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

$$\underset{\mathbf{4a}}{cis\text{-}NH{=}N(C_6H_5)} \rightarrow C_6H_6 + N_2 \qquad (1)$$

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 (^1H 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 ^1H 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 (^2H, ^{15}N).

Acknowledgment. Financial support from the National Science Foundation (Grant CHE-8520329), the donors of the Petroleum Research Fund, administered by the American Chemical Society (17718-AC3), and the Research Corporation is appreciated. The NMR facilities were supported in part through the University of Chicago Cancer Center Grant (NIH-CA-14599).

Supplementary Material Available: Synthetic and experimental details and tables of analytical, NMR (^1H, ^{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 ^1H 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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Received November 5, 1987

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.

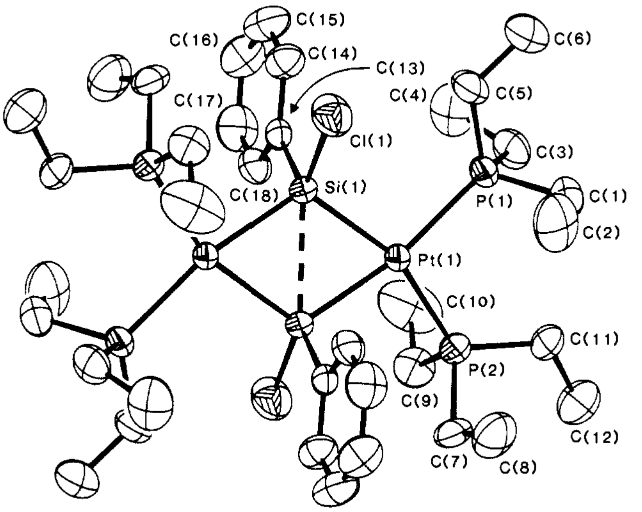
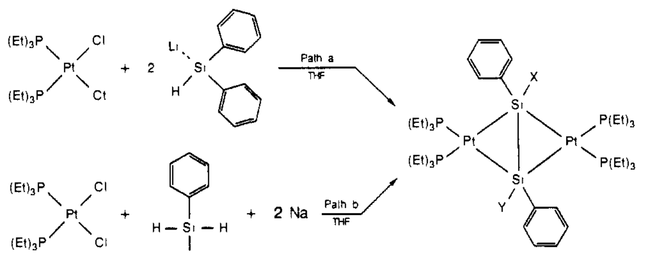


Figure 1. ORTEP labeling diagram of **1a-c** and **1b**. The thermal ellipsoids are drawn at the 20% probability level. Hydrogens are omitted for clarity.

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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[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).

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[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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Crystals of pure **1b** can be obtained by treating toluene solutions of **1a–c** with carbon dioxide followed by recrystallization from benzene. Apparently the Si–H bonds of **1a** and **1c** react with carbon dioxide to yield unidentified complexes, whereas **1b** is unreactive.

Both paths a and b in Scheme I are complicated by partial chlorination of the Si–H bonds. This is not unexpected because Noble metals catalyze chlorination of Si–H bonds using a variety of chloride sources.[8] Path a proceeds with the net loss of a phenyl substituent. We have not determined whether this can be attributed to a metal-catalyzed disproportionation of the substituents[2a,d,3a,9,10] or to rearrangement of the silyllithium reagent.[11]

The addition of catalytic quantities of **1a–c** to phenylsilane yields di- and trisilanes, with some scrambling of the phenyl and hydride substituents.[12] The di- and trisilanes are also produced by the addition of $PtCl_2(PEt_3)_2$ to excess SiH_3Ph and are byproducts of path b.[12]

Field desorption mass spectrometry of **1a–c** clearly shows that all three dimers are present in the crystalline compound. The X-ray study of the product from path a was performed.[13] Alternating refinements to convergence holding the thermal parameters of the chlorine atom fixed while the occupancy factor was freed and vice versa shows that a silyl chloride is present in place of a silyl hydride approximately 65% of the time in this particular crystalline mixture.[13] Pure **1b** has also been crystallographically characterized.[14] All products were further characterized by IR and NMR spectroscopy.[15,16]

An ORTEP drawing of the structure of **1a–c** and pure **1b** is shown in Figure 1. The silicon atoms and H or Cl and phenyl substituents lie in a plane which is perpendicular to the Pt–Pt vector and the plane defined by the platinum–silicon ring. The Si–Si separations in **1a–c** (2.575 (15)–2.602 (4) Å) are within the range of known single Si–Si bonds (2.33–2.70 Å)[17] and are the shortest cross-ring Si–Si distances in any metal–silicon four-membered ring.[18-20] The Pt–Si bonds (2.355 (7)–2.383 (8) Å) are long when compared to other Pt–Si bonds in environments of similar steric demands.[10,18] The acute deviation of the angle at the "square-planar" platinum atoms (Si–Pt–Si = 65.9 (3)–66.5 (1)°) and the increase in the angles of the "tetrahedral" silicon atoms (Pt–Si–Pt = 113.6 (1)–114.2 (3)°) suggest that the Si–Si interaction forms an integral part of the bonding scheme. The acute Si–Pt–Si angle is not a result of van der Waals repulsions between the platinum atoms because the Pt–Pt distances range from 3.973 (1)–3.997 (2) Å, whereas platinum has a van der Waals radius of 1.7–1.8 Å.[22] The large cross-ring Si–Si separations (3.852–4.225 Å),[21] acute M–Si–M angles (69.6–75.0°), and short M–M distances (2.708–3.183 Å) of most other metal–silicon dimers are in sharp contrast to those of **1a–c**.[10,18-20] Only $[Cp_2TiSiH_2]_2$ has a similar cross-ring Si–Si distance (2.69 Å)[20] and M–Si–M angle (103°).[20]

The π-coordination of the disilene PhXSi=SiYPh to two $Pt(PEt_3)_2$ moieties provides a bonding picture of the complexes **1a–c** which is consistent with their geometry. This bonding picture of **1a–c** has been supported by a recent theoretical investigation.[23] The π-coordination of a bulky disilene to a single platinum has been reported, but crystallographic data are not available.[24] As a consequence of π-coordination, the Si–Si distance of **1a–c** is lengthened by 19–22% from that in free disilenes (2.13–2.16 Å).[25] This percent lengthening can be compared to the 12% or 27% lengthening of the C–C distance in $CH_2{=}CH_2$ on π-coordination to two zirconium centers in $Zr_2X_6(PEt_3)_4(CH_2{=}CH_2)$ (X = Br or Cl, respectively).[26] In **1a–c** and $Zr_2X_6(PEt_3)_4(CH_2CH_2)$ the resultant Si–Si (2.58–2.60 Å) or C–C (1.56 and 1.69 Å) separations are longer than the "typical" single bond distances (Si–Si = 2.34 Å and C–C = 1.54 Å).[22] The bonding descriptions of **1a–c** and the zirconium–ethylene complexes[26] are extensions of the Dewar–Chatt–Duncason (DCD) model, which recently has also been applied to the cross-ring Si–Si interactions in $[R_2SiX]_2$ (X = CH_2, NH, O, PH, or S).[27] The chemistry of **1a–c** shows similarities to that of π-coordinated diphosphene complexes because the synthesis of $M(\eta^2\text{-}RP{=}PR)L_n$ can involve monophosphorus reagents[28,29] and similar DCD bonding schemes have been developed.[29] As a consequence of the bonding scheme the silicons of **1a–c** are pentacoordinate in a highly distorted trigonal bipyramidal geometry.[30,31] Placing the platinum atoms in the axial positions is consistent with the relatively long Pt–Si bonds,[30] and this results in positioning the hydrides in their favored

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(13) (a) Crystallographic data for **1a–c**: space group, $P2_1/n$, a = 10.985 (2) Å, b = 11.803 (2) Å, c = 17.636 (3) Å, β = 99.62 (2)°, V = 2254.4 (8) Å^3, and Z = 2. Intensity data were collected from $3.0 < 2\theta < 50.0°$. Refinement on the basis of 1946 reflections ($I \geq 3\sigma$) resulted in a final R = 0.068 and R_w = 0.070. (b) UCLA Crystallographic Computing Package, December 2, 1985. Numerical absorption correction was applied.

(14) Crystallographic data for **1b**: space group $P2_1/n$, a = 10.962 (2) Å, b = 11.833 (2) Å, c = 17.609 (4) Å, b = 99.62 (2)°, V = 2252.2 (8) Å^3, and Z = 2. Intensity data were collected from $3.0 < 2\theta < 52.0°$. Refinement on the basis of 4116 reflections ($I \geq 0\sigma$) resulted in a final R = 0.054 and R_w = 0.043. See ref 13b.

(15) Selected spectral data for the mixture **1a–c**: IR (Nujol mull) ν_{Si-H} = 1955 (m) and 1980 (m) cm^{-1}; ^{1}H NMR (C_6D_6) 0.85 (m, CH_3), 1.72–1.83 (m, CH_2), 4.37 (m, SiH), 7.25, 7.71, and 7.94 (t, d, and d, respectively, C_6H_5). Except for the absence of the Si–H signals, the IR and NMR data for **1b** are virtually identical with those of **1a–c**.

(16) Hydride bridges on the metal–silicon bonds are a common feature in the structures of metal–silicon four-membered rings.[10] We find no evidence of such in the crystallographic or spectra data of **1a–c** or **1b**.

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equatorial sites.[32] The inclusion of the Si–Si bond in two fused three-membered rings can help explain its length.[33]

Acknowledgment. We thank Dr. William Kroenke of BFGoodrich Co. for mass spectra, Professor Robert West for providing information prior to publication, and the Office of Naval Research for support.

Registry No. 1a, 113999-66-9; **1b**, 113999-67-0; **1c**, 113999-68-1; $PtCl_2(PEt_3)_2$, 15390-95-1; $LiSiHPh_2$, 17950-77-5; $PhSiH_3$, 694-53-1.

Supplementary Material Available: Tables of data collection and refinement details, atomic positional parameters, thermal parameters, and bond lengths and angles for the cocrystallized dimers **1a–c** and dichloride dimer **1b** (10 pages); observed and calculated structure factors for **1a–c** and **1b** (27 pages). Ordering information is given on any current masthead page.

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Diallyl- and Bis(2-methylallyl)tetrakis(dimethylamido)ditungsten: $W_2(\mu\text{-}\eta^3\text{-}C_3H_5)_2(NMe_2)_4$ and $W_2(\eta^1\text{-}C_4H_7)_2(NMe_2)_4$ (M≡M). Comments on Ligand–Metal π-Interactions at $(W{\equiv}W)^{6+}$ Centers

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Received February 8, 1988

We have now established a fairly extensive chemistry surrounding d^3–d^3 dinuclear compounds of molybdenum and tungsten.[1] We are currently examining the relative π-donating abilities of ligands in unbridged ethane-like dimers and recently reported[2] the preparation and characterization of 1,2-$M_2(P(t\text{-}Bu)_2)_2(NMe_2)_4$ compounds. The relative π-donating abilities of the ligands were in the order $NMe_2^- > P(t\text{-}Bu)_2^-$. We were curious to examine how allyl ligands might compete with NMe_2^- ligands in compounds of formula 1,2-$M_2X_2(NMe_2)_4$ (X = allyl). The compounds could be analogues to the alkyl, aryl, and benzyl complexes (X = R, Ar, or Bz) previously reported having M–C σ-bonds,[3,4] or alternatively the π-donating properties of the hydrocarbyl ligands could compete with the NMe_2 ligands causing quite different structures. We report here our initial findings.

The reaction between allylmagnesium bromide (2 equiv) and 1,2-$W_2Cl_2(NMe_2)_4$ in ether leads to a brown, hexane-soluble crystalline product. The variable temperature ^1H and ^{13}C NMR spectra are complex and indicate the presence of two isomers in solution.[5] Exchange between these isomers is not rapid on the NMR time-scale. Crystals suitable for an X-ray study[6] were obtained, and the molecular structure in the solid state is shown in Figure 1.

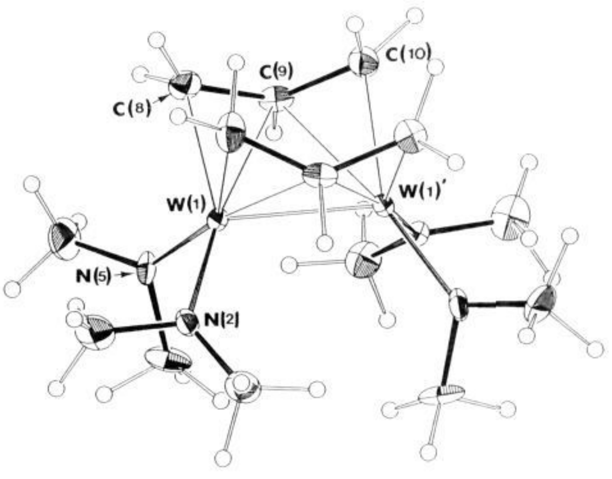
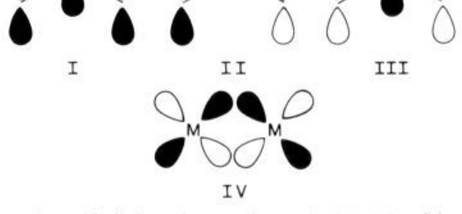


Figure 1. An ORTEP drawing of the $W_2(allyl)_2(NMe_2)_4$ molecule giving the atom number scheme for the pertinent atoms. Thermal ellipsoids are drawn at a 50% probability limit. H atoms, which were refined isotropically, have been given an artificially small thermal parameter and are shown as open circles. Pertinent bond distances (Å) and angles (deg) are as follows: W–W = 2.480 (1); W(1)–N(2) = 1.97 (1), W(1)–N(5) = 1.99 (1), W(1)–C(8) = 2.22 (1), W(1)–C(9) = 2.44 (2), W(1)–C(9)′ = 2.46 (1), W(1)′–C(10) = 2.22 (1), C(8)–C(9) = 1.474 (19), C(9)–C(10) = 1.465 (19), W(1)′–W(1)–N(2) = 112.2 (3), W(1)′–W(1)–N(5) = 115.6 (3), W(1)′–W(1)–C(8) = 94.7 (3), W(1)′–W(1)–C(9) = 60.1 (3), W(1)′–W(1)–C(10) = 89.4 (4), and C(8)–C(9)–C(10) = 129.7 (12).

The structure is quite unlike any other seen for a d^3–d^3 ditungsten compound, and it is apparent that the μ-allyl ligand has caused a significant change in the bonding of the central $(W{\equiv}W)^{6+}$ unit. For example, in contrast to ethane-like $W_2X_2(NMe_2)_4$ or bridged $W_2(L\text{-}L')_2(NMe_2)_4$ structures (L-L = triazine[7] or the anion derived from 2-hydroxypyridine[8]) the W–W–N angles (112° and 116°) are notably larger than the typical values of 103–105°. Moreover the planar W–NC_2 units are not aligned along the M–M axis in the present compound suggesting a rehybridization of the tungsten d_π orbitals.

The well-known p orbitals of the allyl fragment are depicted by I, II, and III below. The allyl anion can act as a four-electron donor by using I and II to interact with tungsten-based orbitals



in the *xy* plane (defining the *z* axis as the M–M axis). It then becomes apparent that the antibonding orbital of allyl, III, has

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[5] ^{13}C NMR (−60 °C, toluene-d_8) isomer 1: 85.5 ($^1J_{C\text{-}H}$ = 174 Hz), *C*H; 56.7 ($^1J_{C\text{-}W}$ = 39 Hz, $^1J_{C\text{-}H}$ = 145 Hz), *C*H_2; 41.5 ($^1J_{C\text{-}H}$ = 151 Hz), CH_2; isomer 2: 76.3 ($^1J_{C\text{-}H}$ = 149 Hz), *C*H; 67.3 ($^1J_{C\text{-}W}$ = 21 Hz, $^1J_{C\text{-}H}$ = 149 Hz), *C*H_2; N(*C*H_3)$_2$, 48.8, 46.0, 45.9.

[6] Crystal data for $W_2(allyl)_2(NMe_2)_4$ at −155 °C: $a = 10.840\ (2)$ Å, $b = 7.886\ (1)$ Å, $c = 11.159\ (3)$ Å, $\beta = 96.24\ (2)°$, $Z = 2$, $d_{calcd} = 2.193$ g cm^{-3}. Of 2017 reflections collected, $6° < 2\theta < 45°$, 1241 were unique, and the 1145 having $F > 2.33\sigma$ were used in the refinement. Final residuals are $R(F) = 0.037$ and $R_w(F) = 0.041$.

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