Hydrosilylations Catalyzed by Iron-Doped Metal–Organic Layers

**Significance:** Metal–organic layers (MOLs) composed of \([\text{Hf}_6\text{O}_4(\text{OH})_4(\text{HCO}_2)_6]\) secondary building units and 4,4′,4′′-benzene-1,3,5-triyltribenzoate (BTB) bridging ligands were prepared. The MOL structures were doped with 4′-(4-carboxylatephenyl)-2,2′:6′,2″-terpyridine-5,5″-dicarboxylate (TPY) and FeBr₂ to afford the solid material Fe-TPY-MOL, which catalyzed the hydrosilylation of terminal olefins. For example, the reaction of styrene (1) with phenylsilane (2) proceeded in the presence of Fe-TPY-MOL to give the linear silane 3 in quantitative yield.

**Comment:** In the reaction of styrene (1) with phenylsilane (2), the Fe-TPY-MOL catalyst showed a better performance than the metal–organic framework-based catalysts Fe-TPY-MOF1 (prepared from an interlocked Hf-MOF instead of the MOLs), Fe-TPY-MOF2 (prepared from a stacked Hf-MOF instead of the MOLs), or the homogeneous counterpart Fe-TPY (prepared from FeBr₂, TPY, and NaBHEt₃). When Fe-TPY-MOF1, Fe-TPY-MOF2, and Fe-TPY were employed as catalysts for the reaction, the ratios of products 3 and 4 were 0:0, 30:0, and 3:43, respectively.

**Examples:**

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\[
\text{Ph} \quad 1 + \quad \text{H}_2\text{SiPh} \quad 2 \quad \xrightarrow{\text{Fe catalyst}} \quad \text{Ph} + \quad \text{H}_2\text{SiPh} \quad 3 \quad \text{(linear)} \quad + \quad \text{Ph} + \quad \text{H}_2\text{SiPh} \quad 4 \quad \text{(branched)}
\]
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**Preparation:**

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\[
\text{TPY} + \text{BTB} \quad \xrightarrow{\text{1. Hf}^+} \quad \text{Fe-TPY-MOL}
\]
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<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Yield (%)</th>
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<tbody>
<tr>
<td>Fe-TPY-MOL (0.02 mol%)</td>
<td>100 / 0</td>
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<tr>
<td>Fe-TPY-MOF1 (0.02 mol%)</td>
<td>0 / 0</td>
</tr>
<tr>
<td>Fe-TPY-MOF2 (0.02 mol%)</td>
<td>30 / 0</td>
</tr>
<tr>
<td>homogeneous Fe-TPY (0.2 mol%)</td>
<td>3 / 43</td>
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