suggests that the catalyst is not stable with low Ph₃SnCH=CH₂ concentrations at the temperature used.

The reaction kinetics are suggestive of the mechanism shown in Scheme 4. The initial step is a reversible dissociation of one of the two Ph₃SnCH=CH₂ moieties from **1b** to generate the unobserved species (ⁱPr₃P)Ni(η^2 -Ph₃SnCH=CH₂) (4) with forward rate constant k_1 and reverse rate constant k_{-1} . This step is consistent with the reduction in reaction rate upon increased Ph₃SnCH=CH₂ concentration. The rate-determining step is a reaction between **4** and C₆F₅H, with rate constant k_2 . Though



Fig. 3 Rate of $C_6F_5SnPh_3$ formation *versus* [1b][C_6F_5H]/ [Ph₃SnCH=CH₂] at 338 K for the catalytic stannylation of C_6F_5H with Ph₃SnCH=CH₂, shown for nine different sets of concentrations for the reagents but identical catalyst concentration, [1b]. The solid line is a least squares linear fit.

more than one step may be required to reach 5 from 4, little insight into these steps are provided from the rate data. Complex 5 should readily associate $Ph_3SnCH=CH_2$ to generate 2, which can then lose ethylene to form 4, and is in equilibrium with the favoured species 1b, but 5 is a speculative intermediate, and alternate pathways where the ethylene moiety is lost prior to C–Sn bond formation are viable. An alternate mechanism where arene coordination precedes vinyl dissociation also cannot be discounted.

The rate law given in eqn (1) can be derived using a steadystate approximation for the concentration of intermediate **4**. Under catalytic conditions, a simpler rate law can be derived providing that $k_2[C_6F_5H]$ is much less than $k_{-1}[Ph_3SnCH=CH_2]$, and is shown in eqn (2). The rate law is consistent with a rapid pre-equilibrium formation of **4**, followed by rate determining reaction with C_6F_5H . As expected, a plot of reaction rate *versus* [**1b**][C_6F_5H]/[Ph_3SnCH=CH_2] for the catalytic data provided a linear plot as shown in Fig. 3. The observed rate constant, $(k_1/k_{-1}) \times k_2$, can be estimated as 0.0016(2) s⁻¹ at 338 K from these data.

Steady-state rate law:

$$\frac{d[C_6F_5SnPh_3]}{dt} = \frac{k_1k_2[\mathbf{1b}][C_6F_5H]}{k_{-1}[Ph_3SnCH=CH_2] + k_2[C_6F_5H]}$$
(1)

Under catalytic conditions, where

$$\frac{\mathrm{d}[\mathrm{C}_{6}\mathrm{F}_{5}\mathrm{SnPh}_{3}]}{\mathrm{d}t} = \frac{k_{1}k_{2}[\mathbf{1b}][\mathrm{C}_{6}\mathrm{F}_{5}\mathrm{H}]}{k_{-1}[\mathrm{Ph}_{3}\mathrm{SnCH}=\mathrm{CH}_{2}]}$$
(2)

Various studies were performed to gain insight into the nature of the step that cleaves the arene C–H bond in the catalytic stannylation reaction. The catalytic reaction of **1b** with 1,2,4,5-tetrafluorobenzene-d₁ provided an intramolecular kinetic isotope effect (KIE) of 2.0 for the catalytic conversion to Ph₃Sn–2,3,5,6-C₆F₄D and to Ph₃Sn–2,3,5,6-C₆F₄H, as shown in eqn (3). This is similar to the equilibrium isotope effect we previously reported for the reversible C–H/D activation of 1,2,4,5-tetrafluorobenzene-d₁ to a (Et₃P)₂Ni synthon.^{5c} In contrast, the seemingly closely related alkenylation of the C–H bond in *para*-MeOC₆F₄H using a 3% loading of a catalyst obtained from Ni (COD)₂ and P(Cyp)₃ has been reported to have a KIE of 1.0.^{4/}

Table 1Relative reaction rates compared to pentafluorobenzene incompetition experiments with stannylation using $Ph_3SnCH=CH_2$ andcatalyst 1b

Substrate	Relative rate	$\Delta\Delta G^{\ddagger}$ (kcal mol ⁻¹)	Equiv. H	$\Delta\Delta H^{\ddagger}$ (kcal mol ⁻¹)
C ₆ F ₅ H	1.00	0.00	1	0.00
$1,2,4,5-C_6F_4H_2$	0.93	0.05	2	0.51
$1,2,3,5-C_6F_4H_2$	0.32	0.77	2	1.24
1,2,4-C ₆ F ₃ H ₃	0.047	2.05	1	2.05
1,3,5-C ₆ F ₃ H ₃	0.039	2.18	3	2.92
1,3-C ₆ F ₂ H ₄	0.0021	4.13	1	4.13

From DFT calculations, it was hypothesized that this is due to a mechanism where C–H activation and insertion occur in one step,¹⁴ although this analysis does not explain the similarly low KIE that was reported for the oxidative addition of 1,2,4,5-tetrafluorobenzene-d₁ to an (ⁱPr₃P)₂Ni synthon at 298 K.^{5a} The KIE of 2.0 that we report here supports a typical oxidative addition process, though ligand assistance of this process by a barrierless insertion into the vinyl group step cannot be discounted.



Further support for significant formation of a metal-carbon bond in the C-H bond cleaving step was obtained from a comparison of reaction rate with different fluorinated arenes containing two ortho-F substituents. The rates of reaction relative to pentafluorobenzene for the substrates 1,2,4,5-tetrafluorobenzene, 1,2,3,5-tetrafluorobenzene, 1,2,4-trifluorobenzene, 1,3,5-trifluorobenzene and 1,3-difluorobenzene are shown in Table 1. The relative rates were obtained by competition studies between these substrates at 338 K. The ratio of initial products can be used to generate a difference in Gibbs free energy of activation, $\Delta\Delta G^{\ddagger}$, for these substrates relative to pentafluorobenzene. An estimated difference in enthalpy of activation, $\Delta \Delta H^{\ddagger}$, can be obtained by correcting for the statistical increase in activation that occurs due to the presence of multiple identical sites of activation. Previous computational studies allow for an estimate of aryl-H and aryl-Ni bond dissociation energies.¹⁵ The $\Delta\Delta H^{\ddagger}$ values correlate well with the difference between aryl-H and aryl-Ni bond strengths, as shown in Fig. 4. Both the relative enthalpies and relative bond dissociation energy differences are with respect to pentafluorobenzene, the most reactive fluorinated benzene. There are several interesting trends observed from this plot. The first is that there is a clear correlation between the $\Delta \Delta H^{\ddagger}$ and the difference between predicted C-H and C-Ni bond strengths for these substrates. Secondly, there is a clear effect of meta-substitution, where the substrates with more meta-fluorine substituents react faster than similar substrates with para-fluorine substituents, and this correlates with the greater importance of meta-F substituents towards Ni-C bond strength than C-H bond strength. Interestingly, the plot has an initial slope of ~ 1 for the substrates 1,2,4,5- and 1,2,3,5-tetrafluorobenzene, suggestive of a transition state where Ni-C bond formation and C-H bond cleavage is substantial.



Fig. 4 Plot of the estimated difference in relative Ni–aryl *vs.* H–aryl bond dissociation energies, $\Delta D_{C-H} - \Delta D_{Ni-C}$, *versus* the difference in enthalpy of activation for catalytic stannylation, $\Delta \Delta H^{\ddagger}$, determined from competition reactions between a series of fluorinated substrates. The relative ΔD value and $\Delta \Delta H^{\ddagger}$ values are both with respect to pentafluorobenzene.

For the less fluorinated substrates the $\Delta\Delta H^{\ddagger}$ values increase faster than the difference in dissociation energies between the C–H and Ni–C bonds, perhaps indicative of an earlier transition state with less Ni–C bond formation.

The reaction of pentafluorobenzene-d₁ and *cis*-1-propenyl-tributyltin catalysed by **1b** produced primarily *trans*-propene-d₁, as analysed by ¹H and ¹³C{¹H} NMR spectroscopy and shown in eqn (4); this was incorrectly assigned previously⁶ due to a database error in the assignment of the ¹H NMR spectrum of propene.¹⁶ The ¹H NMR spectrum of the reaction mixture features two resonances for *trans*-propene- d_1 . The hydrogen attached to C-1 that is *cis* to the methyl group was at δ 4.99, with a 17.0 Hz coupling to C-2 hydrogen, and a 1.7 Hz quartet coupling to the methyl group. The C-2 hydrogen geminal to the methyl group further revealed the location of the deuterium label, with a 1.5 Hz cis HD coupling providing a small 1:1:1 triplet splitting of the 17 Hz doublet and 6.4 Hz quartet splitting. The ${}^{13}C{}^{1}H$ NMR spectrum was also definitive regarding the carbon to which the deuterium is attached. Only C-1 has a ${}^{1}J_{CD}$ coupling, which was a 1:1:1 triplet with a distinctive 24.5 Hz coupling at δ 115.6. The C-2 carbon was a singlet at δ 133.6. Reaction with a mixture of pentafluorobenzene-d₁ and a mixture of cis- and trans-1-propenyl-tributyltin catalysed by 1b provided both *cis* and *trans*-propene-d₁, which confirmed that the single isotopomer of propene-d₁ obtained using *cis*-1-propenyltributyltin is not due to initial isomerization of the vinyl reagent.



The relative rates of the different fluorinated substrates, as well as the observed KIE with 1,2,4,5-C₆F₄HD, are consistent with a mechanism where the stannylation reaction has a step where both aryl–H bond breaking and Ni–C bond formation to the fluoroaryl moiety occurs in a concerted manner, leading to oxidative addition. We had previously reported that labelling studies suggested a σ -bond metathesis pathway,⁶ but the reassignment as



trans-propene-d₁ is suggestive of an insertion pathway as illustrated in Scheme 5. The first step proceeding from the binding of the pentafluorobenzene may involve distinct oxidative addition and insertion step, or this may be ligand assisted, with no barrier to insertion upon C–H bond breaking. Either β-elimination or β-abstraction could conceivably lead to the product. Future computational studies may provide greater detail to the exact mechanism of this reaction during and after the rate-determining step.

Conclusions

Experimental evidence shows that monophosphine nickel complexes such as $({}^{i}Pr_{3}P)Ni(\eta^{2}-Bu_{3}SnCH=CH_{2})_{2}$ (1a) and $({}^{i}Pr_{3}P)$ $Ni(\eta^2-Ph_3SnCH=CH_2)_2$ (1b) are the active catalysts for the catalytic stannylation of partially fluorinated aromatics such as pentafluorobenzene. Complex 1b is a solid which allowed for facile handling and thus was amenable to mechanistic studies. The observed kinetic data is consistent with a mononuclear nickel complex throughout the key steps of the catalytic cycle, and with a dissociative step with the loss of a Ph₃SnCH=CH₂ moiety prior to reaction with C₆F₅H. The Sn-C bond forming step appears to occur via β-elimination or β-abstraction after hydrogen insertion into the vinyltin moiety. Competition studies suggest that the rate determining step occurs with significant metal-aryl bond formation with highly fluorinated aromatics. Further studies are needed to better understand the importance of stannyl substituents and ancillary donor choice on both catalyst thermal stability and reaction rate.

Experimental

General procedures

Unless otherwise stated, all manipulations were performed under an inert atmosphere of nitrogen using either standard Schlenk techniques or an MBraun glovebox. Benzene-d₆ was dried by refluxing with Na/K and was then vacuum transferred and degassed by three freeze–pump–thaw cycles. All other solvents were purchased anhydrous from Aldrich and further purified using a Grubbs' type column system¹⁷ produced by Innovative Technology. ¹H, ¹³C{¹H}, ¹⁹F{¹H}, ³¹P{¹H} and ¹¹⁹Sn{¹H} NMR spectra were recorded on a Bruker AMX Spectrometer operating at 300 MHz or where stated at 500 MHz with respect to proton nuclei. ¹H NMR spectra were referenced to residual protons (C₆D₆, δ 7.15) with respect to tetramethylsilane at δ 0.00. ${}^{13}C{}^{1}H$ spectra were referenced relative to solvent resonances (C₆D₆, δ 128.0). ¹⁹F{¹H} NMR spectra were referenced to an external sample of 80% CCl₃F in $\overline{CDCl_3}$ at δ 0.0. ³¹P{¹H} NMR spectra were referenced to an external sample of phosphoric acid at δ 0.0. ¹¹⁹Sn{¹H} NMR spectra were referenced to an external sample of SnMe₄ at δ 0.0. C₆D₆ and toluene-d₈ was purchased from Aldrich. The compounds pentafluorobenzene, PⁱPr₃, tributyl(vinyl)tin, and triphenyltin chloride were purchased from Aldrich. The compounds cis-tributyl(1-propenyl) tin, cis/transtributyl(1-propenyl) tin, bromo-2,3,4,5,6-pentafluorobenzene, bromo-2,3,5,6-tetrafluorobenzene and Bn₃SnCl were purchased from Alfa Aesar. The compounds Ni(COD)₂,¹⁸ C₆F₅D,¹⁹ C₆F₄HD,²⁰ Ph₃Sn(vinyl)²¹ were prepared by literature procedures. Elemental analyses were conducted at the Centre for Catalysis and Materials Research at the University of Windsor.

Synthesis of (ⁱPr₃P)Ni[η²-Bu₃SnCH=CH₂]₂ (1a)

A toluene solution of Ni(COD)₂ (500 mg, 1.82 mmol), P¹Pr₃ (291.3 mg, 1.82 mmol), and Bu₃SnCH=CH₂ (1.15 g, 3.64 mmol, 2 equiv) were reacted immediately at room temperature. The solvent was removed under vacuum leaving an oil. The resultant oil was identified by multinuclear NMR spectroscopy to be (P¹Pr₃)Ni(η^2 -C₂H₃SnBu₃)₂, **1a**. ¹H NMR (toluene-d₈, 25 °C, 300.13 MHz): δ 0.93 (overlapping m, 30H, SnCH₃ and SnCH₂CH₂CH₂, ³J_{HH} = 7.3 Hz); 0.97 and 0.99 (d, 18H, Pr-CH₃, ³J_{HH} = 7 Hz); 1.39 (m with Sn satellites, 12H, SnCH₂, ³J_{HSn} = 60.4 Hz, ³J_{HH} = 7.3 Hz); 1.51 (m, 3H, Pr-CH); 1.62 (m, 12H, SnCH₂CH₂); 2.80 (dd with Sn satellites, 2H, vinyl-CH, ³J_{HH} = 6.6 Hz, ³J_{HH} = 2.3 Hz, ³J_{HSn} = 62.1 Hz); 2.86 (m, 2H, vinyl-CH); 3.35 (ddd with Sn satellites, 2H, vinyl-CH, ²J_{PH} = 15.3 Hz, ³J_{HH} = 6.3 Hz, ³J_{HH} = 4.3 Hz, ²J_{HSn} = 67.8 Hz). ³¹P{¹H} NMR (toluene-d₈, 25 °C, 121.5 MHz): δ 50.2 (s with Sn satellites, 1P, ³J_{PSn} = 29.7 Hz). ¹¹⁹Sn{¹H} (toluene-d₈, 25 °C, 111.96 MHz): δ -35.7 (d, 1Sn, ³J_{SnP} = 30.3 Hz).

Synthesis of $({}^{i}Pr_{3}P)Ni[\eta^{2}-Ph_{3}SnCH=CH_{2}]_{2}$, (1b)

To a solution of triphenylvinyl tin (0.719 g, 1.90 mmol) in 15 mL of toluene was added PⁱPr₃ (0.262 g, 0.95 mmol) and Ni (COD)₂ (0.153 g, 0.95 mmol). The solution was stirred for 30 min and the solvent was removed, leaving a yellow solid. (0.898 g, 97% yield). ¹H NMR (C₆D₆, 25 °C, 500.13 MHz): δ 0.64 (dd, 9H, CH₃, ³J_{HH} = 7.1 Hz, ³J_{HP} = 12.3 Hz); 0.77 (dd, 9H, CH₃, ³J_{HH} = 7.1 Hz, ³J_{HP} = 12.3 Hz); 1.90 (d septet, 3H, CH, ²J_{HP} = 7.2 Hz, ³J_{HH} = 6.9 Hz); 3.00 (dd with Sn satellites, 2H, vinyl-CH, ²J_{HH} = 11.7 Hz, ³J_{HH} = 4.1 Hz, ²J_{HSn} = 151 Hz); 3.09 (dd, 2H, vinyl-CH, ³J_{HH} = 14.8 Hz, ²J_{HH} = 9.4 Hz); 4.11 (ddd with Sn satellites, 2H, vinyl-CH, ²J_{HH} = 3.0 Hz, ³J_{HSn} = 61.6 Hz); 7.15 (m, 12H, Ar-H); 7.6 (m with Sn satellites, 12H, Ar-H, ³J_{HSn} = 45.2 Hz). ³¹P{¹H} NMR (C₆D₆, 25 °C, 202.46 MHz): δ 49.8 (s with Sn satellites,

1P, ${}^{3}J_{PSn} = 30.7$ Hz). ${}^{119}Sn\{{}^{1}H\}$ (toluene, 25 °C, 111.96 MHz): δ -122.0 (d, 1Sn, ${}^{3}J_{SnP} = 32.4$ Hz). Anal. Calcd for C₄₉H₅₇NiPSn₂: C, 60.48; H 5.90. Found: C, 60.29; H 5.79%.

Stoichiometric stannylation of C₆F₅H with 1b

The addition of 40 mg C_6F_5H to 40 mg **1b** in benzene-d₆ was monitored by ¹H, ¹⁹F and ¹¹⁹Sn NMR spectroscopy. The product $C_6F_5SnPh_3$ and complexes **2** and **3** were the only species observed. The assignment was confirmed by consistency with the reaction products observed in the reaction of **1b** and ethylene, provided below.

Catalysis and characterization of C₆F₅SnPh₃

A solution of pentafluorobenzene (0.052 g, 0.309 mmol) in C₆D₆ was added to a mixture of triphenyl(vinyl)tin (0.039 g, 0.103 mmol) and (ⁱPr₃P)Ni[η²-Ph₃SnCH=CH₂]₂ (0.003 g, 0.0031 mmol). The solution was heated at 338 K for 0.5 h to allow the reaction to go to completion (95% yield by NMR spectroscopy). ¹H NMR (C₆D₆, 65 °C, 300.13 MHz): δ 7.28 (m, 17H, Ar-*H*); 7.70 (m with Sn satellites, 8H, Ar-*H*, ²J_{HSn} = 55.0 Hz). ¹⁹F{¹H} NMR (C₆D₆, 65 °C, 282.40 MHz): δ –118.6 (AA' MM'N second order with Sn satellites, 2F, 2,6-Ar-*F*); –151.0 (tt with Sn satellites, 1F, 4-Ar-*F*, ³J_{FF} = 19.6 Hz, ⁴J_{FF} = 2.7 Hz); –159.7 (AA'MM'N second order, 2F, 3,5-Ar-*F*). ¹¹⁹Sn{¹H} NMR (C₆D₆, 25 °C, 111.96 MHz): δ –137.9 (m).

Reaction of 1b with ethylene

A solution of **1b** (40 mg) in benzene- d_6 was transferred into an NMR tube equipped with a Teflon valve. The nitrogen atmosphere was removed by two freeze–pump–thaw cycles, and an atmosphere of ethylene was added. The sample was heated at 50 °C for 30 minutes. The probe was then cooled to 25 °C and spectra were collected consistent with **2** and **3**.

Reaction of C₆F₅D, Bu₃Sn(*cis,trans*-propenyl), and 5% catalyst loading (ⁱPr₃P)Ni(η^2 -Ph₃SnCH=CH₂)

A solution of C_6F_5D (0.046 g, 0.2718 mmol), Bu₃Sn(*cis,trans*propenyl) (0.090 g, 0.2718 mmol) in 1 mL of C_6D_6 was mixed with (ⁱPr₃P)Ni(η^2 -Ph₃SnCH=CH₂) (0.013 g, 0.0136 mmol) and placed in a preheated NMR probe at 338 K. After 20 min the ¹H NMR spectrum was used to confirm that both *cis*-propene-d₁ and *trans*-propene-d₁ are produced in equal amounts.

Characterization of (ⁱPr₃P)Ni(η²-Ph₃SnCH=CH₂)(η²-C₂H₄), (2)

¹H NMR (C₆D₆, 25 °C, 500.13 MHz): δ 0.85 (dd, 9H, CH₃, ²J_{HH} = 7 Hz, ³J_{HP} = 12.5 Hz); 0.90 (dd, 9H, CH₃, ²J_{HH} = 7 Hz, ³J_{HP} = 12.5 Hz); 2.00 (m, 3H, CH); 2.70 (2nd order m, 2H, CHH on η^2 ethylene); 2.97 (2nd order m, 2H, CHH on η^2 ethylene); 2.79 (dd, 1H, vinyl-CH, ³J_{HH} = 15.5 Hz, ²J_{HH} = 6.5 Hz); 3.25 (ddd, 1H, vinyl-CH, ³J_{HH} = 12 Hz, ²J_{HH} = 6.5 Hz); 3.25 (ddd, 1H, vinyl-CH, ³J_{HH} = 12 Hz, ³J_{HH} = 15.5 Hz, ³J_{HP} = 3.5 Hz); 7.19 (m, H, Ar-H); 7.60 (m, 2H, Ar-H); 7.78 (m with Sn satellites, 2H, Ar-H, ³J_{HSn} = 44.5 Hz). ³¹P{¹H} NMR (C₆D₆, 25 °C, 121.54 MHz): δ 50.89 (s with Sn satellites, 1P, ${}^{3}J_{\text{SnP}} =$ 24.3Hz). ${}^{119}\text{Sn}\{{}^{1}\text{H}\}$ (C₆D₆, 25 °C, 186.48 MHz): δ –109.8 (d, 1Sn, ${}^{3}J_{\text{SnP}} =$ 24.9 Hz).

Characterization of $({}^{i}Pr_{3}P)Ni(\eta^{2}-C_{2}H_{4})_{2}$, (3)

¹H NMR (C₆D₆, 25 °C, 500.13 MHz): δ 0.97 (dd, 18H, CH₃, ²J_{HH} = 7.5 Hz, ³J_{HP} = 12.5 Hz); 1.93 (m, 3H, CH); 2.76 (s, 4H, C₂H₄). ³¹P{¹H} NMR (C₆D₆, 25 °C, 121.54 MHz): δ 52.46 (s, 1P).

Catalytic reaction rate versus [catalyst]

A stock solution of the reagent Ph₃SnCH=CH₂ (232 mg, 0.62 mmol), the reagent C₆F₅H (107 mg, 0.64 mmol), the internal standard C₆H₅F (60 mg, 0.62 mmol) and the internal standard hexamethyldisiloxane (HMDSO) (100 mg, 0.62 mmol) were dissolved in toluene and the solution was diluted to 3.6 mL, to provide a solution that is 0.172 M of Ph₃SnCH=CH₂, C₆H₅F and HMDSO and 0.177 M of C₆F₅H. Approximate masses of 3, 6, 12, 24 and 48 mg of the catalyst $({}^{1}Pr_{3}P)Ni(\eta^{2}-Ph_{3}SnCH=CH_{2})$ were weighed into a vial and 0.6 mL of the stock solution was added to give approximate catalyst concentrations of 0.005 M, 0.01 M, 0.02 M, 0.04 M and 0.08 M, respectively. The resulting solution was transferred to an NMR tube. The samples did not react appreciably at room temperature, and were introduced into an NMR spectrometer probe preheated to 338 K. The rate of reaction production was monitored via concentration of C₆F₅SnPh₃ formed versus time. The concentration of C₆F₅SnPh₃ formed was estimated from integration of the ¹⁹F NMR signals compared to the internal standard C₆H₅F. Plotting concentration of product formed versus time, the slope was found to be linear for extended periods of time and was recorded as the reaction rate. The observed reactions rates were found to be 1.347×10^{-5} , 2.162×10^{-5} , 3.961×10^{-5} , 8.387×10^{-5} and 1.794×10^{-4} M s⁻¹, respectively. Plotting catalyst concentration versus the respective reaction rates, yields a linear slope.

Catalytic reaction rate versus [C₆F₅H]

A stock solution of the reagent Ph₃SnCH=CH₂ (400 mg, 1.06 mmol), the catalyst $({}^{i}Pr_{3}P)Ni(\eta^{2}-Ph_{3}SiCH=CH_{2})_{2}$, 1b, (25 mg, 0.026 mmol) and the internal standard C_6H_5F (100 mg, 1.04 mmol) were dissolved in 5 mL toluene to provide a solution that was 0.212 M, 0.0052 M and 0.208 M in these three components, respectively. Approximate masses of 12, 25, 50, 100 and 200 mg of C₆F₅H were weighed directly into five 5 mm NMR tubes, and the stock solution was added to dilute the solution to a total volume of 0.64 mL. The samples did not react appreciably at room temperature. The samples were introduced into an NMR spectrometer probe preheated to 338 K, and the concentration of C₆F₅SnPh₃ was monitored versus time by ¹⁹F NMR spectroscopy. The slope of this plot was found to be linear for extended periods, and the slope was recorded as the reaction rate. The concentrations of C₆F₅H for the five separate samples were estimated from integration compared to the internal standard to be 0.123, 0.218, 0.480, 0.82 and 1.97 M, and the

observed reaction rates were 3.64×10^{-6} , 6.76×10^{-6} , 1.68×10^{-5} , 2.72×10^{-5} , and 7.64×10^{-5} M s⁻¹, respectively.

Catalytic reaction rate versus [Ph₃SnCH=CH₂]

A stock solution of the reagent Ph₃SnCH=CH₂ (100 mg, 0.265 mmol), the reagent C_6F_5H (400 mg, 2.38 mmol) the catalyst (${}^{i}Pr_{3}P$)Ni(η^{2} -Ph₃SnCH=CH₂)₂ 25 mg, 0.026 mmol) and the internal standard C₆H₅F (100 mg, 1.04 mmol) was dissolved in 5 mL toluene, to provide a solution that was 0.053 M, 0.476 M 0.0052 M and 0.208 M in these four components, respectively. Five NMR tubes were loaded with 0, 10, 30, 70 and 162 mg of Ph₃SnCH=CH₂, and the stock solution was added to dilute the solution to a total volume of 0.64 mL. No reaction was observed at room temperature. The samples were introduced into an NMR spectrometer probe preheated to 338 K, and the rate of production of concentration of C₆F₅SnPh₃ was monitored versus time by ¹⁹F NMR spectroscopy. The slope of this plot was found to be linear for extended periods, and the slope was recorded as the reaction rate. The initial concentrations of Ph₃SnCH=CH₂ for the five separate samples are calculated to be 0.053, 0.094, 0.177, 0.342, and 0.722 M, and the observed reaction rates were 1.18×10^{-4} , 4.39×10^{-5} , 1.80×10^{-5} , 7.45×10^{-6} , and 3.12×10^{-6} 10^{-6} M s⁻¹, respectively.

Reaction of 1,2,4,5-C₆F₄HD, Ph₃Sn(vinyl), and 5% catalyst loading (${}^{1}Pr_{3}P$)Ni(η^{2} -Ph₃SnCH=CH₂)

A solution of 1,2,4,5-C₆F₄HD (0.015 g, 0.103 mmol), triphenyl (vinyl)tin (0.039 g, 0.103 mmol) in 1 mL of C₆D₆ was mixed with $({}^{i}Pr_{3}P)Ni(\eta^{2}-Ph_{3}SnCH=CH_{2})$ (0.005 g, 0.005 mmol) and placed in a preheated NMR probe at 338 K. The ¹⁹F NMR spectrum of the reaction mixture was recorded after 5 min of initiation of the reaction in order to determine the initial deuterium isotope effect for C-H vs. C-D activation. Activation of hydrogen over deuterium can be confirmed by a ~ 0.3 ppm shift of any ortho fluorine adjacent to the remaining deuterium in the product and the isotope effect can be determined through integration. Oxidative addition is favoured for C-H over C-D bonds, and the ratio of integrals for the products Ph₃Sn(2,3,5,6- C_6F_4D) and $Ph_3Sn(2,3,5,6-C_6F_4H)$ were found to be 2.0:1 at 338 K. ¹⁹F{¹H} NMR (C₆D₆, 65 °C, 282.40 MHz): -118.7 (AA'BB' second order, 3F, 2,6-Ar-F); -136.9 (AA'BB' second order, 1F, 3,5-Ar(H)-F); -137.2 (AA'BB' second order, 2F, 3,5-Ar(D)-F).

Fluorinated aromatic competition reactions

A stock solution of Ph₃SnCH=CH₂ (400 mg, 1.06 mmol), catalyst **1b** (30 mg, 0.031 mmol) and the internal standard monofluorobenzene (100 mg, 1.04 mmol) were dissolved in 5 mL of toluene. Equimolar amounts of fluorinated aromatics were added. The following proportions were used with each competition: (a) C_6F_5H (100 mg, 0.595 mmol) *vs.* 1,2,4,5- $C_6F_4H_2$ (89 mg, 0.595 mmol); (b) 1,2,4,5- $C_6F_4H_2$ (100 mg, 0.666 mmol) *vs.* 1,2,3,5- $C_6F_4H_2$ (100 mg, 0.666 mmol); (c) 1,2,3,5- $C_6F_4H_2$ (100 mg, 0.666 mmol); vs. 1,2,4- $C_6F_3H_3$ (88 mg, 0.666 mmol); (d) 1,2,4- $C_6F_3H_3$ (100 mg, 0.757 mmol) *vs.* 1,3,5-

 $C_6F_3H_3$ (100 mg, 0.757 mmol); and (e) 1,2,4- $C_6F_3H_3$ (100 mg, 0.757 mmol) vs. 1,3- $C_6F_2H_4$ (86 mg, 0.757 mmol). Soon after the reactants were mixed ¹⁹F NMR spectroscopy was used to analyze the sample at 338 K. At this point the conversion was minimal relative to the starting materials, which allowed integration of the products ¹⁹F NMR resonances to be used to determine relative rates. Using the relative rate constant, the change in Gibbs free energy of activation and change in enthalpy of activation *versus* pentafluorobenzene were also determined.

Reaction of C_6F_5D , $Bu_3Sn(cis,trans-propenyl)$, and 5% catalyst loading (ⁱPr₃P)Ni(η^2 -Ph₃SnCH=CH₂)

A solution of C_6F_5D (0.046 g, 0.2718 mmol), Bu₃Sn(*cis,trans*propenyl) (0.090 g, 0.2718 mmol) in 1 mL of C_6D_6 was mixed with **1b** (0.013 g, 0.0136 mmol) and placed in a preheated NMR probe at 338 K. After 20 min the ¹H NMR spectrum was used to confirm that both the ratio of *cis*-propene-d₁ to *trans*-propene-d₁ was equal to the *trans* : *cis* ratio of the Bu₃Sn-propenyl starting material.

X-ray crystallography

The X-ray structure of 1b was obtained at -100 °C, with the crystal covered in Paratone and placed rapidly into the cold N₂ stream of the Kryo-Flex low-temperature device. The data was collected using the SMART²² software on a Bruker APEX CCD diffractometer using a graphite monochromator with MoKa radiation ($\lambda = 0.71073$ Å). A hemisphere of data was collected using a counting time of 10 s per frame. Data reductions were performed using the SAINT²³ software, and the data were corrected for absorption using SADABS.²⁴ The structures were solved by direct methods using SIR97²⁵ and refined by full-matrix leastsquares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELX-97²⁶ and the WinGX²⁷ software package, and thermal ellipsoid plots were produced using ORTEP32.²⁸ The hydrogen atoms on the coordinated carbon atoms of the vinyl moiety were located in the electron-density difference map and their positions were refined. The remaining hydrogen atoms were placed in idealized locations using the AFIX command in SHELX.

Details of crystal data, data collection, and structure refinement data for **1b**: empirical formula, $C_{49}H_{57}NiPSn_2$; formula weight, 973.01 g mol⁻¹; monoclinic; a = 9.6240(12), b = 44.359(6), c = 11.7793(11) Å; $\beta = 114.822(8)^{\circ}$; V = 4564.1(9) Å³; space group $P2_1/c$; Z = 4; $D_{calc} = 1.416$ g cm⁻³; μ (MoK α) = 1.560 mm⁻¹; temperature = 173(2) K; $2\theta_{max}$ 50.0°; total no. of reflns = 43 373; no. unique reflns = 8037; $R_{int} = 0.0527$; transmission factors = 0.93–0.56; no. with $I \ge 2\sigma(I) = 6953$; no. variables = 508, reflections/parameters = 15.3, wR² (all data) = 0.121; GOF = 1.274; residual density = 1.14; -1.363 e⁻ Å⁻³.

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