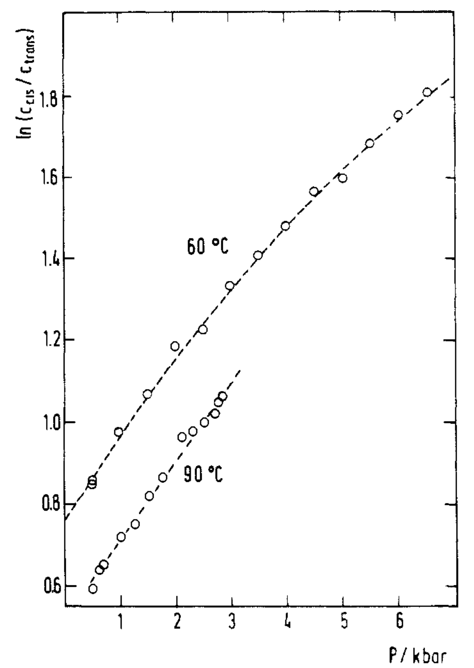

Figure 2. Pressure dependence of diastereoselectivity, in terms of ln (c_{cis}/c_{trans}), for the cycloaddition of **1** and **2** in CH_2Cl_2 solution at 60 and 90 °C.

centration of the ether **2** exceeding that of the *hetero* diene **1** by more than two orders of magnitude. The Kezdy–Swinbourne plot[10] for the pseudo-first-order reaction yields a straight line over the whole range up to complete conversion of the diene **1**. From the first-order rate coefficient and from the known amount of **2**, the second-order Diels–Alder rate coefficient *k* was obtained. The *k* values presented in Figure 1 for 90 °C as a function of pressure refer to a rate law with concentrations in terms of mole per kilogram of solution. The rate coefficient increases with pressure. For reactions at 90 °C with the vinyl ether **2** in a large excess concentration of 1 mol·kg^{-1}, the half-life of **1** decreases from 6.2 h at ambient pressure to 34 min at 3 kbar. From the slope of the straight line fitted to the ln *k* vs *P* data in Figure 1, the overall activation volume found was $-\Delta V^{\neq} = 24.2 \pm 1.0$ cm^3·mol^{-1}, which is very close to the value measured for a similar *hetero*-Diels–Alder reaction.[1] Both values are, however, relatively small in comparison to $-\Delta V^{\neq} > 30$ cm^3·mol^{-1} which is normally found for intermolecular Diels–Alder reactions.[3,4] An explanation for this discrepancy might be that the transition state in the reaction of **1** and **2** has a lower polarity compared to the ground state.[11]

Since the diastereomeric cycloadducts **3** and **4** could not be distinguished by IR spectra (C=O) under high pressure conditions, pressure-induced diastereoselectivity was investigated by HPLC analysis of the reaction mixture after complete conversion of **1**. For these studies cycloadditions were performed in a 7-kbar cell without windows. The logarithm of the concentration ratio of **3** and **4**, ln (c_{cis}/c_{trans}), plotted vs pressure at 60 and 90 °C is shown in Figure 2. For the 60 °C curve a slight deviation from linearity is observed. This corresponds to a pressure-dependent decrease of activation volume as found for many other reactions.[3] At 60 °C the ratio fo **3** and **4** changes from 2.15:1 up to 6.07:1 between ambient pressure and 6.5 kbar. From the slope of both isomers, for *P* approaching ambient pressure, the difference in activation volume between the reaction paths leading to diastereomers **3** and **4**, respectively, was found to be $-\Delta\Delta V^{\neq} = 5.8 \pm 0.5$ cm^3·mol^{-1}. From $\Delta\Delta V^{\neq}$ the individual $\Delta V^{\neq}$ values for the endo and exo cycloadditions were found to be -26.0 ± 1.5 cm^3·mol^{-1} and -20.1 ± 1.5 cm^3·mol^{-1}, respectively. The temperature dependence of diastereoselectivity in Figure 2 corresponds to a difference in activation energy of $-\Delta\Delta H^{\neq} = 8.1 \pm 2.4$ kJ·mol^{-1}. It should be noted that the observed diastereoselectivity comes from kinetic control. Isomers **3** and **4** do not interconvert within typical reaction times, even at 90 °C and 6 kbar. From thermodynamics the trans product **4** is strongly favored. Isomerization of **3** with boron trifluoride etherate followed by crystallization allows an almost complete transformation of **3** into **4**.[7]

In the system studied our experiments show there is a twofold advantage of applying high pressure: (1) According to the remarkable large difference in activation volume, $\Delta\Delta V^{\neq}$, diastereoselectivity is enhanced toward high pressure at constant temperature. (2) From the experimental $\Delta\Delta H^{\neq}$ it can be deduced that diastereoselectivity also increases toward lower temperature. As $\Delta V^{\neq}$ is fairly large and negative, high pressure enables the cycloaddition to be run with reasonable rate even at and below 0 °C. High selectivity for **3** can therefore be achieved in transformations at high pressure and low temperature. Thus, **3** and **4** are formed at 90 °C and 1 bar only in a 1.67:1 ratio, whereas at 0.5 °C and 6 kbar at 13.6:1 ratio is obtained. The corresponding ln (c_{cis}/c_{trans}) values (cf. Figure 2) are 0.51 and 2.61, respectively.

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(11) le Noble, W. J.; Ojosipe, B. J. *J. Am. Chem. Soc.* **1975**, *97*, 5939.

Stereoselective Synthesis of Monosubstituted *cis*-Aryldiazenes, NH=NR†

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Monosubstituted diazenes (NH=NR) are invoked as reactive intermediates in numerous important organic reactions including oxidations of arylhydrazines,[1] Wolff–Kishner reductions,[2] the McFadyen–Stevens conversion of carboxylic acids to aldehydes,[3] and reductive deaminations.[4] However, this elusive molecular class was not detected until 1965 when Kosower and Huang observed *trans*-phenyldiazene as the product of the decarboxylation of phenyldiazenecarboxylic acid.[5] Several monoalkyl- and monoaryldiazenes have since been prepared by various routes.[6-9] Diazenes possessing a hydrogen atom(s) attached to a diazenyl nitrogen differ from their disubstituted cousins (NR=NR) in two important ways: (1) diimine (NH=NH)[10] and NH=NR[11] are reactive, thermally unstable species, usually decomposing with extrusion of dinitrogen well below ambient temperature, in contrast to the relatively inert disubstituted derivatives (like azobenzene), and (2) although both cis and trans isomers of disubstituted diazenes are well-known,[12] only *trans*-NH=NH[13,14] and *trans*-

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† Dedicated to our colleague Professor Gerhard L. Closs on the occasion of his 60th birthday.

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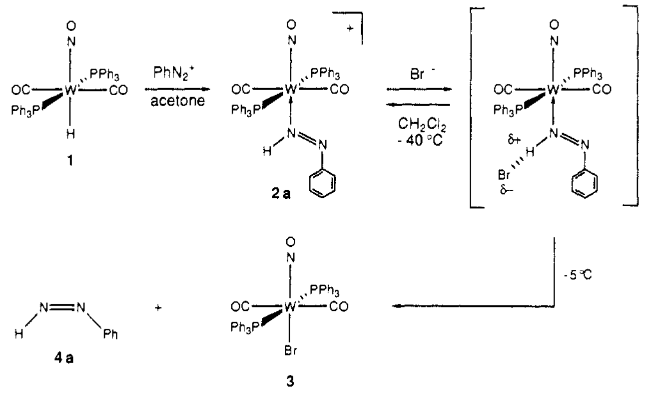
Scheme I



$NH{=}NR$[5-9,11] have been directly observed. This latter point is especially significant because a trans → cis isomerism is generally regarded as a key feature in the reactions of both $NH{=}NH$ and $NH{=}NR$, with the cis isomers being responsible for their interesting chemistries.[10,11]

Although they have never been observed, *cis*-$NH{=}NR$ molecules are classic examples of reactive species that can be stabilized by coordination to transition metals. These complexes are commonly prepared by 1,1-insertions of aryldiazonium cations into metal-hydride bonds.[15] The diazene ligands in such complexes are often labile and can be displaced by various nucleophiles, but these displacement reactions occur at temperatures too high (at or above ambient temperature) to allow for direct detection of the free $NH{=}NR$ molecule.[15c,d,16] We report here a low-temperature displacement of coordinated *cis*-$NH{=}NR$ from a tungsten complex, a reaction that provides a general method for the stereoselective synthesis of *cis*-aryldiazenes.

The hydrido complex *trans,trans*-$W(H)(CO)_2(NO)(PPh_3)_2$ (**1**)[17] reacts with aryldiazonium salts $[RNN][PF_6]$ ($R = C_6H_5$, $p\text{-}C_6H_4CH_3$, $p\text{-}C_6H_4OCH_3$, $p\text{-}C_6H_4CF_3$) to afford red, air-stable, cationic aryldiazene complexes [*trans,trans*-$W(NH{=}NR)(CO)_2(NO)(PPh_3)_2^+][PF_6^-]$ (**2a**, $R = C_6H_5$; **2b**, $R = p\text{-}C_6H_4CH_3$; **2c**, $R = p\text{-}C_6H_4OCH_3$; **2d**, $R = p\text{-}C_6H_4CF_3$) in high yield (70–85%).[18] The $|^2J_{NH}| = 3.0$ Hz for [*trans,trans*-$W(^{15}NH{=}^{15}NPh)(CO)_2(NO)(PPh_3)_2^+$] (**2a**-$\alpha,\beta^{15}N$) shows that the diazene ligand adopts a cis geometry (vide infra).[15,19] Titration of cold (−40 °C) methylene chloride solutions of **2a**-$\alpha,\beta^{15}N$ with $[n\text{-}Bu_4N^+][Br^-]$ results in strong ion-pairing between the cationic metal complex and Br^- as indicated by a gradual downfield shift of the resonance for the diazenyl proton (^1H NMR) from δ 11.98 (no Br^-) to δ 14.01 (1 equiv of Br^-).[20] Warming solutions of **2** containing 1 equiv of $[n\text{-}Bu_4N^+][Br^-]$ to −5 °C results in formation of the neutral bromo complex *trans,trans*-$WBr(CO)_2(NO)(PPh_3)_2$ (**3**)[17] with displacement of the free aryldiazene as *cis*-$NH{=}NR$ (**4a**, $R = C_6H_5$; **4b**, $R = p\text{-}C_6H_4CH_3$; **4c**, $R = p\text{-}C_6H_4OCH_3$; **4d**, $R = p\text{-}C_6H_4CF_3$). The overall sequence is illustrated for **4a** in Scheme I. Compounds **4a–d**, the first examples of the key cis isomers of monosubstituted diazenes, exhibit moderate thermal stability at the temperature (−5 °C) at which the displacements are effected and have been characterized spectroscopically[21] and by their reactivities.

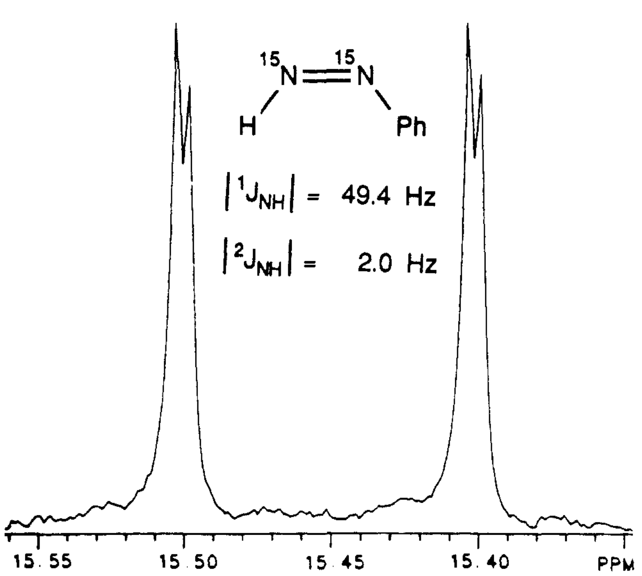


Figure 1. 500-MHz ^1H NMR spectrum showing the diazenyl proton resonance (δ 15.45) of **4a**-$\alpha,\beta^{15}N$ (CD_2Cl_2 solution, −5 °C).

Three features of the diazenyl proton resonance of **4a**-$\alpha,\beta^{15}N$ (Figure 1) merit comment since they provide unambiguous evidence that the free *cis*-aryldiazene has indeed been prepared. First, the chemical shift of δ 15.45 compares favorably with that reported for *trans*-$NH{=}NMe$ (δ 15.6).[6] Second, the $|^2J_{NH}| = 2.0$ Hz is diagnostic of a cis geometry about the N–N double bond. The magnitudes and signs of such two-bond coupling constants are highly sensitive to spatial orientations of the nuclei. For example, in acetaloxime ($MeHC{=}N\text{-}OH$), $^2J_{NH} = 2.9$ Hz for the isomer where the coupled protion is anti to the nitrogen lone pair, and it is −15.9 Hz for the isomer where the proton is syn to the lone pair.[19] Third, the unusually small $|^1J_{NH}| = 49.4$ Hz indicates that the *cis*-$NH{=}NPh$ moiety is no longer coordinated to the metal. Nuclear spin-electron orbital interactions between the hydrogen nucleus and the highly anisotropic nitrogen lone pair in molecules like diphenylketimine ($Ph_2C{=}NH$, $|^1J_{NH}| = 52.4$ Hz) give one-bond NH coupling that is not determined solely by the Fermi contact term.[22] Protonation of the lone pair (or, in our case, coordination to a metal as in **2a**, $|^1J_{NH}| = 62.8$ Hz) results in a "normal" $N(sp^2)$-H coupling (for $[Ph_2C{=}NH_2^+]$, $|^1J_{NH}| = 92.6$ Hz). The $^1J_{NH}$ values for **4a–d** are the smallest one-bond NH couplings yet reported,[21] and it is interesting that Roberts predicted years ago that $^1J_{NH}$ for $NH{=}NPh$ should not be determined by the contact interaction alone![23]

With the first examples of *cis*-$NH{=}NR$ in hand, we are commencing an investigation of the chemistry of these species. As is the case for *trans*-$NH{=}NPh$,[5,11] solutions of **4a–d** show

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(14) 1,1-Diimine ($N{=}NH_2$) has also been prepared and characterized: Sylwester, A. P.; Dervan, P. B. *J. Am. Chem. Soc.* **1984**, *106*, 4648.

(15) Typical examples include the following: (a) Parshall, G. W. *J. Am. Chem. Soc.* **1967**, *89*, 1822. (b) Parshall, G. W. *Ibid.* **1965**, *87*, 2133. (c) Haymore, B. L.; Ibers, J. A. *Ibid.* **1975**, *97*, 5369. (d) Albertin, G.; Antoniutti, S.; Lanfranchi, M.; Pelizzi, G.; Bordignon, E. *Inorg. Chem.* **1986**, *25*, 950 (and references therein).

(16) $Cu_4Cl_4(NH{=}NPh)$ releases phenyldiazene, probably as the trans isomer (based on X-ray data for the $NMe{=}NMe$ derivative[16a]) when dissolved in acetonitrile.[16b] (a) Brown, I. D.; Dunitz, J. D. *Acta Crystallogr.* **1960**, *13*, 28. (b) Petredis, D.; Burke, A.; Balch, A. L. *J. Am. Chem. Soc.* **1970**, *92*, 428.

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(18) Compounds **2a–d** (and their ^{15}N labeled derivatives) were prepared according to the literature procedure[17] for **2a**. ^1H NMR ($CDCl_3$, 500 MHz) for the diazenyl proton ($W\text{-}NH{=}NR$): **2a**-$\alpha,\beta^{15}N$, δ 12.25, dd, $|^1J_{NH}| = 63.8$ Hz, $|^2J_{NH}| = 3.0$ Hz; **2b**-$\alpha^{15}N$, δ 12.03, d, $|^1J_{NH}| = 63.5$ Hz; **2c**-$\alpha^{15}N$, δ 11.62, d, $|^1J_{NH}| = 63.8$ Hz; **2d**-$\alpha^{15}N$, δ 12.53, d, $|^1J_{NH}| = 63.9$ Hz. See Supplementary Material for complete (^1H, ^{31}P NMR; IR) spectroscopic and analytical data.

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(20) The dynamic equilibrium is also manifested by substantial broadening of the NH resonance on addition of Br^- (FWHM ~ 10 Hz, $|^1J_{NH}| = 66.3$ Hz, $^2J_{NH}$ unresolved); the ^{31}P NMR chemical shift is virtually unaffected ($\Delta\delta \sim 0.1$ ppm).

(21) See Supplementary Material for experimental details of the displacement reaction. ^1H NMR (CD_2Cl_2, 500 MHz, −5 °C) for the diazenyl proton ($NH{=}NR$): **4a**-$\alpha,\beta^{15}N$, δ 15.45, dd, $|^1J_{NH}| = 49.4$ Hz, $|^2J_{NH}| = 2.0$ Hz; **4b**-$\alpha^{15}N$, δ 15.27, d, $|^1J_{NH}| = 49.3$ Hz; **4c**-$\alpha^{15}N$, δ 15.03, d, $|^1J_{NH}| = 49.5$ Hz; **4d**-$\alpha^{15}N$, δ 15.73, d, $|^1J_{NH}| = 49.3$ Hz. UV–vis ($n \rightarrow \pi^*$, CH_2Cl_2/CH_3CN, 1:2) of **4a**, $\lambda_{max} = 4150$ Å ($\epsilon \leq 50$). It is noteworthy that, contrary to the prediction,[11b] the $n \rightarrow \pi^*$ transition for **4a** appears to be at a shorter wavelength than that for the trans isomer.

(22) Binsch, G.; Lambert, J. B.; Roberts, B. W.; Roberts, J. D. *J. Am. Chem. Soc.* **1964**, *86*, 5564.

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thermal instability above about +5 °C. The predominant products from the thermal decomposition of **4a** are dinitrogen and benzene (eq 1).[24] It is noteworthy that the analogous decomposition of

$$\underset{\mathbf{4a}}{cis\text{-NH}{=}\text{N}(\text{C}_6\text{H}_5)} \rightarrow \text{C}_6\text{H}_6 + \text{N}_2 \qquad (1)$$

trans-NH=NPh is a second-order process, with the interpretation that the rate-determining step is a bimolecular trans → cis isomerization.[5,11] Our preliminary kinetic studies (^{1}H NMR) suggest that for **4a** this is a first-order process ($t_{1/2}$ ~85 min, +5 °C),[25] an important result that appears to put us in a good position to address fundamental details of the nitrogen extrusion reactions of these species. Moreover, this system is well-suited for such studies because of the following: (1) the diazenes are prepared with known cis stereochemistry (and cis → trans isomerization does not occur under our reaction conditions), (2) the *cis*-NH=NR can be prepared under conditions and in solvents that allow for their study by conventional ^{1}H NMR and UV spectroscopic techniques, (3) various substituted aryldiazenes can be generated, allowing us to probe electronic effects in their decompositions, and (4) since the sources of the diazenes are aryldiazonium salts and a metal-hydride (or deuteride), we can easily prepare salient isotopomers (^{2}H, ^{15}N).

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Supplementary Material Available: Synthetic and experimental details and tables of analytical, NMR (^{1}H, ^{31}P), IR, and UV data (2 pages). Ordering information is given on any current masthead page.

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(24) A Toepler measurement showed that 1.06 equiv of N_2/W was produced in the room temperature reaction of 0.21 g (0.194 mmol) of **2a** with 0.3 mmol of *n*-Bu_4NBr (CH_2Cl_2 solution). Benzene was analyzed by capillary GC-MS and ^{1}H NMR.

(25) Note that the first-order lifetime for **4a** at +5 °C is about the same order of magnitude as the second-order lifetime estimated for the same concentration of *trans*-NH=NPh. A detailed kinetic investigation of the decomposition of **4a** is now in progress.

Synthesis and Structural Characterization of Pt-Si Dimers with Unusually Short Cross-Ring Silicon-Silicon Interactions

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Polysilanes have use in applications where photosensitivity is required and as precursors to β-SiC.[1] Polysilanes are usually prepared from dichloroorganosilanes and sodium at ~100 °C.[1] Several reports of transition-metal-catalyzed formation of polysilanes from R_2SiH_2 and $RSiH_3$ have appeared in which product distributions have been the main focus.[2] The mechanism of this catalytic process is poorly understood.[2b–d,3] Dimeric silyl- or hydride-bridged complexes of titanium and zirconium are the only reported metal-containing species isolated from catalytic silane polymerizations.[4] Herein we report the synthesis and structural characterization of a series of platinum–silyl dimers with unusually short cross-ring Si-Si distances. These dimers are catalysts or catalyst precursors in silane oligomerization reactions.

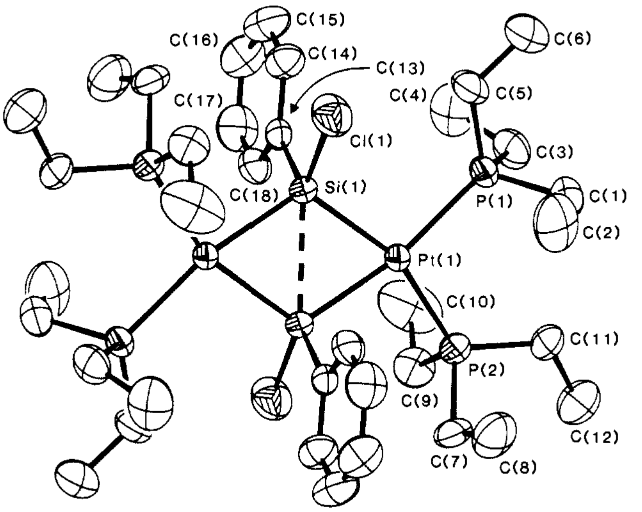
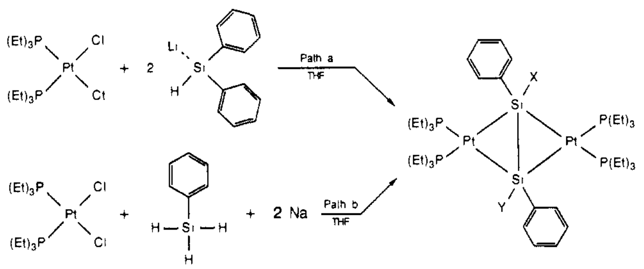


Figure 1. ORTEP labeling diagram of **1a–c** and **1b**. The thermal ellipsoids are drawn at the 20% probability level. Hydrogens are omitted for clarity.

Scheme I[a]



[a] **1a**, X = Y = H; **1b**, X = Y = Cl; **1c**, X = H, Y = Cl.

The preparation of cocrystallized mixtures of three platinum-silyl dimers $[(Et_3P)_2Pt(SiPhX)(SiPhY)Pt(PEt_3)_2]$ (**1a**, X = Y = H; **1b**, X = Y = Cl; and **1c**, X = H and Y = Cl) from two very different reaction paths is shown in Scheme I. The reaction of $PtCl_2(PEt_3)_2$[5] with $LiSiHPh_2$[6] in THF (path a, Scheme I) yields a small quantity of the cocrystallized mixture **1a–c** as air stable yellow crystals suitable for X-ray diffraction studies. The complexes **1a–c** are the major platinum-containing products produced by the reaction of $PtCl_2(PEt_3)_2$ with SiH_3Ph in THF with the addition of a slight excess of sodium powder (path b, Scheme I).[7]

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(1) For a recent review, see: West, R. *J. Organomet. Chem.* **1986**, *300*, 327–346.

(2) (a) Ojima, I.; Inaba, S.-I.; Kogure, T.; Nagai, Y. *J. Organomet. Chem.* **1973**, *55*, C7–C8. (b) Yamamoto, K.; Okinoshima, H.; Kumada, M. *J. Organomet. Chem.* **1971**, *27*, C31–C32; **1970**, *23*, C7–C8. (c) Corey, J. Y.; Chang, L. S.; Corey, E. R. *Organometallics* **1987**, *6*, 1595–1596. (d) Brown-Wensley, K. A. *Organometallics* **1987**, *6*, 1590–1591. (e) Lappert, M. F.; Maskell, R. K. *J. Organomet. Chem.* **1984**, *264*, 217–228.

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(5) $PtCl_2(PEt_3)_2$ was prepared from $PtCl_2(NC\text{-}Ph)_2$ and PEt_3. Its properties were as reported by Jensen (Jensen, K. A. *Z. Anorg. Allg. Chem.* **1936**, *229*, 225–281).

(6) Gilman, H.; Steudel, W. *Chem. Ind.* **1959**, 1094.

(7) All reactions were conducted under an argon atmosphere. The product from path a was obtained by removing the THF under vacuum followed by extraction with and recrystallization from hexane. The reaction mixture of path b showed the evolution of gas, presumably H_2. Filtration of the mixture and removal of the solvent leaves a dark brown oil which when *quickly* washed with acetone yields the yellow solid **1a–c**. Low isolated yields (10–20%) of pure **1a–c** from path b are due to reaction of acetone with **1a–c** and to difficulties in completely removing traces of the liquid oligomeric silanes from **1a–c** via subsequent recrystallizations from hexane.

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