Supporting Information for:

Heck Coupling of Olefins to Mixed Methyl/Thienyl Monolayers on Si(111) Surfaces

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A. XP spectra

Figure SA1. C 1s (100 scans), Si 2p (40 scans), S 2s (200 scans), and survey (4 scans)

XP spectra of a mixed CH$_3$/SC$_4$H$_3$-Si(111) with $\theta_{SC_4H_3} \approx 0.20$. 
Figure SA2. C 1s (15 scans), Si 2p (20 scans), S 2s (30 scans), and survey (2 scans) XP spectra of a mixed CH₃/SC₄H₃-Si(111) with $\theta_{SC_4H_3} \approx 0.35$. 
**Figure SA3.** Br 3d (50 scans), Si 2p (30 scans), S 2s (60 scans), and survey (4 scans) XP spectra of a mixed CH\textsubscript{3}/SC\textsubscript{4}H\textsubscript{2}Br-Si(111) with $\theta_{\text{SC}_4\text{H}_3} \approx 0.25$, $\theta_{\text{Br-SC}_4\text{H}_2} = 0.16$, and $\theta_{\text{Br-Si}} = 0.05$. 
Figure SA4. Br 3d (100 scans), F 1s (120 scans), Pd 3d (120 scans), Si 2p (33 scans), S 2s (30 scans), and survey (2 scans) XP spectra of a mixed CH₃/FSsty-SC₄H₂-Si(111) with θ_{SC₄H₂} ≈ 0.20 and θ_{FSsty} = 0.11.
Figure SA5. F 1s (150 scans), S 2s (200 scans), Si 2p (70 scans), and survey (4 scans) XP spectra of CH₃SC₄H₃-Si(111) after exposure to Pd(PPh₃)₄ (toluene, RT), then 4-fluorostyrene (DMF, 100 °C), but with no exposure to NBS. No F was detected using XPS.
Figure SA6. Br 3d (250 scans), Pd 3d (250 scans), Si 2p (70 scans), and survey (40 scans) XP spectra of a Br-Si(111) surface after exposure to Pd(PPh₃)₄ (toluene, RT). θₚd = 0.06.
Figures SA7. S 2s (150 scans), Br 3d (200 scans), Pd 3d (200 scans), F 1s (100 scans), Si 2p (20 scans), and survey (4 scans) XP spectra of Pd activated Br-Si(111) after reaction with 4-fluorostyrene (DMF, 100 °C). Pd catalyzed hydrosilylation takes place under these conditions.
Figure SA8. Br 3d (250 scans), Pd (250 scans), Si (70 scans), and survey (4 scans) spectra of H-Si(111) after exposure to Pd(PPh₃)₄ (toluene, RT).
Figure SA9. Br 3d (150 scans), Si 2p (40 scans), Pd 3d (100 scans), and survey (4 scans) spectra of CH₃SC₄H₂Br-Si(111) surfaces after exposure to Pd(dba)₂ (toluene, RT).
Figures SA10. Fe (200 scans) XP spectrum of the CH$_3$/Fe-SC$_4$H$_2$-Si(111) surface after cyclic voltammetry experiments. $\theta_{\text{Fe}} = 0.082$, and $\theta_{\text{SC}_4\text{H}_3 + \text{SC}_4\text{H}_2-\text{Fe}} = 0.24.$
B. Cyclic Voltammetry

Figure SB1. Cyclic voltammogram of vinyl ferrocene modified n-Si, $\theta_{Fc} = 0.12$. 1.0 M LiClO$_4$ in acetonitrile, 2500 mV s$^{-1}$. The asymmetry is due to the electron transfer dynamics at non-degenerately doped semiconductor electrodes. The small splitting, 0.01 V, between the potentials where the cathodic and anodic currents exhibited peaks suggests facile electron transfer through the conjugated linker.
C. Substrate overlayer model

The substrate overlayer model can be used here, as described in the text:

\[ d_{ov} = \ln \left( \frac{I_{ov}}{I_{Si}} \frac{SF_{Si}}{SF_{ov}} \frac{\rho_{Si}}{\rho_{ov}} \right) + 1 \lambda \sin(\theta) \]

\( d_{ov} \) is the thickness of the overlayer, \( I_{ov} \) and \( I_{Si} \) are the signal intensity of the C_{Si} and Si_{bulk} 2p(3/2) XPS signals respectively. \( SF_{ov} \) and \( SF_{Si} \) are the modified sensitivity factors for the Si 2p(3/2) and C 1s signals. \( \rho_{ov} \) (0.14 mol cm\(^{-3}\) based on \( d_{CH3} \)) and \( \rho_{Si} \) (0.083 mol cm\(^{-3}\) based on Si crystal structure) are the atomic density of C in the overlayer and in the Si crystal. \( \lambda \) is the mean free path of electrons, determined empirically as 3.5 nm for Si 2p electrons,\{haber; laibinis 1991; tufts 1992\} and \( \theta \) is the angle from the horizontal to the detector (35°).

\[ SF_x = SF_{scof} \left( \frac{1486 - BE_{x}}{1486 - 284} \right)^{S_{exp}} \]

Modified sensitivity factors are calculated based on the binding energy of the electron (BE), and the configuration dependent sensitivity exponent (\( S_{exp} \)). In this case, \( S_{exp} = 0.6 \) and \( SF_{Si} = 0.9 \) for the 2p electrons.

\( d_{ov} = 0.097 \) for the CH3-Si(111) surface. \( d_{o} \) for a methyl group is 0.234 nm, and thus gives 0.41 ML CH3 groups. 1 monolayer of CH3 groups having a density of 1.89 × 10\(^{15}\) (based on \( d_{CH3} = 2.3 \) Å), gives \( \Gamma_{CH3} = 8.0 \times 10^{14} \) cm\(^{-2}\) or \( \theta_{CH3-Si} = 0.99 \pm 0.06 \) (based on \( \Gamma_{Si(111)} = 7.83 \times 10^{14} \) cm\(^{-2}\)).

Similarly, the fractional overlayer equation

\[ \Phi_{ov} = \left( \frac{\lambda \sin \theta}{a_{ov}} \right) \left( \frac{SF_{Si}}{SF_{ov}} \right) \left( \frac{\rho_{Si}}{\rho_{ov}} \right) \left( \frac{I_{ov}}{I_{Si}} \right) \]

gives a similar value of \( \Phi_{ov} = 0.43 \) or \( \theta_{CH3-Si} = 1.04 \pm 0.06 \).
D. Molecular Modelling of Surface Species

Figure SD1. Geometry optimized molecular model of the proposed Pd-activated species, namely CH$_3$/Br-Pd(PPh$_3$)$_2$-SC$_4$H$_2$-Si(111), on a small portion of hexagonal Si(111) surface: (left) space-filling model of the species, (middle) ball-and-stick model of the same species, (right) ball-and-stick model of the species with H's omitted for clarity. The overall 'planar' rigidity of the Si(111) framework was in this case was enforced by substituting methyl groups in the basal plane. The Pd-ligated surface was modeled using the 3-21G basis set and the functional PW91.$^1$ The geometries were optimized to a low root mean square gradient (GRMS < 0.001) in Firefly,$^2$ and the resulting models were visualized in Mercury.$^3$
Figure SD2. Geometry optimized molecular model of the proposed Pd-activated species, namely CH$_3$/Br-Pd(PPh$_3$)$_2$-SC$_4$H$_2$-Si(111), on a small portion of hexagonal Si(111) surface: (above) ball-and-stick model of the species with H's omitted for clarity. The overall 'planar' rigidity of the Si(111) framework was in this case was enforced by substituting methyl groups in the basal plane. The Pd-ligated surface was modeled using the 3-21G basis set and the functional PW91. The geometries were optimized to a low root mean square gradient (GRMS < 0.001) in Firefly, and the resulting models were visualized in Mercury.

References
(3) http://www.ccdc.cam.ac.uk/free_services/mercury/downloads/