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# High-Selectivity Bis(imino)pyridine Iron Catalysts for the Hydrosilylation of 1,2,4-Trivinylcyclohexane

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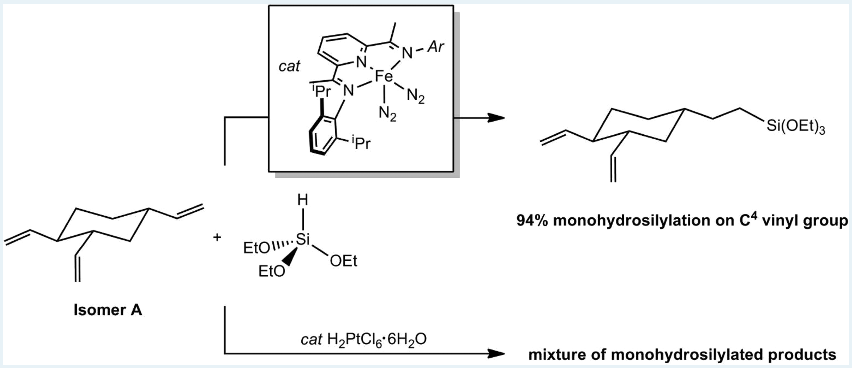
Supporting Information

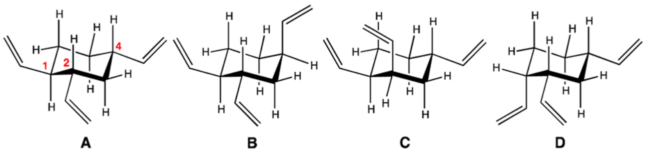


**ABSTRACT:** Aryl-substituted bis(imino)pyridine iron dinitrogen complexes are active for the hydrosilylation of 1,2,4-trivinylcyclohexane with tertiary alkoxy silanes, a process used in the manufacture of low rolling resistance tires. The iron compounds exhibit unprecedented selectivity for the monohydrosilylation of the desired 4-alkene that far exceeds results obtained with commercially used platinum compounds.

**KEYWORDS:** *iron, catalysis, hydrosilylation, silane, trivinylcyclohexene*

Selectivity and specificity are often enabling features of homogeneous catalysis.[1,2] Structure−activity relationships and rational ligand design are well-demonstrated approaches to modulate and improve reactivity to achieve a desired outcome. A particularly intriguing challenge for selective catalysis is the anti-Markovnikov hydrosilylation of the mixture of the four stereoisomers (A−D) present in commercial samples of 1,2,4-trivinylcyclohexane (TVCH, Chart 1). These hydrosilylation products have a wide range of applications, including silicone coatings,[3−5] aerospace lubricants,[6] cross-linkers for contact lens materials,[7] and coupling agents in silica-filled automotive tires with low rolling resistance and improved wear.[8] While the other applications necessitate hydrosilylation of all three alkenes, the tire chemistry requires the addition of a single [Si−H] from an alkoxysilane to a single alkene. Two vinyl groups must be left intact, ideally those that are adjacent, for subsequent functionalization with sulfur and cross-linking into the rubber matrix. Thus, it is advantageous to have the monohydrosilylation occur exclusively at the 4-position (Chart 1).[9] Alkoxysilanes are required for bonding to a silica surface.

**Chart 1. Four Stereoisomers (A−D) of 1,2,4-Trivinylcyclohexane**



Performing the hydrosilylation of the isomers of TVCH with commercially employed platinum catalysts such as Karstedt's and Speier's catalysts, $Pt_2\{[CH_2{=}CH)SiMe_2]_2O\}_3$ and $H_2PtCl_6{\cdot}6H_2O/{}^iPrOH$,[10,11] yields a mixture of products arising from multiple silylations with poor regioselectivity among the various alkene positions.[8] Even when a slow addition of a substoichiometric amount of trialkoxysilane ($(RO)_3Si{-}H$/TVCH ratio of 0.8:1) is used, a 50:30 mixture (by weight) of mono to disilylated products is obtained, with the balance being unreacted TVCH isomers. Within the monoaddition products, the hydrosilylation occurs statistically at the three different alkene positions. This lack of selectivity requires purification by

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**Table 1. Evaluation of Bis(imino)pyridine Iron Dinitrogen and Traditional Pt Complexes for the Hydrosilylation of the Isomers of TVCH with MD′M or TES.**[a]

| compound | TVCH | silane | time (min) | remaining silane (mol %) | remaining TVCH (mol %) | mono-silylation (mol %) | disilylation (mol %) |
|---|---|---|---|---|---|---|---|
| $(^{iPr}PDI)Fe(N_2)_2$ | A | MD′M | 180 | 30 | 37 | 33 (98% C4) | trace |
| $(4\text{-}NMe_2\text{-}^{iPr}PDI)Fe(N_2)_2$ | A | MD′M | 180 | 17 | 19 | 60 (98% C4) | 4 |
| $[(^{iPr,Et}PDI)FeN_2]_2(\mu_2\text{-}N_2)$ | A | MD′M | 60 | trace | 16 | 72 (94% C4) | 12 |
| $[(^{Et}PDI)FeN_2]_2(\mu_2\text{-}N_2)$ | A | MD′M | <5 | trace | 7 | 74 (92% C4) | 19 |
| $[(^{Me}PDI)FeN_2]_2(\mu_2\text{-}N_2)$ | A | MD′M | <5 | trace | 11 | 72 (92% C4) | 17 |
| $(^{iPr}PDI)Fe(N_2)_2$ | A | TES | <5 | trace | 21 | 62 (94% C4) | 16 |
| $(4\text{-}NMe_2\text{-}^{iPr}PDI)Fe(N_2)_2$ | A | TES | <5 | trace | 20 | 64 (95% C4) | 16 |
| $[(^{iPr,Et}PDI)FeN_2]_2(\mu_2\text{-}N_2)$ | A | TES | <5 | trace | 27 | 54 (86% C4) | 19 |
| $[(^{Et}PDI)FeN_2]_2(\mu_2\text{-}N_2)$ | A | TES | <5 | trace | 19 | 58 (81% C4) | 23 |
| $[(^{Me}PDI)FeN_2]_2(\mu_2\text{-}N_2)$ | A | TES | <5 | trace | 30 | 49 (78% C4) | 21 |
| $[(^{Et}PDI)FeN_2]_2(\mu_2\text{-}N_2)$ | B | MD′M | <5 | trace | 12 | 56 (70% C4) | 32 |
| $[(^{Et}PDI)FeN_2]_2(\mu_2\text{-}N_2)$ | B | TES | <5 | trace | 25 | 43 (78% C4) | 32 |
| $[(^{Et}PDI)FeN_2]_2(\mu_2\text{-}N_2)$ | C | MD′M | <5 | trace | 17 | 56 (1:1 C1:C4) | 27 |
| $[(^{Et}PDI)FeN_2]_2(\mu_2\text{-}N_2)$ | C | TES | <5 | trace | 23 | 53 (1:1 C1:C4) | 23 |
| Speier's catalyst[b] | A | MD′M | 30 | trace | 23 | 50 (1:1.17:1.46)[c] | 27 |
| Speier's catalyst[b] | A | TES | 960 | trace | 34 | 41(1:1:0.74)[c] | 5[e] |
| Speier's catalyst (optimized)[d] | A | TES | 210 | trace | 37 | 46(1:1:1.65)[c] | 14[f] |

[a] Each reaction was conducted neat at 23 °C with 1:1 TVCH/silane and 0.4 mol % Fe metal; the numbers reported are based on the composition of the mixture at the specified time. [b] Identical conditions as in footnote a, using 0.4 mol % Pt metal. [c] Ratio of C1/C2/C4. [d] Conducted neat at 95 °C with 1:0.8 TVCH/silane, 0.003 mol % Pt, and slow addition of the silane. These are optimized industrial conditions.[10] [e] 20 mol % TEOS was observed. [f] 1 mol % trisilylated product and 2 mol % TEOS were observed.

distillation, generates waste, limits commercialization, and motivates the exploration of new catalyst platforms to overcome the selectivity challenge presented by the isomers of TVCH.

Aryl-substituted bis(imino)pyridine iron dinitrogen[12,13] and dialkyl complexes[14] are highly active and selective for the hydrosilylation of terminal alkenes and offer distinct advantages over traditional precious metal catalysts. For example, $[(^{Me}PDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$ ($^{Me}PDI$ = 2,6-(2,6-$Me_2$-$C_6H_3N{=}CMe)_2C_5H_3N$) promotes the hydrosilylation of 1-octene with tertiary silanes at parts per million level catalyst loadings in <15 min with no evidence for byproducts arising from olefin isomerization or dehydrogenative silylation.[13] Inspired by these observations, the selective hydrosilylation of the isomers of TVCH was explored with this class of iron catalyst. This specific substrate presents unique chemo-, regio-, and stereoselectivity challenges that have not been encountered with the more traditional $\alpha$-olefins studied to date. Here, we describe that iron catalysis provided unprecedented levels of selectivity for the hydrosilylation of TVCH.

To further expand the library of aryl-substituted bis(imino)pyridine iron dinitrogen complexes and to determine its selectivity in the hydrosilylation of TVCH, $[(^{iPr,Et}PDI)FeN_2]_2(\mu_2\text{-}N_2)$ ($^{iPr,Et}PDI$ = 2,6-(2-Et-6-$^i$Pr-$C_6H_3N{=}CMe)_2C_5H_3N$) was synthesized using established methods.[12,15] Interest in this particular aryl substitution pattern derived, in part, from the observation of exclusively monomeric dinitrogen compounds for $(^{iPr}PDI)Fe(N_2)_2$,[16] whereas dimeric species are obtained when the 2,6-aryl substituents are reduced to ethyl and methyl.[15] Single crystal X-ray diffraction established that $[(^{iPr,Et}PDI)FeN_2]_2(\mu_2\text{-}N_2)$ is dimeric in the solid state as the meso diastereomer with the ethyl groups oriented toward the bridging dinitrogen. This is also evident from the solid-state (KBr) infrared spectrum of the complex. However, analysis of bulk samples by pentane solution infrared spectroscopy established detectable concentrations of both the four- and five-coordinate monomeric bis(imino)pyridine iron dinitrogen complexes, $(^{iPr,Et}PDI)FeN_2$ and $(^{iPr,Et}PDI)Fe(N_2)_2$ (see Supporting Information). We note that the iron dinitrogen complexes are sensitive to air and water.

Initial evaluation of the iron catalysts for TVCH hydrosilylation was conducted using the mixture of isomers used commercially (53% A, 16% B, 31% C/D). Because of its industrial predominance, $(EtO)_3SiH$ (TES) was chosen as the alkoxysilane.[17] Each reaction was conducted neat at 23 °C without slow addition or substoichiometric quantities of reagents. In the presence of 0.4 mol % $(^{iPr}PDI)Fe(N_2)_2$, complete consumption of the silane was observed in <5 min, establishing high activity for the iron catalyst. Analysis of the product mixture by GC established 53% monosilylated products, with the major of these (64%) being the 4-vinyl product of isomer A. The balance of the material consisted of disilylated products (18%) and unreacted TVCH isomers (29%). With $[(^{Et}PDI)FeN_2]_2(\mu_2\text{-}N_2)$, the amount of monosilylated product dropped to 48% with 56% selectivity for the 4-vinyl position of isomer A. The disilylated products increased slightly to 23% with 29% unreacted TVCH.

The observation of high activity, slightly improved selectivity, and lack of requirement for special reaction conditions prompted more systematic investigations into the reactivity of the individual TVCH isomers with various bis(imino)pyridine iron dinitrogen derivatives. Two silanes were evaluated, TES and $(Me_3SiO)_2MeSiH$ (MD′M). The results of these studies are summarized in Table 1. The values reported are based on the composition of the mixture at the specified time. Also included in Table 1 are results with Speier's catalyst and TVCH-A, the all-equatorial isomer that is the major component of the commercially used substrate mixture. The reactions were conducted under neat conditions at 23 °C using a 1:1 mixture of TVCH and silane to which 0.4 mol % of the catalyst (Fe or Pt) was added.

In general, the bis(imino)pyridine iron dinitrogen complexes exhibit higher activity and selectivity for TVCH-A hydrosilylation than Speier's catalyst. The most sterically protected iron compounds in the series, $(^{iPr}PDI)Fe(N_2)_2$ and $(4\text{-}Me_2N\text{-}^{iPr}PDI)Fe(N_2)_2$ ($^{iPr}PDI$ = $2,6\text{-}(2,6\text{-}^{i}Pr_2{-}C_6H_3N{=}CMe)_2C_5H_3N$ and ($4\text{-}Me_2N\text{-}^{iPr}PDI$ = $2,6\text{-}(2,6\text{-}^{i}Pr_2{-}C_6H_3N{=}CMe)_2\text{-}4\text{-}Me_2N{-}C_5H_2N$), were the most selective for monohydrosilylation with MD′M and exhibited >98% selectivity for the desired 4-vinyl position. Slightly reduced selectivities were obtained when MD′M was replaced with TES, as evidenced by formation of 16% of disilylated product. Selectivity for the 4-vinyl group remained high (94 and 95%) within the monohydrosilylated product. Hydrosilylations with TES were more active than those with MD′M because the former reached completion in <5 min at 23 °C, whereas the latter required 180 min to reach 52% conversion (Table 2).

**Table 2. Comparison of the Activity and Selectivity of $(^{iPr}PDI)Fe(N_2)_2$ and $(4\text{-}Me_2N\text{-}^{iPr}PDI)Fe(N_2)_2$ As a Function of Time for the Hydrosilylation of TVCH-A with MD′M**

| | $(^{iPr}PDI)Fe(N_2)_2$ | | |
|---|---|---|---|
| time (min) | % MDM | % TVCH-A | % mono[c] (conversion) |
| 30 | 41 | 48 | 11 (21) |
| 60 | 36 | 43 | 21 (37) |
| 120 | 32 | 39 | 29 (48) |
| 180 | 30 | 37 | 33 (52) |
| 960 | 26 | 35 | 39 (60) |
| | $(4\text{-}Me_2N\text{-}^{iPr}PDI)Fe(N_2)_2$ | | |
| time (min) | % MDM[a] | % TVCH-A[b] | % mono[c] (conversion) |
| 30 | 41 | 44 | 15 (27) |
| 60 | 35 | 38 | 27 (44) |
| 120 | 23 | 24 | 50 (71) |
| 180 | 17 | 19 | 60 (80) |
| 960 | 0 | 8 | 83 (100) |

[a] Reported numbers are based on the composition of the mixture at the specified time with the balance being disilylated products. [c] Monosilylated product is 98% on C4 in all entries. % conversion is based on % silane consumed.

Reducing the size of the aryl substituents from $[2,6\text{-}^{i}Pr_2]$ dramatically improved the activity of the catalyst but with diminished selectivity. Replacing a single $[^{i}Pr]$ group with an [Et] substituent on each aryl ring increased formation of the disilylated product, although 4-vinyl selectivity for the monohydrosilylated product remained at 94%. As expected, $[(^{Et}PDI)FeN_2]_2(\mu\text{-}N_2)_2$ and $[(^{Me}PDI)FeN_2]_2(\mu_2\text{-}N_2)$ were extremely active, completing the hydrosilylation almost immediately upon mixing at 23 °C with both silanes. However, only 74% of the monohydrosilylated product was obtained with 92% selectivity for the 4-vinyl group.

Using a different TVCH epimer at either the 2- (TVCH-C) or 4-positions (TVCH-B) reduced the selectivity of the iron-catalyzed hydrosilylation. Using $[(^{Et}PDI)FeN_2]_2(\mu_2\text{-}N_2)$ as a representative precatalyst, the hydrosilylation of TVCH-B with MD′M yielded 56% monohydrosilylated product with 70% selectivity for the 4-alkene. With TES, the selectivity for monohydrosilylation and the 4-position also eroded to 43 and 78%, respectively. Comparable results were obtained with TVCH-C, for which the iron precatalyst exhibits equal preference for the 1- and 4-positions of the monohydrosilylated product. These results demonstrate the importance of the stereochemistry of both the 2- and 4-positions for the preference for mono- versus disilylation, as well as for the hydrosilylation of the 4-vinyl position. With the more open iron dinitrogen compound, $[(^{Et}PDI)FeN_2]_2(\mu_2\text{-}N_2)$, both di- and trisilylated TVCH were intentionally synthesized and isolated using an excess of silane (see Supporting Information).

Performing the hydrosilylation of TVCH-A using Speier's catalyst under the same conditions demonstrated a decrease in both activity and selectivity of platinum compared with the iron compounds. A near statistical mixture of the 1-, 2-, and 4-vinyl products was obtained from the monohydrosilylation. In the case of TES, 20% of tetraethoxysilane (TEOS) was also obtained from the disproportionation of the silane. No product was detected during the first few hours of the reaction, indicating a significant induction period for the platinum catalyst at room temperature. These factors necessitate the slow addition of the silane and higher reaction temperatures in the large-scale Pt-catalyzed hydrosilylation of TVCH.

To gain insight into the relative rates of iron-catalyzed hydrosilylation of isomers A, B, and C, a competition experiment was conducted. A 1:1:1 mixture of the three TVCH isomers (31% A, 34% B, and 35% C) and 0.5 equiv of MD′M were mixed for 5 min at 23 °C in the presence of 0.2 mol % of $[(^{Et}PDI)FeN_2]_2(\mu_2\text{-}N_2)$. Analysis of the remaining olefin isomers by GC revealed 35% TVCH-A, 34% TVCH-B, and 31% TVCH-C. Importantly, no products of disilylation were observed under these conditions, which thereby establishes that the rate of hydrosilylation of all three isomers is approximately equal with this specific iron dinitrogen complex.

The high selectivity but relatively low activity of $(^{iPr}PDI)Fe(N_2)_2$ and $(4\text{-}Me_2N\text{-}^{iPr}PDI)Fe(N_2)_2$ prompted more careful investigation of the time course of the catalytic hydrosilylation with these compounds (Table 2). Under the conditions used in Table 1, considerable amounts of silane and TVCH-A remained after 180 min. Stirring $(^{iPr}PDI)Fe(N_2)_2$ with TVCH-A and MD′M for longer times (960 min) resulted in additional conversion to product, although only slightly more than was observed at 180 min, suggesting catalyst deactivation. Introduction of a $[Me_2N]$ substituent into the 4-position of the pyridine ring alleviated this limitation because complete conversion was observed after 960 min. Comparing conversions between $(^{iPr}PDI)Fe(N_2)_2$ and $(4\text{-}Me_2N\text{-}^{iPr}PDI)Fe(N_2)_2$ at earlier reaction times demonstrates that the latter compound is more active for hydrosilylation, similar to recent observations in olefin hydrogenation catalysis.[18]

In summary, a family of aryl-substituted bis(imino)pyridine iron dinitrogen complexes has been discovered for the hydrosilylation of 1,2,4-trivinylcyclohexane. The activity and selectivity of the iron compounds is unprecedented and surpasses commercially deployed platinum catalysts, demonstrating the potential advantages of base metal catalysis. The origins of the selectivity, structure−reactivity relationships, and a deeper mechanistic understanding of iron-catalyzed hydrosilylation are currently under investigation.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Complete experimental details, characterization of hydrosilylation products and crystallographic data for $[(^{iPr,Et}PDI)FeN_2]_2(\mu\text{-}N_2)_2$. 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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