Dehydrogenative Coupling Reactions To Form Silazane Oligomers Promoted by Binuclear Rhodium Complexes

Wei-Dong Wang and Richard Eisenberg*

Department of Chemistry, University of Rochester, Rochester, New York 14627

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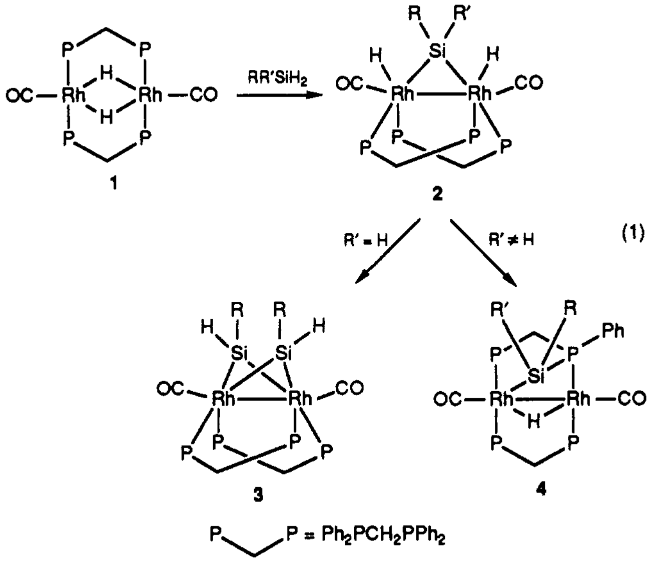
Primary and secondary silanes $RR'SiH_2$ (R = Ph, R′ = H; R = Et, R′ = H; R = C_6H_{13}, R′ = H; R = R′ = Me; R = R′ = Et; R = Me, R′ = Ph) react with ammonia and simple amines $R''NH_2$ (R″ = Me, *i*-Bu, *i*-Pr) in the presence of the binuclear rhodium complexes $Rh_2H_2(CO)_2(dppm)_2$ (**1**; dppm = bis(diphenylphosphino)methane) and $Rh_2(\mu\text{-}SiRH)_2(CO)_2(dppm)_2$ (**3a**, R = Ph; **3b**, R = Et; **3c**, R = C_6H_{13}) at ambient temperature to form small silazane oligomers. The effects of silane and amine on the extent of dehydrogenative coupling have been investigated. For the reaction of primary silanes with methylamine, oligomers with a degree of coupling greater than 3 have been observed. When complex **3** is used as the catalyst, a μ-SiRNHR″ dihydride intermediate similar to $Rh_2(\mu\text{-}SiRH)H_2(CO)_2(dppm)_2$ (**2**) is formed, as characterized by ^1H and ^{31}P NMR spectroscopy.

Introduction

In this paper we describe studies on the reaction chemistry of binuclear rhodium complexes with silanes and amines leading to Si–N bond formation and the synthesis of small silazane oligomers. Our study was stimulated by previous work on the synthesis and characterization of μ-SiRR′ complexes via eq 1.[1] The dihydride species **2** was observed to be fluxional, and the mechanism of fluxionality was proposed as facile Si–H reductive elimination and oxidative addition. The unsaturated intermediate thus generated appeared as an interesting target for further reaction with nucleophiles such as amines.



The work described here involves reactions of **1**–**3** with silanes and simple amines leading to Si–N bond formation. This is a subject of current interest because silazane oligomers and polymers can serve as precursors to silicon nitride (Si_3N_4).[2] While silazanes have been prepared traditionally by the ammonolysis or aminolysis of chlorosilanes,[3] recent efforts have focused on dehydrogenative coupling of silanes and amines with transition-metal complexes as catalysts.[4-7] Notable in this regard is the work of Laine and co-workers, who have investigated eq 2 using various homogeneous and heterogeneous catalyst systems, including $Ru_3(CO)_{12}$ and Pd/C.[4] This work followed from

$$Et_3SiH + R'NH_2 \xrightarrow{\text{catalyst}} H_2 + Et_3Si\text{-}NHR' \quad (2)$$

earlier efforts on transition-metal-catalyzed ring opening of cyclic silazanes, which by necessity involves Si–N bond cleavage. Prior reports of metal-catalyzed dehydrogenative Si–N coupling include the work of Sommer and Citron with Pd/C, which Laine and co-workers have confirmed as being most effective for eq 2.[5] Independently, Barton and co-workers have examined dehydrogenative coupling of silanes and amines and have found $PdCl_2$ to be a superior catalyst for the synthesis of a diaminosilane from Et_2SiH_2 and BuMeNH.[6] As was found in kinetic studies of the ruthenium-catalyzed reaction of Et_3SiH with RNH_2 (R = *n*-Pr, *n*-Bu, *sec*-Bu, *t*-Bu),[5b] these investigators observed that the reaction between silanes and amines is very sensitive to steric factors.

Results and Discussion

Silazane Formation Promoted by Binuclear Rhodium Complexes. Reactions between silanes and amines catalyzed by binuclear Rh complexes were examined by ^1H NMR spectroscopy, and the products of dehydrogenative coupling of Si–H and N–H bonds were definitively established by GC–mass spectrometry.

In a typical experiment, 10 μL of $PhSiH_3$ and 10 μL of *i*-$BuNH_2$ were added to a C_6D_6 solution containing 5 mg of $Rh_2(\mu\text{-}SiHPh)_2(CO)_2(dppm)_2$ (**3a**). The ratio of reactants to complex was thus approximately 20:1. Within 10 min, new signals appeared in the ^1H NMR spectrum of the solution, including resonances at δ 2.64 (multiplet), 2.47

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(pseudo-triplet), 5.19 (t), and 5.07 (d) ppm. After 1 h, 33% of the starting silane had reacted to form the initial coupling products described below. The more volatile components of the sample were separated from the nonvolatiles and examined independently. The major new component of the volatiles corresponded to the resonances at δ 2.47 and 5.07 ppm, which occur in a 1:1 ratio and which are both coupled to a single amine proton contained in a broad resonance at ~0.5 ppm. On the basis of the ^{1}H NMR data, this product was assigned as $\mathrm{PhH_2SiNH}(i\text{-Bu})$ with the resonance at 5.07 ppm belonging to Si-H and the resonance at 2.47 ppm corresponding to the $-\mathrm{C}H_2-$ protons of the i-Bu group. Confirmation of the assignment was provided by GC–MS, which showed a parent ion peak at m/e 179 and major fragmentation peaks at m/e 136 and 107 corresponding to loss of a propyl group and $-\mathrm{NH}(i\text{-Bu})$, respectively.

The major new nonvolatile product of the reaction after 1 h has ^{1}H NMR resonances at δ 2.64 and 5.19, both of which are coupled to amine protons, a parent ion at m/e 250, and major fragmentation peaks corresponding to the same mass losses as seen for the major volatile product. On the basis of these data, the nonvolatile product is assigned as $\mathrm{PhHSi(NH}(i\text{-Bu}))_2$.

When the complex $\mathrm{Rh_2H_2(CO)_2(dppm)_2}$ (**1**) is employed in the reaction between $\mathrm{PhSiH_3}$ and $i\text{-BuNH}_2$, the same initial coupling products as described above are seen. Prolonged reaction leads to further coupling products, which were characterized when the reaction was scaled up. In this experiment, 400 μL of $\mathrm{PhSiH_3}$ and 400 μL of $i\text{-BuNH}_2$ were added to a THF solution containing 5 mg of **1**, after which a vigorous reaction occurred accompanied by the evolution of $\mathrm{H_2}$. After 36 h, several products had formed and only a small amount of free $\mathrm{PhSiH_3}$ remained in the sample. By GC–mass spectrometry, three major products were seen with parent ion peaks at m/e 250, 285, and 356. The first corresponds to $\mathrm{PhHSi(NH}(i\text{-Bu}))_2$ described above while the second and third are assigned as the Si–N–Si and Si–N–Si–N coupling products $\mathrm{(PhH_2Si)_2N}(i\text{-Bu})$ and $\mathrm{PhH_2SiN}(i\text{-Bu})\mathrm{SiPhHNH}(i\text{-Bu})$, on the basis of the parent ion peaks and fragmentation data (see Table I). In addition to the major products, smaller amounts of the initial coupling product $\mathrm{PhH_2SiNH}(i\text{-Bu})$ and a larger oligomer are also observed. The latter is assigned as the N–Si–N–Si–N product $(\mathrm{NH}(i\text{-Bu})\mathrm{SiPhH})_2\mathrm{N}(i\text{-Bu})$ and exhibits a mass peak at m/e 426 corresponding to (M − 1) and fragmentation peaks showing mass losses identical with those seen above. No cyclic coupling products were observed in this reaction. When the same reaction was performed in $\mathrm{C_6H_6}$ rather than THF, the same coupling products as described above were obtained. A control experiment with $\mathrm{PhSiH_3}$ and $i\text{-BuNH}_2$ in $\mathrm{C_6D_6}$ showed no evidence for coupling by ^{1}H NMR spectroscopy after 24 h at 60 °C.

Table I. Mass Spectrometric Data for the Products Formed in the Reaction of $\mathrm{PhSiH_3}$ with i-$\mathrm{BuNH_2}$ in the Presence of 1

coupling products	extent of coupling	major mass fragments, m/e (mass loss, proposed assignt of mass loss)
$\mathrm{PhH_2SiNH}(i\text{-Bu})$	Si–N	179 ($\mathrm{M^+}$) 136 (−43, $-\mathrm{CHMe_2}$)[a] 107 (−72, $-\mathrm{NHCH_2CHMe_2}$)[b]
$(i\text{-Bu})\mathrm{NHSiHPhNH}(i\text{-Bu})$	N–Si–N	250 ($\mathrm{M^+}$) 207 (−43, $-\mathrm{CHMe_2}$) 178 (−72, $-\mathrm{NHCH_2CHMe_2}$) 136 (−114, $-\mathrm{NH{=}CHCHMe_2}$, $-\mathrm{CHMe_2}$)[c] 107
$\mathrm{PhH_2SiN}(i\text{-Bu})\mathrm{SiPhH_2}$	Si–N–Si	285 ($\mathrm{M^+}$) 242 (−43, $-\mathrm{CHMe_2}$) 226 (−59, $-\mathrm{CH_2CHMe_2}$, −2H) 164 (−121, $-\mathrm{CHMe_2}$, −PhH) 134 (−151, $-\mathrm{PhSiH_3}$, $-\mathrm{CHMe_2}$) 107
$\mathrm{H(PhHSiN}(i\text{-Bu}))_2\mathrm{H}$	Si–N–Si–N	356 ($\mathrm{M^+}$) 313 (−43, $-\mathrm{CHMe_2}$) 284 (−72, $-\mathrm{NHCH_2CHMe_2}$) 242 (−114, $-\mathrm{NH{=}CHCHMe_2}$, $-\mathrm{CHMe_2}$) 226; 164; 134; 107
$(i\text{-Bu})\mathrm{NH(PhHSiN}(i\text{-Bu}))_2\mathrm{H}$	N–Si–N–Si–N	426 ($\mathrm{M^+} - 1$) 355 (−72, $-\mathrm{NHCH_2CHMe_2}$) 313 (−114, $-\mathrm{NH{=}CHCHMe_2}$, $-\mathrm{CHMe_2}$) 311[d] 255; 226; 164; 134; 107

[a] The most intense peak. All of the coupling products exhibit an intense peak of ($\mathrm{M^+} - 43$) except the N–Si–N–Si–N coupling product. [b] The peak at m/e 107 corresponds to $\mathrm{PhSiH_2}$. [c] $\mathrm{PhH_2SiNHCH_2}$ (m/e 136) is obtained by losing $\mathrm{NH{=}CHCH(CH_3)_2}$ through β-hydrogen elimination. [d] $\mathrm{PhH\underline{SiNHCH_2SiPhHN}}(i\text{-Bu})$ (m/e 312) is probably formed, which leads to the mass ion peaks of m/e 311 and 255 through loss of one H and i-Bu, respectively.

For secondary silanes, only the simplest coupling products are formed. This is undoubtedly a consequence of the increased steric bulk of the silane. For example, when the reaction of $i\text{-BuNH}_2$ with $\mathrm{Et_2SiH_2}$ in the presence of **1** is performed at room temperature for 36 h, all of the silane is consumed and only one product is seen by ^{1}H NMR spectroscopy. This product exhibits a multiplet at δ 4.48 ppm, a pseudo-triplet at 2.49 ppm, and other resonances in the 0–1 ppm region of the spectrum. On the basis of resonance intensities and homonuclear decoupling, the compound is formulated as $\mathrm{Et_2HSiNH}(i\text{-Bu})$ with the Si-H resonance at 4.48 ppm coupled to the SiEt methylene protons at 0.58 ppm and the NH proton at 0.33 ppm. The resonance at δ 2.49 ppm corresponds to the methylene protons of the $\mathrm{NH}(i\text{-Bu})$ moiety with coupling to the methine proton at 1.39 ppm and the NH proton at 0.33 ppm. GC–MS analysis of the same sample shows the predominant product to have a parent ion peak at m/e 159 in accord with the simple coupling formulation given above. A trace amount of a second coupling product with a parent ion at m/e 230 is also observed by GC–MS, and it is assigned as $\mathrm{Et_2Si(NH}(i\text{-Bu}))_2$. These results are identical for reactions carried out in THF and $\mathrm{C_6H_6}$. In addition, when $\mathrm{MePhSiH_2}$ is employed in the reaction with $i\text{-BuNH}_2$ catalyzed by **1**, both ^{1}H NMR and GC–MS data show that the simplest coupling product $\mathrm{MePhHSiNH}(i\text{-Bu})$ predominates.

The catalytic dehydrogenative coupling reactions are also affected by the nature of the amine $\mathrm{RNH_2}$. The chain length of the silazane product decreases as the R group becomes bulky. For example, the reaction of $\mathrm{PhSiH_3}$ (100 μL) with $\mathrm{MeNH_2}$ (60 mL, 300 Torr) in a 1-mL benzene solution of $\mathrm{Rh_2H_2(CO)_2(dppm)_2}$ (5 mg; **1**) was carried out at room temperature for 36 h, and the coupling products were characterized by GC–mass spectrometry. Among several silazane products listed in Table II, the acyclic species $\mathrm{H(PhHSiNMe)_3H}$ was formed as the highest molecular weight product. Under the same conditions, the reaction of $\mathrm{PhSiH_3}$ with $i\text{-PrNH}_2$ in the presence of **1** yielded $\mathrm{PhHSi(NH}(i\text{-Pr}))_2$ as the highest coupling product.

The dehydrogenative coupling reaction can be accelerated, and the extent of oligomerization can be increased, upon heating. For instance, identical samples of $\mathrm{PhSiH_3}$, $\mathrm{MeNH_2}$, and **1** in benzene were allowed to react at room temperature and 60 °C and were monitored by ^{1}H NMR spectroscopy. As expected, $\mathrm{PhSiH_3}$ was consumed faster in the 60 °C reaction than in the one at room temperature. The reaction samples were increased in scale and allowed

Table II. Mass Spectrometric Data for the Products Formed in the Reaction of $PhSiH_3$ with $MeNH_2$ in the Presence of 1

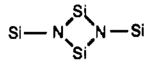
coupling products	extent of coupling	major mass fragments, m/e (mass loss, proposed assignt of mass loss)
MeNHSiHPhNHMe	N-Si-N	166 (M^+) 136 (-30, -NHMe) 107 (-59, -NHMe, $-NH{=}CH_2$)[a]
$H(PhHSiNMe)_2H$	Si-N-Si-N	272 (M^+) 240 (-32, $-NH_2Me$, -H) 195 (-77, -Ph) 164 (-108, $-PhSiH_3$) 136; 107
$H(MeNSiPhH)_2NMeH$[b]	N-Si-N-Si-N	301 (M^+) 271 (-30, -NHMe) 240 (-61, -NHMe, $-NH_2Me$) 193 (-108, $PhSiH_3$) 164; 136; 107
$H(PhHSiNMe)_2SiPhH_2$	Si-N-Si-N-Si	378 (M^+) 363 (-15, -Me) 270 (-108, $-PhSiH_3$) 240 (-30, -NHMe) 193; 164; 136; 107
$(PhHSiNMe)_3$	$(Si-N)_3$	405 (M^+) 327 (-78, -PhH) 270; 240; 164; 107
$H(PhHSiNMe)_3H$[b]	Si-N-Si-N-Si-N	407 (M^+) 376 (-31, $-NH_2Me$) 329 (-78, -PhH) 300 (-107, $-PhSiH_2$) 270; 240; 193; 164; 107

[a] The peak at m/e 107 corresponds to $PhSiH_2$, which may result from losing $NH{=}CH_2$ through β-hydrogen elimination. [b] The branched isomer cannot be ruled out on the basis of only the mass spectrometric data.

Table III. Mass Spectrometric Data for the Products Formed in the Reaction of Me_2SiH_2 with NH_3 in the Presence of 1

coupling products	extent of coupling	major mass fragments, m/e (mass loss, proposed assignt of mass loss)
$H(Me_2SiNH)_2H$	Si-N-Si-N	148 (M^+) 133 (-15, -NH or -Me) 116 (-32, $-NH_2$, MeH) 100; 74[a]
$(Me_2HSi)_3N$[b]	$(Si)_3N$	191 (M^+) 190 (-1, -H) 176 (-15, -Me) 130 (-61, $-Me_2SiH$, -2H) 116; 100; 86; 73; 59
$H(Me_2SiNH)_2$-$SiMe_2H$[c]	Si-N-Si-N-Si	205 ($M^+ - 1$) 191 (-15, -Me or -NH) 175 (-31, -MeH, -Me) 147; 131; 117; 100; 73; 59
$(Me_2SiNH)_3$[b]	$(Si-N)_3$	204 (M - 15) 187; 171; 157; 130; 114; 95; 86
$(Me_2HSi)_2NSiMe_2$-$NHSiMe_2H$	$(Si)_2N$-Si-N-Si	264 (M^+) 262 (-2, -2H)[d] 247 (-17, -2H, -Me) 205 (-59, $-SiMe_2H$) 190 (-74, $-HNSiMe_2H$) 189 (-75, $-SiMe_2H$, -MeH) 175; 173; 130; 116; 100; 73; 59

[a] The peaks at m/e 74 and 59 correspond to Me_2HSiNH and Me_2SiH, respectively. [b] These products are confirmed by comparison with the mass fragmentation data of authentic samples. [c] The branched isomer was also observed with a parent ion at m/e 206 and a similar mass fragmentation pattern. [d] Intensity equal with that of the parent ion peak. The cyclic product



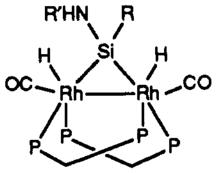
is probably formed after losing H_2.

to react for 20 h, after which the silazane products were characterized by GC–mass spectrometry. For the room-temperature sample, a parent ion at m/e 272 and the fragmentation pattern given in Table II show that the highest molecular weight product is $H(PhHSiNMe)_2H$, while for the reaction at 60 °C, products containing up to six couplings are observed along with smaller silazanes listed in Table II.

Reaction with NH_3. As described above, the dehydrogenative coupling reactions promoted by $Rh_2H_2(CO)_2(dppm)_2$ (1) are influenced by both the amines and silanes. In order to minimize the steric effects of the amine and silane and to characterize the silazane products more easily, the reaction of Me_2SiH_2 with NH_3 in the presence of 1 was performed. In a typical experiment with this system, 10 mL of NH_3 at 760 Torr and 30 mL of Me_2SiH_2 at 280 Torr were condensed onto a frozen C_6H_6 solution of 10 mg of 1. The reaction was carried out at room temperature for 20 h, and the coupling products were characterized by GC–MS. The data are given in Table III along with assignments showing the formation of linear, branched, and cyclic silazane products. For example, the species that shows a parent ion peak at m/e 148 and major fragmentation peaks at m/e 133, 116, and 74 corresponding to the loss of Me (or NH), NH_2 + MeH, and Me_2HSiNH, respectively, is assigned as the Si–N–Si–N linear coupling product $H(Me_2SiNH)_2H$. A second product with a parent ion peak at m/e 191 is assigned as $(Me_2HSi)_3N$ on the basis of the fact that its fragmentation pattern agrees closely with that of an authentic sample. A third product exhibits its most intense peak at m/e 204 and is assigned as the cyclic trisilazane coupling product $(Me_2SiNH)_3$ on the basis of the similarity of its fragmentation pattern with that of an authentic sample. It is noteworthy that neither the trisilazane $(Me_2SiNH)_3$ nor the tetrasilazane $(Me_2SiNH)_4$ exhibits a parent ion peak under the operating conditions used here. The intense peak at m/e 204 for the cyclic trisilazane corresponds to (M – 15).

Observation of the $Rh_2(\mu\text{-}SiR(NHR'))H_2(CO)_2(dppm)_2$ Intermediate. When $MeNH_2$ (10 mL at 200 Torr) was condensed into a C_6D_6 solution of $Rh_2(\mu\text{-}SiEtH)_2(CO)_2(dppm)_2$ (**3b**) in the absence of silane, a metal complex intermediate was observed that contains three different dppm $-CH_2-$ proton resonances at 4.27, 3.80, and 2.87 ppm in a 1:1:2 ratio and a hydride resonance at –9.43 ppm with a relative intensity of 2. The hydride resonance at 23 °C was a triplet of multiplets with a triplet splitting of 40 Hz. These resonances were accompanied by a doublet at δ 2.79, an unsymmetric triplet at 1.75 ppm, and a multiplet resonance at 1.68 ppm, which also belong to the metal hydride intermediate. The doublet at 2.79 ppm with 6.5-Hz coupling is assigned to the $-CH_3$ protons of the $-NHCH_3$ moiety with coupling from the NH proton. This coupling is very close to $^3J_{HH}$ observed in the organic silazane products. The resonances at 1.75 and 1.68 ppm in a 3:2 ratio result from the ethyl group on silicon. No resonance for an Si–H proton assignable to this intermediate complex was seen. The $^{31}P\{^1H\}$ NMR spectrum of the species exhibited two doublet of doublets resonances with a very small difference in chemical shifts.

This species is unstable under the reaction conditions and decomposes over 1 h at 23 °C to produce the known metal complexes $Rh_2H_2(CO)_2(dppm)_2$ (1) and $Rh_2(CO)_3(dppm)_2$ on the basis of their $^{31}P\{^1H\}$ and ^1H NMR spectra. From the relative ratios of the proton resonances, the intermediate is assigned as $Rh_2(\mu\text{-}SiEt(NHMe))H_2(CO)_2(dppm)_2$ (**5b**) with a "cradle" type structure similar to **2** in eq 1. While **5b** exhibits a well-resolved metal hydride resonance as does $Rh_2(\mu\text{-}SiEt_2)H_2(CO)_2(dppm)_2$ (**2d**) at room temperature, it appears that it is fluxional, as is **2d**, on the basis of substantial broadening of its hydride and ^{31}P resonances at low temperature. However, efforts to



5b: R = Et, R′ = Me
c: R = *n*-C_6H_{13}, R′ = Me
d: R = Et, R′ = H
e: R = *n*-C_6H_{13}, R′ = H

obtain a slow exchange limiting spectrum of **5b** have been unsuccessful to date.

Support for the structural assignment of **5** is obtained from the reaction of $Rh_2(\mu\text{-}Si(n\text{-}C_6H_{13})H)_2(CO)_2(dppm)_2$ (**3c**) with NH_3, yielding the results shown in Figure 1. An intermediate similar to **5b** rapidly forms, which in its $^{31}P\{^1H\}$ NMR spectrum exhibits two doublet of doublets resonances at 27.11 and 31.01 ppm (see Figure 1a). The only other major species observed by ^{31}P NMR spectroscopy at this time (<10 min) corresponds to the starting complex **3c**. By ^1H NMR spectroscopy, the intermediate is found to possess a triplet of multiplets hydride resonance. Selective P decoupling of this resonance gives the results shown in Figure 1b. Specifically, decoupling of the ^{31}P resonance at 27.11 ppm yields a signal similar to the fully coupled hydride resonance, whereas irradiation of the ^{31}P resonance at 31.01 ppm causes the signal to collapse to a single broad resonance. These results indicate that only the phosphine donor corresponding to the latter resonance has a large coupling with the hydride, consistent with structure **5**, in which the H ligand is trans to only one of the two P donors at each Rh center. Similar results were observed for the complexes $Rh_2H_2(\mu\text{-}SiEt(NH_2))(CO)_2(dppm)_2$ and $Rh_2H_2(\mu\text{-}SiMe(NHMe))(CO)_2(dppm)_2$. In both cases, only one P resonance significantly coupled with the hydride resonance.

As in the reaction of $Rh_2(\mu\text{-}SiEtH)_2(CO)_2(dppm)_2$ (**3b**) with $MeNH_2$, the reaction of $Rh_2(\mu\text{-}SiH(n\text{-}C_6H_{13}))_2(CO)_2(dppm)_2$ (**3c**) with $MeNH_2$ led to the analogous intermediate $Rh_2(\mu\text{-}Si(NHMe)(C_6H_{13}))H_2(CO)_2(dppm)_2$ (**5c**) on the basis of similarities of the dppm $-CH_2-$, *N*-methyl, and metal hydride resonances in the ^1H NMR spectrum with those of **5b**. Moreover, the same species forms when $MeNH_2$ is added to a benzene solution of the μ-silylene dihydride complex $Rh_2(\mu\text{-}SiH(n\text{-}C_6H_{13}))H_2(CO)_2(dppm)_2$ (**2c**). In the reaction of **3b** with other amines RNH_2 (R = *i*-Bu, *i*-Pr), similar metal hydride resonances of reaction intermediates appear as triplets of multiplets. As noted above, the reactivity of RNH_2 with $Rh_2(\mu\text{-}SiHEt)_2(CO)_2(dppm)_2$ decreases with increasing substitution on the α- and β-positions of the amine. This is supported by the observation that whereas **5** forms within 10 min for the reactions of **3b** with $MeNH_2$ and *i*-$BuNH_2$, the reaction with *i*-$PrNH_2$ takes more than 30 min to change color from yellow to red with concomitant formation of the metal hydride intermediate.

When the reaction of the secondary-silylene-bridged species $Rh_2(\mu\text{-}SiEt_2)H_2(CO)_2(dppm)_2$ (**2d**) with $MeNH_2$ was carried out in C_6D_6, $Et_2HSiNHMe$ was detected by ^1H NMR and mass spectrometry. While ^1H and $^{31}P\{^1H\}$ NMR spectra of the solution indicated that **1** and $Rh_2(CO)_3(dppm)_2$ were formed, no other metal species were observed.

Relative Activity of 1 as Catalyst. A comparison between the two catalysts $Rh_2H_2(CO)_2(dppm)_2$ (**1**) and $Ru_3(CO)_{12}$ for the reaction of $PhSiH_3$ and *i*-$BuNH_2$ was performed. The reaction conditions and initial concentrations of substrates and catalysts were made the same for the two runs in THF-d_8 at 50 °C, and the reaction was followed by ^1H NMR spectroscopy. After 10 h, all of the $PhSiH_3$ was consumed in the $Ru_3(CO)_{12}$-catalyzed reaction, while ca. 10% of the silane remained in the sample catalyzed by **1**. Both systems showed the same coupling products at this stage, corresponding mainly to (*i*-Bu)NHSiHPhNH(*i*-Bu) (N–Si–N) and $PhH_2SiN(i\text{-}Bu)SiPhH_2$ (Si–N–Si) on the basis of the growing Si–H resonances in the 4.3–5.5 ppm region of the spectrum and GC–mass spectrometric data.

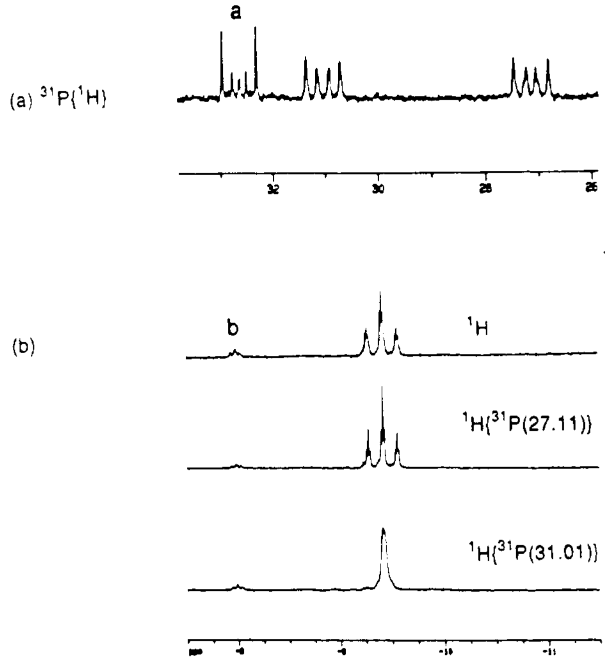
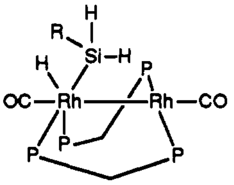


Figure 1. $^{31}P\{^1H\}$, ^1H, and $^1H\{^{31}P\}$ NMR spectra of $Rh_2H_2(\mu\text{-}Si(n\text{-}C_6H_{13})(NH_2))(CO)_2(dppm)_2$ (**5e**). The resonances marked a and b correspond to **3c** and **1**, respectively.

Comments on the Mechanism of the Coupling Reaction. It has been established previously that primary and secondary silanes react rapidly with $Rh_2H_2(CO)_2(dppm)_2$ (**1**), leading to formation of the reactive dihydride species $Rh_2(\mu\text{-}SiRR')H_2(CO)_2(dppm)_2$ (**2**) at room temperature.[1] Under the same conditions, $MeNH_2$ does not react with **1**. It therefore appears that **2** is an entry point into the catalytic cycle. Species **2** is fluxional, and its fluxionality is thought to proceed by facile Si–H reductive elimination to generate the coordinatively unsaturated intermediate A. While details leading to dehydrogenative



A

Si–N coupling and the formation of **5** are not established, one can envision activation of silane at the unsaturated site of A and nucleophilic attack by amine on terminal or bridging silyl groups, as has been proposed previously for Si–O[8] and Si–N[7] coupling reactions. Species **5**, $Rh_2H_2(\mu\text{-}SiR(NHR'))(CO)_2(dppm)_2$, is clearly an intermediate, but it is uncertain whether it is part of the catalytic cycle or is simply connected to the catalytic cycle by a facile

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[8] (a) Corriu, R. J. P.; Moreau, J. J. E. *J. Organomet. Chem.* **1976**, *114*, 135. (b) Luo, X.-L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1989**, *111*, 2527.

equilibrium. Further studies to elucidate the mechanism of dehydrogenative Si–N coupling catalyzed by binuclear Rh complexes are planned.

Conclusions. We have shown that dehydrogenative coupling of Si–H and N–H bonds to form small silazane oligomers is promoted by several dppm-bridged binuclear rhodium complexes. The steric effects of silanes and amines play a role in determining the efficacy of this reaction, with the degree of coupling decreasing as the silanes and amines become more bulky. For the reaction of $PhSiH_3$ and RNH_2 with 1, linear coupling silazane products are formed when R = *i*-Bu, whereas branched coupling products are observed for R = H, Me. The stable cradle complex $Rh_2(\mu\text{-}SiRH)_2(CO)_2(dppm)_2$ is reactive toward amines, possibly due to the favorable driving force of Si–N bond formation. In these reactions, an intermediate has been characterized and identified as $Rh_2(\mu\text{-}SiR(NHR'))H_2(CO)_2(dppm)_2$ (5).

Experimental Section

All procedures were performed on a high-vacuum line or in a glovebox. NMR samples were usually prepared in resealable NMR tubes fitted with Teflon valves from J. Young. The NMR samples were sealed under vacuum or under a known amount of specified gas. Silanes were stored under nitrogen after being received and were used without further purification. Liquid amines were dried over K_2SO_4 and stored under nitrogen after distillation. Benzene-d_6 (MSD, 99.6% D) was vacuum-distilled from sodium-benzophenone ketyl. Anhydrous ammonia (Matheson) and anhydrous methylamine (Aldrich, 98%) were used as received.

^1H and $^{31}P\{^1H\}$ NMR spectra were recorded at 400.13 and 161.98 MHz, respectively, on Bruker WH-400 and AMX-400 spectrometers. ^1H chemical shifts are reported in ppm downfield from TMS but were measured relative to the residual ^1H in the solvent. ^{31}P chemical shifts are reported in ppm downfield from phosphoric acid and were referenced to external 85% H_3PO_4. Mass spectral analyses were performed with a Hewlett-Packard 5890 GC–MS instrument equipped with an HP-1 (cross-linked Me silicon gum, 12 m × 0.2 mm × 0.33 μm film thickness) or HP-5 (cross-linked 5% PhMe silicon, 25 m × 0.2 mm × 0.5 μm film thickness) capillary column. The GC parameters used were as follows: injection port, 150 °C; detector, 250 °C; oven, temperature ramp from 150 °C (hold 10 min) to 200 °C (hold 25 min) at 20 °C/min. Ionization was by electron impact, operating at 70 eV.

$Rh_2H_2(CO)_2(dppm)_2$[9] and $Rh_2(\mu\text{-}SiRR')H_2(CO)_2(dppm)_2$ and $Rh_2(\mu\text{-}SiRH)_2(CO)_2(dppm)_2$[1] were prepared by literature procedures.

Reaction of $PhSiH_3$ and *i*-$BuNH_2$ with $Rh_2H_2(CO)_2(dppm)_2$ (1). For the NMR measurements, the samples were prepared by the following procedures. A C_6D_6 solution of $PhSiH_3$ (10 μL, 80.2 μmol) and *i*-$BuNH_2$ (10 μL, 100.6 μmol) was transferred into an NMR tube containing 1 (5 mg, 4.84 μmol). After the mixture was thawed, the reaction was followed by ^1H NMR spectroscopy. The volatiles were separated from the nonvolatiles by vacuum transfer after 1 h. The major new component of the volatiles, identified as $PhH_2SiNH(i\text{-}Bu)$, showed the following ^1H NMR resonances in C_6D_6: 7.64 (m, 2 H); 7.20 (m, 3 H); 5.07 (d, J = 2.2 Hz, 2 H); 2.47 (dd, J_1 = 8.2 Hz, J_2 = 6.5 Hz, 2 H); 1.39 (m, 1 H); 0.72 (d, J = 8.2 Hz, 6 H); 0.50 (v br). The residue was redissolved in C_6D_6 and the major new nonvolatile component, corresponding to $PhHSi(NH(i\text{-}Bu))_2$, exhibited the following ^1H NMR data: 7.73 (m, 2 H); 7.26 (m, 3 H); 5.19 (t, J = 2.2 Hz, 1 H); 2.64 (m, 4 H); 1.45 (m, 2 H); 0.80 (d, J = 8.2 Hz, 12 H).

For a large-scale reaction, a THF or C_6H_6 solution of $PhSiH_3$ (400 μL, 3.21 mmol) and *i*-$BuNH_2$ (400 μL, 4.02 mmol) was added to a reaction vessel containing 5 mg of 1. After 36 h, the solution was checked by ^1H NMR spectroscopy and characterized by GC–mass spectrometry.

Reaction of RR'_2SiH_2 (R = R' = Et; R = Me, R' = Ph) and *i*-$BuNH_2$ with $Rh_2H_2(CO)_2(dppm)_2$ (1). A THF or C_6H_6 (400 μL) solution of Et_2SiH_2 (400 μL, 3.10 mmol) and *i*-$BuNH_2$ (400 μL, 4.02 mmol) was added to a reaction vessel containing 7 mg of 1. After 36 h, about 0.25 mL of the reaction solution was put in an NMR tube containing 0.25 mL of C_6D_6. This solution was checked by ^1H NMR spectroscopy and characterized by GC–mass spectrometry. ^1H NMR of $Et_2HSiNH(i\text{-}Bu)$ in C_6D_6: 4.48 (m, 1 H); 2.49 (dd, J_1 = 8.2 Hz, J_2 = 6.5 Hz, 2 H); 1.39 (m, 1 H); 0.95 (t, J = 8.0 Hz, 6 H); 0.80 (d, J = 8.2 Hz, 6 H); 0.52 (dq, J = 8.0 Hz, J = 2.4 Hz, 4 H); 0.33 (v br). Major fragmentation pattern of $Et_2HSiNH(i\text{-}Bu)$ with proposed mass losses: (*m/e*): 159 (M^+); 144 (–15, –Me); 130 (–29, –Et); 116 (–43, $-CHMe_2$); 102 (–57, –*i*-Bu); 88 (–71, $-NH{=}CHCHMe_2$); 59 (–29, –Et of Et_2SiH_2 (88)). The higher coupling product $Et_2Si(NH(i\text{-}Bu))_2$, not observed by ^1H NMR spectroscopy, was characterized by GC–mass spectrometric data. Major fragmentation pattern of $Et_2Si(NH(i\text{-}Bu))_2$ (*m/e*): 230 (M^+); 201 (–29, –Et); 173 (–57, –*i*-Bu); 158 (–72, –NH(*i*-Bu)); 130 (–28, $-CH_2CH_2$); 116; 87; 59.

The reaction of $MePhSiH_2$ and *i*-$BuNH_2$ with 1 was performed in an NMR tube in a manner similar to the reaction of $PhSiH_3$ and *i*-$BuNH_2$ with 1 described above. Only one product was observed by ^1H NMR spectroscopy and was characterized on the basis of intensities of the ^1H NMR resonances and GC–mass spectrometric data. ^1H NMR of $MePhHSiNH(i\text{-}Bu)$ in C_6D_6: 7.62 (m, 2 H); 7.21 (m, 3 H); 5.62 (m, 1 H); 2.48 (dd, J_1 = 8.2 Hz, J_2 = 6.5 Hz, 2 H); 1.38 (m, 1 H); 0.80 (d, J = 8.2 Hz, 6 H); 0.28 (d, J = 3.0 Hz, 3 H). Major fragmentation pattern of $MePhHSiNH(i\text{-}Bu)$: 193 (M^+); 192 (M – 1); 178 (–15, –Me); 150 (–43, $-CHMe_2$); 121 (–72, –NH(*i*-Bu)).

Reaction of $PhSiH_3$ and $MeNH_2$ with 1. Two samples were prepared identically. After three freeze–pump–thaw cycles at –78 °C, a C_6H_6 *solution of* 300 μL of $PhSiH_3$ (2.4 mmol) was transferred into a reaction vessel containing 5 mg of 1 (4.84 μmol). Subsequently, $MeNH_2$ (340 Torr, 45 mL, 0.82 mmol) was condensed onto the frozen benzene solution. One of the samples was allowed to react at room temperature, while the other was heated at 60 °C. After 20 h, the reaction products of both samples were characterized by GC–mass spectrometry. For the reaction at 60 °C, three isomers with the same parent ion of *m/e* 434 and similar mass fragmentation patterns were observed in addition to the coupling products listed in Table II. These isomers had retention times of 29.82, 33.14, and 33.93 min and are possibly due to the cyclic isomers $(\underline{\mathrm{NMeSiPhHNMeSi}}\mathrm{Ph})\mathrm{NMeSiPhNHMe}$, $\mathrm{MeHN}\text{-}(\underline{\mathrm{SiPhNMeSiPh(NMeSiPhH_2)N}}\mathrm{Me})$ and $\mathrm{NM}\underline{\mathrm{e(SiPhHN}}\text{-}\mathrm{Me)_2SiPhNHMe}$. Mass fragmentation pattern of the product with retention time of 33.14 min (*m/e*): 434 (M^+); 403 (–31, –NHMe, –H); 356 (–78, –PhH); 313 (–121; –Ph, $-NH{=}CH_2$, –Me); 270; 240; 164; 148; 107.

Reaction of $Rh_2(\mu\text{-}SiEt_2)H_2(CO)_2(dppm)_2$ (2d) with $MeNH_2$. This reaction was carried out in C_6D_6 and monitored by ^1H NMR spectroscopy. After 20 h, the reaction product was characterized by GC–mass spectroscopy. ^1H NMR of $Et_2HSiNHMe$ in C_6D_6: 4.49 (m, 1 H); 2.38 (d, J = 6.5 Hz, 3 H); 1.10 (t, J = 8.0 Hz, 6 H); 0.55 (dq, J = 2.3 Hz, J = 8.0 Hz, 4 H); –0.16 (br). Coupling between the NH proton at –0.16 and the Si–H proton at 4.49 ppm was observed. Mass fragmentation pattern of $Et_2HSiNHMe$: 117 (M^+); 88 (–29, –Et or $-NHCH_2$); 60 (–57, –NHMe, $-CH_2CH_2$).

Reaction of $PhSiH_3$ and *i*-$PrNH_2$ with 1. This reaction was carried out in an NMR tube with use of the same procedure as for other NMR-scale reactions described above. Two products were observed by NMR spectroscopy, and the resonances for Si–N and N–Si–N coupling products were assigned by the intensities of their ^1H NMR signals. Characterization data for the Si–N coupling product $PhH_2SiNH(i\text{-}Pr)$: ^1H NMR (C_6D_6) 7.61 (m, 2 H), 7.19 (m, 3 H), 5.01 (d, J = 2.2 Hz, 2 H), 2.96 (m, 1 H), 0.94 (d, J = 8.2 Hz, 6 H); mass fragmentation pattern (*m/e*) 165 (M^+), 150 (–15, –Me), 121 (–43, $-CHMe_2$), 107 (–58, $-NHCHMe_2$). Characterization data for the N–Si–N coupling product $(i\text{-}Pr)NHSiPhHNH(i\text{-}Pr)$: ^1H NMR (C_6D_6) 7.68 (m, 2 H), 7.23 (m, 3 H), 5.12 (t, J = 2.2 Hz, 1 H), 3.17 (m, 2 H), 1.03 (m, 12 H); mass fragmentation pattern (*m/e*) 222 (M^+), 207 (–15, –Me), 164 (–58, $NHCHMe_2$), 150 (–72, $-NH{=}CMe_2$, –Me), 121, 107.

Reaction of Ammonia and Me_2SiH_2 with 1. After 1.5 mL of C_6H_6 was transferred into a reaction vessel containing 10 mg of 1 (9.68 μmol), NH_3 (10 mL, 760 Torr, 0.41 mmol) and Me_2SiH_2 (30 mL, 280 Torr, 0.45 mmol) were condensed onto the frozen

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benzene solution. After the mixture was thawed, the reaction was carried out at room temperature for 20 h, at which time the products were characterized by GC–mass spectrometry.

Observation of $Rh_2H_2(\mu$-SiR(NHR′))$(CO)_2(dppm)_2$ (5b, R = Et, R′ = Me; 5c, R = *n*-C_6H_{13}, R′ = Me). Complex 5 was only observed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy and could not be isolated. The following general procedures were used for the preparation of NMR samples. A 0.5-mL portion of C_6D_6 was transferred into an NMR tube containing 10 mg of 3, followed by the addition of $MeNH_2$ (10 mL, 200 Torr). After the mixture was thawed, the reaction was followed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. Spectroscopic data for **5b**: ^1H NMR (C_6D_6) 7.62 (br s, 10 H), 7.33 (s, 2 H), 7.22 (s, 4 H), 6.85–6.63 (m, 24 H), 4.27 (m, 1 H), 3.80 (m, 1 H), 2.87 (m, 2 H), 2.72 (d, J = 6.5 Hz, 3 H), 1.72 (t, J = 8.0 Hz, 3 H), 1.65 (m, 2 H), −9.43 (t of m, J_t = 40 Hz, 2 H); $^{31}P\{^1H\}$ NMR 30.15 (dd, J_1 = 71 Hz, J_2 = 36 Hz), 29.33 (dd, J_1 = 68 Hz, J_2 = 39 Hz). Selective spectroscopic data for **5c**: ^1H NMR (C_6D_6) 7.66 (br s, 10 H), 7.36 (s, 2 H), 7.22 (s, 4 H), 6.9–6.6 (m, 24 H), 4.24 (m, 1 H), 3.77 (m, 1 H), 2.86 (m, 2 H), 2.79 (d, J = 6.5 Hz, 3 H), −9.36 (t of m, J_t = 45 Hz, 2 H); $^{31}P\{^1H\}$ NMR 30.43 (dd, J_1 = 71 Hz, J_2 = 36 Hz), 29.60 (dd, J_1 = 68 Hz, J_2 = 39 Hz). Selective spectroscopic data for **5d**: ^1H NMR (C_6D_6) 4.41 (m, 1 H), 3.80 (m, 1 H), 2.93 (m, 1 H), 2.79 (m, 1 H), 1.72 (m, 5 H), −9.40 (t of m, J_t = 57 Hz, 2 H); $^{31}P\{^1H\}$ NMR 30.94 (dd, J_1 = 72 Hz, J_2 = 34 Hz), 27.00 (dd, J_1 = 67 Hz, J_2 = 38 Hz). Selective spectroscopic data for **5e**: ^1H NMR (C_6D_6) 4.42 (m, 1 H), 3.83 (m, 1 H), 2.94 (m, 1 H), 2.81 (m, 1 H), −9.42 (t of m, J_t = 57 Hz, 2 H); $^{31}P\{^1H\}$ NMR 31.01 (dd, J_1 = 72 Hz, J_2 = 34 Hz), 27.11 (dd, J_1 = 67 Hz, J_2 = 38 Hz).

The intermediate $Rh_2H_2(\mu$-SiMe(NHMe))$(CO)_2(dppm)_2$, which was formed in the reaction of $Rh_2(\mu\text{-SiMeH})_2(CO)_2(dppm)_2$ with $MeNH_2$ in CD_2Cl_2, was identified by ^1H, $^1H\{^{31}P\}$, and $^{31}P\{^1H\}$ NMR spectroscopy with the following selective data: ^1H NMR (CD_2Cl_2) 4.17 (m, 1 H), 3.82 (m, 1 H), 2.70 (m, 2 H), 2.63 (d, J = 8 Hz, 3 H), 0.55 (s, 3 H), −9.92 (m, 2 H); $^{31}P\{^1H\}$ NMR 30.53 (dd, J_1 = 69 Hz, J_2 = 38 Hz), 27.74 (dd, J_1 = 71 Hz, J_2 = 35 Hz).

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Assembling Ethylene, Alkyl, Hydride, and CO Ligands at Iridium

Pierluigi Barbaro, Claudio Bianchini,* Andrea Meli, Maurizio Peruzzini, Alberto Vacca, and Francesco Vizza

Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione, CNR,
Via J. Nardi 39, 50132 Firenze, Italy

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The iridacyclopropane complex $[(triphos)Ir(Cl)(C_2H_4)]$ is the starting point to synthesize a number of stable iridium complexes containing various combinations of *participative* ligands such as hydride, ethylene, alkyls and heteroalkyls, alkynes, and carbon monoxide: $Ir(H)(C_2H_4)$, $Ir(H)_2(C_2H_4)$, $Ir(C_2H_5)(C_2H_4)$, $Ir(CO)_2$, $Ir(H)(C_2H_5)(CO)$, $Ir(H)_2(CO)$, $Ir(H)_2(CH_2CH_2PEt_3)$, $Ir(H)_3$, $Ir(H)_2(C_2H_5)$, $Ir(H)_2(C_3H_7)$, $Ir(C_2H_4)_2$, $Ir(RC{\equiv}CR)$, $IrH(\mu\text{-}H)_2HIr$, and $IrH(\mu\text{-}Cl)_2HIr$. Due to the tripodlike structure of the ligand $MeC(CH_2PPh_2)_3$ (triphos), all the complexes invariably exhibit a facial arrangement of the phosphorus and non-phosphorus ligands. The contemporaneous availability of so many related species has allowed a comparative experimental study on several important reactions. These include (i) reductive elimination of C–H and H–H bonds from dihydride alkyl complexes, (ii) reductive elimination of H–H bonds vs hydride migration in dihydride ethylene species, (iii) nucleophilic additions to coordinated double bonds, (iv) phosphine arm dissociation in triphos complexes, and β-H elimination vs C–H bond reductive elimination in hydride alkyl complexes. In most instances, such reactions are characterized by stereo- and chemoselectivity. Valuable information on the role played by the nature of the metal and of the phosphine ligands in determining the reactivity has been provided by a comparison among strictly related Rh and Ir complexes containing either triphos or three comparable monophosphines.

Introduction

Olefin-based reactions such as hydroformylation, hydrogenation, isomerization, polymerization, amination, and related nucleophilic additions contribute a large percentage of the whole body of metal-catalyzed homogeneous transformations of organic compounds. All of these reactions take place through multistep sequences involving (i) olefin or CO binding to the metal center, (ii) insertion of CO or olefins across M–H and M–C bonds, (iii) oxidative addition of H_2 or C–H bonds at the metal, and (iv) reductive elimination from the metal center to form C–H bonds. A good catalyst performs such reaction sequences very rapidly so that the observation of intermediates is generally difficult. This limitation can be overcome with the use of model complexes exhibiting high kinetic stability.

Due to the large radial extension of the dπ orbitals and the readily attainable π-d^6 electron configuration, third-row transition metals, particularly iridium, are being largely used to design model compounds for homogeneously catalyzed reactions.[1] A second, less common strategy to gain information about the structure of reaction intermediates involves the use of ancillary ligands that are capable of

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