

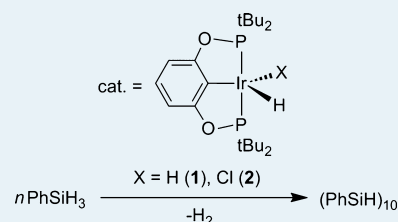
High Activity and Selectivity for Silane Dehydrocoupling by an Iridium Catalyst

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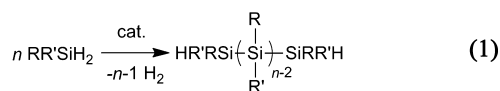
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ABSTRACT: Iridium complexes bearing a bis(phosphinite) pincer ligand are highly active for the dehydrocoupling of phenylsilane, comparable to other catalysts for this reaction. Interestingly, this catalysis produces primarily a single product, the decasilane ring *cyclo*-(PhSiH)₁₀ in what is unusually high selectivity for a single product in silane dehydrocoupling.

KEYWORDS: dehydrocoupling, iridium, pincer, silane, polysilane



Prospects for materials that contain earth-abundant elements such as silicon are highly desirable in light of global economic and sustainability considerations.¹ Therefore, the preparation of high molecular weight, linear polysilanes remains of great interest due primarily to the unique electronic and optical properties that result from strong σ -delocalization along the silicon backbone.² There has been a nearly four decade pursuit of metal-catalyzed dehydropolymerization strategies for organosilanes (eq 1) given the limitations



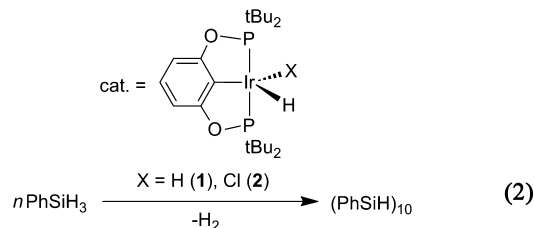
associated with classic, Würtz-type reductive coupling methods.^{3–7} These investigations have, in part, precipitated a broader application of dehydrocoupling for inorganic polymers and synthesis.^{8–14}

To date, the study of group 4 metallocenes has been the primary focus for catalytic silane dehydrocoupling, with key scientific exploits and mechanistic insight most frequently arising from the groups of Corey, Harrod, and Tilley.^{3–6} While the first example of silane dehydrocoupling involved Wilkinson's catalyst,¹⁵ the use of electron-rich late transition metals as catalysts has been less frequent than early metals, stymied by early observations of lower activity for such compounds.^{16–18} However, a series of investigations in more recent years illustrated activity comparable to early metals and invigorated the interrogation of late metals for this catalysis.^{19–27} Despite tremendous advances, this kind of polymerization still generally suffers from lower than desired molecular weights,²⁸ mixtures of linear and cyclic products,²⁹ and relatively high polydispersities, even for short-chain oligomers.³⁰

Iridium complexes bearing bis(phosphinite) pincer ligands are of acute interest because of their high reactivity. In particular, these complexes have shown unique activity in dehydrogenation of alkanes and other substrates including

amine-boranes.³¹ Beyond the high activity of these complexes as catalysts, the selectivity of such species is also remarkable. For example, Goldberg and Heinekey reported that (POCOP)-Ir(H)₂ (**1**, POCOP = 2,6-(^tBu₂PO)₂C₆H₃) as a highly active catalyst for the liberation of hydrogen from ammonia borane with formation of cyclic pentaazaborane, (NH₂BH₂)₅.^{32,33} In 2008, Manners and co-workers revisited this catalyst and found that linear poly(aminoboranes) can be solicited from the dehydrocoupling reaction under alternative conditions.^{34,35} This high reactivity and selectivity prompted investigation of these pincer complexes in catalytic silane dehydrocoupling. In this initial report, high activity was observed with an unusually high selectivity for a single cyclosilane product.

Treatment of phenylsilane with 0.8 mol % of (POCOP)-IrHCl (**2**) results in complete consumption of starting silane and liberation of copious hydrogen gas (eq 2). The reaction of



2 with neat PhSiH₃ in a vented reaction vessel at ambient temperature leads to the consumption of nearly all of the starting silane within 12 h. Optimal conditions for completion were found to be neat silane under reflux, which allowed hydrogen gas to efficiently vent, and gave nearly complete consumption (>95%) of silane in under 2 h. All reactions produced the cyclic decasilane, *cyclo*-(PhSiH)₁₀ (**3**), as the final product in no less than 92% conversion as assessed by ¹H NMR

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spectroscopy as compared to an internal standard. Highly related dihydride **1** is an equally effective precatalyst for the reaction. Under identical conditions, catalytic runs with complex **1** gave complete consumption of phenylsilane and the decasilane as the sole product in similarly high conversion as observed for complex **2**.

Initial characterization of the silane product **3** was achieved via ^1H NMR spectroscopy. The diagnostic Si–H resonance was a singlet at δ 5.07 corresponding to **3**. Minor byproducts, which represented no more than 8% of the silane products present by integration included trace of 1,2-diphenyldisilane, $(\text{PhSiH}_2)_2$, linear oligomers observed in the range δ 4.3–4.8, and other cyclic oligomers with resonances between δ 5.2–5.9.³⁶ Given that these products have a variable number of protons per silicon atom, the percent conversion is, at best, an estimate. However, a highly conservative estimate has been made including integration of the baseline, which is slightly elevated (Figure 1). It is clear from the silane region of a ^1H NMR

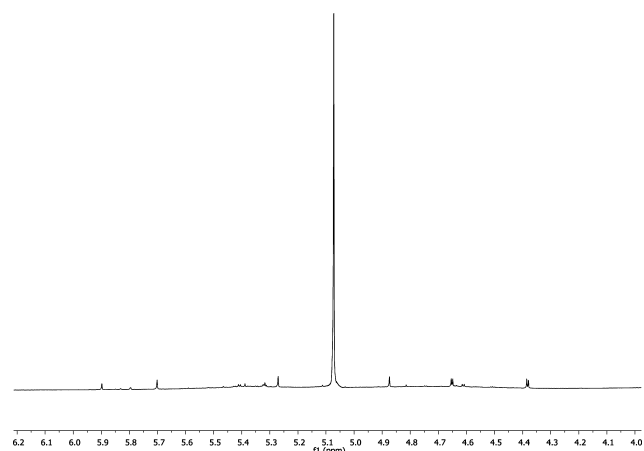


Figure 1. Silane Si–H region of the ^1H NMR spectrum of **3** in benzene- d_6 after filtration through Fluorisoril.

spectrum of the product after filtration through Fluorisoril in toluene that the vastly dominant product is a singlet in cyclic silane region of the spectrum (Figure 1). That a dehydrocoupling product has been formed is supported by observation of $^2J_{\text{SiH}} = 12$ Hz. What is even more interesting is that no redistribution products were observed, despite a very recent report of a phosphine-supported iridium complex catalyzing silane redistribution via proposed silylene intermediates.³⁷

To further elucidate the identity of the cyclic species, ^{29}Si NMR data were collected. Only one resonance was observed from the reaction at δ –34.1. This chemical shift is in good agreement with the range for cyclic silanes.³⁸ Gel permeation chromatography (GPC) was employed as a means of estimating the ring size of compound **3** against polystyrene standards. Triplicate runs on multiple samples yielded two peaks with average retention volumes of 10.02 and 11.48 mL (1 mL/min) for two major peaks (Figure 2). The calculated average molecular weight for the compound of the first peak is 972(2) amu, which allowed for either a nine- or ten-membered silane ring. The calculated average molecular weight for the other peak is 166(2) amu, which can be attributed to $\text{PhSi}(\text{OH})_3$ (MW = 156.21 amu), was not observed in the ^1H NMR spectra of samples prior to GPC and appears to be a consequence of hydrolysis of **3** by adventitious water in the mobile phase (THF) of the GPC, a known reaction for

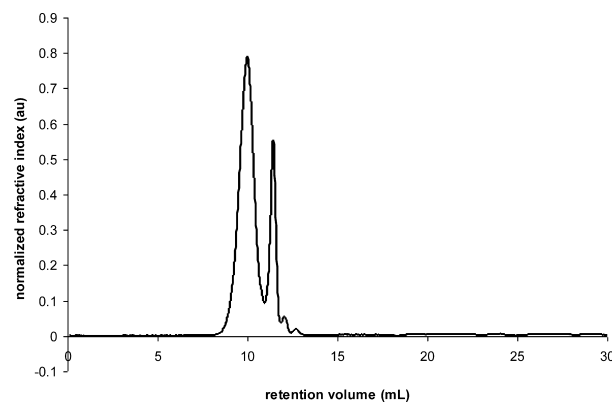


Figure 2. Representative GPC trace of product **3**.

silanes.³⁹ Because it is well established that GPC can be inaccurate when comparing silanes to polystyrene standards whereby the calculated masses are typically low, a GPC validation experiment with phenylsilane was undertaken. A retention peak appeared at a volume of 11.75 mL, resulting in a calculated molecular weight of 120(2) amu, which deviated by approximately 12% from the actual mass. This experiment also gave a retention peak 11.48 mL, consistent with phenylsilanetriol from silane hydrolysis.

Mass spectrometry provided additional data to distinguishing between potential cyclic silane products. Efforts to obtain a mass spectrum of compound **3** by LCMS while bypassing the liquid chromatography column failed to provide reproducible data, which was attributed to a difficulty in ionizing the silane sample. It was hypothesized that a charged species would be more likely to be observed. It was anticipated that a transient cation could be generated in an analogy to silyl cation chemistry.⁴⁰ Therefore, **3** was reacted with approximately 1 equiv of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$, and $m/z = 1059.1$ was detected in electrospray ionization (ESI) mode of a mass spectrum. The mass spectrum also contained a number of byproducts that were likely the result of the data being collected under nonideal conditions.⁴¹ Control experiments where each PhSiH_3 and Ph_2SiH_2 were reacted with 1 equiv of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ under identical conditions failed to produce $m/z = 1059.1$. It is anticipated that a cationic derivative of compound **3** would be highly reactive, and isolation of the product was not attempted. ^1H NMR spectra of samples of the reaction of **3** with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ prior to MS data collection gave a mixture of products at ambient temperature, none of which could be definitively identified as a cationic product. Regardless, the sum of the available spectroscopic, chromatographic, and spectrometric data is consistent with a ten-membered cyclosilane product.

The reaction of **2** with phenylsilane was monitored by ^1H NMR spectroscopy at lower catalyst loadings including 5, 10, and 50 mol %. Hydrogen gas evolution was observed immediately and confirmed in the ^1H NMR spectra of these reactions. Two sharp resonances with ^{29}Si satellites were observed at δ 4.49, unique from H_2 at δ 4.48, and δ 5.07, corresponding to 1,2-diphenyldisilane ($\text{PhH}_2\text{Si}-\text{SiH}_2\text{Ph}$) and **3**, respectively. As the reaction proceeds to completion, the starting silane and disilane are gradually observed by ^1H NMR spectroscopy to be converted to the single cyclic product **3**. It is likely that there are multiple other intermediates en route to **3**, but the absence of other appreciable resonances suggests that larger intermediates (e.g., $\text{PhH}_2\text{Si}(\text{SiHPh})_n\text{SiH}_2\text{Ph}$, $n = 1-7$)

are more reactive with respect to formation of the final product. It is important to note that the reaction is inhibited by hydrogen, as evidenced by the decreased qualitative rate with increased H₂ pressure or added H₂, whereas degassing reaction mixtures accelerated the qualitative rate.

It is very reasonable to suspect iridium silyl complex intermediates in this catalysis.^{42,43} While efforts were made to isolate reaction products of **1** or **2** with stoichiometric amounts of phenylsilane, clean compounds were not produced. In both cases, complexes **1** and **2** convert to the same products, which are also observed in the catalytic reactions. Two of the most prominent intermediates are characterized by resonances at δ 174.9 and 153.6 in ³¹P NMR spectra in benzene-*d*₆ solution. Additionally, several hydride resonances were observed at δ -8.3, -10.2, and -11.5 in ¹H NMR spectra throughout the course of the catalytic reaction. Unfortunately, these resonances were routinely broad. Though these compounds have eluded isolation, the recent preparation of (POCOP)Ir(H)_{*n*}(SiEt₂H) (*n* = 1 or 3) by Brookhart and co-workers provide an excellent model for possible structures. The ³¹P NMR chemical shifts of intermediates in the dehydrocoupling catalysis appear to be similar to these Ir(III) and (V) silyl derivatives, with an expected change in chemical shift for the change in substitution at silicon. Our working hypothesis is that complex **2** is reduced to a hydride because some PhClSiH₂ was observed by ¹H NMR spectroscopy and that silyl hydride complexes, akin to those reported by Brookhart, are operant species in the catalysis.

The selectivity for **3** in the catalysis may arise from steric constraints derived by the POCOP ligand. To test this, an attempt to catalytically dehydrocouple triethylsilane was undertaken. Heating a benzene-*d*₆ solution of triethylsilane with 10 mol % of **2** gradually resulted in liberation of hydrogen over a period of days with concomitant formation of (SiEt₃)₂. The reaction was indeed sluggish. With daily removal of any hydrogen gas from the head space, only 50% conversion to (SiEt₃)₂ was observed after 4 days. This initial observation is consistent with steric effects, but the substantial change in electronic properties of these substrates can not be discounted and further study is warranted.

In summary, (POCOP)Ir-hydride complexes catalytically dehydrocouple phenylsilane to predominantly a single cyclic product, which appears to be a unique event in silane dehydrocoupling catalysis. As with the dehydrocoupling of amine-boranes using the same catalysts,^{34,35} further tuning of reaction conditions is a probable route to selectivity for different silane products. Efforts to expand this catalysis and devise conditions for forming alternative silane products with similarly high selectivity are underway.

■ EXPERIMENTAL SECTION

General experimental procedures have been described elsewhere.⁴⁴ NMR spectra were recorded on a Bruker AXR 500 MHz spectrometer where ¹H and ¹³C, NMR spectra were referenced to residual benzene-*d*₆ resonances (δ 7.16 and 128.0) and ³¹P and ²⁹Si NMR were referenced to external 85% H₃PO₄ and internal tetramethylsilane standards, respectively. Mass spectra were collected on an Applied Biosystems 4000QTrap Pro. Gel Permeation Chromatography (GPC) data was collected using a Hewlett-Packard 1100 series HPLC equipped with refractive index, intrinsic viscosity, and right angle light scattering detectors. Samples were eluted through a Waters μ Styragel 103 Å (7.8 × 300 mm) column using tetrahydrofuran (THF) at a flow rate of 1 mL min⁻¹. The

average molecular weights of the polyphenylsilane samples were determined relative to four polystyrene standards obtained from Waters with molecular weights ranging from 489–6480 amu. Infrared spectra were collected on a Bruker Alpha FT-IR with an ATR head. Bis(phosphinite) pincer complexes PCPIr(H)₂ (**1**),⁴⁵ PCPIrHCl (**2**),⁴⁶ and [Ph₃C][B(C₆F₅)₄]⁴⁷ were prepared via literature methods.

Typical Procedure for Catalytic Dehydrocoupling of PhSiH₃. A Schlenk flask with an attached condenser was charged with either **1** or **2** (0.174 mmol) and 2.69 mL (21.8 mmol, 125 equiv) of phenylsilane. Hydrogen evolved immediately. The solution was refluxed for 2 h under an N₂ atmosphere. The reaction was diluted with toluene (~10 mL) then filtered through a bed of Florisil and dried under reduced pressure to afford *cyclo*-(PhSiH)₁₀ as a viscous dark red liquid (2.02 g, 1.90 mmol, 87%). ¹H NMR (500 MHz): δ 7.50 (d, 2 H, C₆H₅), 7.09–7.14 (m, 3 H, C₆H₅), 5.07 (s, 1 H, ¹J_{SiH} = 195 Hz, ²J_{SiH} = 12 Hz, SiH). ²⁹Si NMR (99 Hz): δ -34.1. IR: 3065 m, 3048 m, 3008 m, 2098 s (ν _{SiH}), 1428 s, 1100 s, 839 s, 714 m, 698 m, 588 m cm⁻¹. The reaction can also be run at ambient temperature for 16 h to obtain a similar yield. Closed vessels may also be used, but hydrogen must be purged periodically and a longer reaction time was noted.

Example Observation by NMR Spectroscopy. A PTFE-valved NMR tube was charged with PhSiH₃ (0.1739 g, 1.605 mmol), **2** (0.0201 g, 0.032 mmol), and enough benzene-*d*₆ to bring the volume to approximately 0.5 mL. Upon combination of the PhSiH₃ and **2**, H₂ evolved vigorously, which was allowed to subside prior to sealing the NMR tube. The dark red homogeneous mixture slowly lightened to an orange-red color after 1 day at ambient temperature. The reaction was then heated gently at 65 °C for several days to monitor for changes. Numerous ¹H and ³¹P NMR spectra were collected over the reaction period.

Dehydrocoupling of Et₃SiH. A PTFE-valved NMR tube was charged with Et₃SiH (0.040 g, 0.350 mmol), **2** (0.022 g, 0.035 mmol), and enough benzene-*d*₆ to bring the volume to approximately 0.5 mL. There was no obvious reaction, and the solution was degassed and the NMR tube sealed. The reaction was then heated gently at 65 °C for several days to monitor for changes. Numerous ¹H and ³¹P NMR spectra were collected over the reaction period.

Reaction of [PhSiH]₁₀ with [Ph₃C][B(C₆F₅)₄]. In a round-bottom flask, *cyclo*-(PhSiH)₁₀ (0.124 g, 0.117 mmol) was dissolved in 2 mL of benzene and added to a 2 mL of benzene solution of [Ph₃C][B(C₆F₅)₄] (0.1199 g, 0.130 mmol). The reaction was stirred at ambient temperature for 1 h to 2 days under an inert N₂ atmosphere resulting in a burnt orange solution with a ring of burnt orange precipitate around the inside of the flask. The solution was decanted and diluted for mass spectrometry.

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Stanier, C.; Hutchinson, J. *A Sustainable Global Society. How Materials Science Can Help*; Chemical Sciences and Society Summit (CS3): London, U.K., 2001.
- (2) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359.
- (3) Corey, J. Y. *Adv. Organomet. Chem.* **2004**, *51*, 1.
- (4) Gauvin, F.; Harrod, J. F.; Woo, H. G. *Adv. Organomet. Chem.* **1998**, *42*, 363.
- (5) Tilley, T. D. *Comments Inorg. Chem.* **1990**, *10*, 37.
- (6) Tilley, T. D. *Acc. Chem. Res.* **1993**, *26*, 22.
- (7) Hill, M. S. *Struct. Bonding (Berlin)* **2010**, *136*, 189.
- (8) Braunstein, P.; Morise, X. *Chem. Rev.* **2000**, *100*, 3541.
- (9) Clark, T. J.; Lee, K.; Manners, I. *Chem.—Eur. J.* **2006**, *12*, 8634.
- (10) Harrod, J. F.; Mu, Y.; Samuel, E. *Polyhedron* **1991**, *10*, 1239.
- (11) Jaska, C. A.; Bartole-Scott, A.; Manners, I. *Phosphorus, Sulfur Silicon Relat. Elem.* **2004**, *179*, 685.
- (12) Jaska, C. A.; Manners, I. *Inorg. Chem. Focus II* **2005**, 53.
- (13) Waterman, R. *Curr. Org. Chem.* **2008**, *12*, 1322.
- (14) Waterman, R. *Dalton Trans.* **2009**, 18.
- (15) Ojima, I.; Inaba, S.; Kogure, T.; Nagai, Y. *J. Organomet. Chem.* **1976**, *55*, C7.
- (16) Brown-Wensley, K. A. *Organometallics* **1987**, *6*, 1590.
- (17) Chang, L. S.; Corey, J. Y. *Organometallics* **1989**, *8*, 1885.
- (18) Fryzuk, M. D.; Rosenberg, L.; Rettig, S. J. *Inorg. Chim. Acta* **1994**, *222*, 345.
- (19) Rosenberg, L.; Davis, C. W.; Yao, J. *J. Am. Chem. Soc.* **2001**, *123*, 5120.
- (20) Fontaine, F.-G.; Kadkhodazadeh, T.; Zargarian, D. *Chem. Commun.* **1998**, 1253.
- (21) Chauhan, B. P. S.; Shimizu, T.; Tanaka, M. *Chem. Lett.* **1997**, *26*, 785.
- (22) Itazaki, M.; Ueda, K.; Nakazawa, H. *Angew. Chem., Int. Ed.* **2009**, *48*, 3313.
- (23) Diversi, P.; Marchetti, F.; Erminia, V.; Matteoni, S. *J. Organomet. Chem.* **2000**, 593–594, 154.
- (24) Fontaine, F.-G.; Zargarian, D. *Organometallics* **2002**, *21*, 401.
- (25) Fontaine, F.-G.; Zargarian, D. *J. Am. Chem. Soc.* **2004**, *126*, 8786.
- (26) Smith, E. E.; Du, G.-D.; Fanwick, P. E.; Abu-Omar, M. M. *Organometallics* **2010**, *29*, 6527.
- (27) Jackson, S. M.; Chisholm, D. M.; McIndoe, J. S.; Rosenberg, L. *Eur. J. Inorg. Chem.* **2011**, 327.
- (28) Imori, T.; Tilley, T. D. *Polyhedron* **1994**, *13*, 2231.
- (29) Dioumaev, V. K.; Harrod, J. F. *J. Organomet. Chem.* **1996**, *521*, 133.
- (30) Rosenberg, L.; Kobus, D. N. *J. Organomet. Chem.* **2003**, *685*, 107.
- (31) Choi, J.; MacArthur, A. H. R.; Brookhart, M.; Goldman, A. S. *Chem. Rev.* **2011**, *111*, 1761.
- (32) Denney, M. C.; Pons, V.; Hebden, T. J.; Heinekey, D. M.; Goldberg, K. I. *J. Am. Chem. Soc.* **2006**, *128*, 12048.
- (33) Dietrich, B. L.; Goldberg, K. I.; Heinekey, D. M.; Autrey, T.; Linehan, J. C. *Inorg. Chem.* **2008**, *47*, 8583.
- (34) Staubitz, A.; Sloan, M. E.; Robertson, A. P. M.; Friedrich, A.; Schneider, S.; Gates, P. J.; Schmedt, a. d. G. J.; Manners, I. *J. Am. Chem. Soc.* **2010**, *132*, 13332.
- (35) Staubitz, A.; Soto, A. P.; Manners, I. *Angew. Chem., Int. Ed.* **2008**, *47*, 6212.
- (36) Woo, H. G.; Walzer, J. F.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 7047.
- (37) Park, S.; Kim, B. G.; Göttker-Schnetmann, I.; Brookhart, M. *ACS Catal.* **2012**, *2*, 307.
- (38) Dioumaev, V. K.; Rahimian, K.; Gauvin, F.; Harrod, J. F. *Organometallics* **1999**, *18*, 2249.
- (39) Korkin, S. D.; Buzin, M. I.; Matukhina, E. V.; Zherlitsyna, L. N.; Auner, N.; Shchegolikhina, O. I. *J. Organomet. Chem.* **2003**, *686*, 313.
- (40) Lambert, J. C.; Zhao, Y.; Zhang, S. M. *J. Phys. Org. Chem.* **2001**, *14*, 370.
- (41) Lubben, A. T.; McIndoe, J. S.; Weller, A. S. *Organometallics* **2008**, *27*, 3303.
- (42) Corey, J. Y. *Chem. Rev.* **2011**, *111*, 863.
- (43) Corey, J. Y.; Braddock-Wilking, J. *Chem. Rev.* **1999**, *99*, 175.
- (44) Roering, A. J.; Leshinski, S. E.; Chan, S. M.; MacMillan, S. N.; Tanski, J. M.; Waterman, R. *Organometallics* **2010**, *29*, 2557.
- (45) Goettker-Schnetmann, I.; White, P. S.; Brookhart, M. *Organometallics* **2004**, *23*, 1766.
- (46) Goettker-Schnetmann, I.; White, P.; Brookhart, M. *J. Am. Chem. Soc.* **2004**, *126*, 1804.
- (47) Ihara, E.; Young, J.; Victor, G.; Jordan, R. F. *J. Am. Chem. Soc.* **1998**, *120*, 8277.