Synthesis and study of platinum silylene complexes of the type $(R_3P)_2Pt=SiMes_2$ (Mes = 2,4,6-trimethylphenyl)¹

Jay D. Feldman, Gregory P. Mitchell, Jörn-Oliver Nolte, and T. Don Tilley

Abstract: The synthesis and characterization of neutral platinum silylene complexes $(R_3P)_2Pt=SiMes_2$ (R = i-Pr (1) or cyclohexyl (2), Mes = 2,4,6-trimethylphenyl) is reported. The dimesitylsilylene ligand in 2 is displaced by a number of ligands including phosphines, alkenes, alkynes, and O₂. Complex 2 reacts with *R*OH substrates (R = H, Me, Et) to give $(Cy_3P)_2Pt$ and Mes₂Si(OR)(H) and with H₂ to give *trans*-(Cy₃P)₂Pt(H)SiHMes₂ (3). Reaction of H₂SiMes₂ with (Cy₃P)₂Pt gave *cis*-(Cy₃P)₂Pt(H)SiHMes₂ (4). EXSY NMR experiments of 4 reveal that exchange of silicon and platinum hydrides occurs via reductive elimination – oxidative addition and not via a silylene intermediate.

Key words: silylene, EXSY, platinum, hydride.

Résumé : On a effectué la synthèse et la caractérisation de complexes neutres de silylène de platine, $(R_3P)_2Pt=SiMes_2$ (R = isopropyle (1) ou cyclohexyle (2); Mes = 2,4,6-triméthylphényle). Le ligand diméthylsilylène du composé 2 est déplacé par un grand nombre de ligands, dont les phosphines, les alcènes, les alcynes et le dioxygène. Le complexe 2 réagit avec des substrats de formule *R*OH (R = H, Me, Et) pour conduire à la formation de (Cy₃P)₂Pt et de Mes₂Si(OR)(H); il réagit aussi avec H₂ pour donner le *trans*-(Cy₃P)₂Pt(H)SiHMes₂ (3). La réaction du H₃SiMes₂ avec le (Cy₃P)₂Pt conduit à la formation du *cis*-(Cy₃P)₂Pt(H)SiHMes₃ (4). Des expériences de RMN de type « EXSY » effectuées sur le composé 4 révèlent qu'il se produit un échange des hydrures de silicium et de platine par le biais d'une réaction d'élimination réductrice – addition oxydante et non pas par le biais d'un intermédiaire silylène.

Mots clés : silylène, « EXSY », platine, hydrure.

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Introduction

Platinum complexes play an important role as catalysts in transformations of organosilanes. These metal species are used to effect olefin hydrosilylation (1), dehydrogenative coupling of silanes to produce oligomers (2), and redistribution of substituents on silicon (3, 4). The latter two transformations occur extensively with low-valent platinum catalysts and are usually observed concurrently. Because these processes occur together it is likely that they involve a common intermediate. One possible mechanism for this redistribution–oligomerization reaction involves an intermediate silylene complex (L_n Pt=Si R_2) and migration chemistry (Scheme 1), although a mechanism involving reductive elimination – oxidative addition (Scheme 2) is preferred by some (4). While many of the proposed steps for redistribution via

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J.D. Feldman, G.P. Mitchell, J.-O. Nolte, and T.D. Tilley.² Department of Chemistry, University of California at Berkeley, Berkeley, CA 94720–1460, U.S.A.

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²Corresponding author (email: tdtilley@socrates.berkeley.edu).

the latter mechanism have precedent (e.g., Si–H oxidative addition and reductive elimination), there is little evidence to support the direct addition of an Si–C bond to platinum.

In 1971 Kumada and co-workers discovered the first hydrosilane oligomerization and redistribution reactions catalyzed by a platinum complex (3*b*, 5). In the presence of *trans*-(Et₃P)₂PtCl₂ as a precatalyst, Me₃SiSiMe₂H was transformed into Me₃SiH (redistribution product) and Me-(SiMe₂)_nH (n = 3-6, oligomerization products). The investigators subsequently found that introducing diphenylacetylene into the reaction resulted in formation of a disilacyclohexadiene (eq. [1]), which was proposed to result from the trapping of dimethylsilylene (5).

[1]

2 Me₃SiSiMe₂H + 2 PhC=CPh

$$\xrightarrow{[Pt]} 2 Me_3SiH + Ph Si Ph Ph Si Ph Ph Si Ph Me_2 Ph Ph Si Ph Me_2 Ph Ph Si Ph Me_2 Ph Ph Si Ph Si Ph Ph Si Ph Si Ph Ph Si Ph Si Ph Si Ph Ph Si Ph$$

More recently, Tanaka suggested that the formation of a platina-sila-cyclohexadiene, by the addition of phenylacetylene to a similar oligomerization–redistribution system, resulted from the trapping of a Pt^0 silylene complex (6) (eq. [2]). Although these results suggested a mechanism involving intermediate platinum silylene species, the goal of isolating and probing the reactivity of such a complex still remained. Additionally, given the utility of carbene comScheme 1.



plexes as catalysts and synthons in organic and polymer chemistry (7), it is likely that development of silylene chemistry will lead to similar advancements in organosilicon chemistry.

[2]



Many synthetic efforts have targeted the isolation of complexes featuring silylene ligands. In recent years, these efforts have culminated in the syntheses of a number of transition metal compounds containing sp^2 -hybridized silicon (8). For the most part, these compounds are cationic, having been obtained via an "anion-abstraction" method (8*a*-*e*). However, some neutral silylene complexes have been prepared via coordination of a stable free diamidosilylene (of which there are very few) to a transition metal (8*k*-*o*). The free silylenes are conjugated, five-membered rings in which the Si atoms are stabilized via heteroatom coordination to nitrogen.





Only two platinum silylene complexes have been previously reported, [*trans*-(Cy₃P)₂(H)Pt=Si(SEt)₂][BPh₄] (8*c*) and [(*i*-Pr₂PCH₂CH₂P-*i*-Pr₂)(H)Pt=SiMes₂][MeB(C₆F₅)₃] (8*f*). Neither of these cationic compounds is a good model for silylenes of the type $(R_3P)_2Pt=SiR_2$, which have been the primary focus of speculation regarding catalytic silylene intermediates (9). In an effort to prepare netural platinum(0) silylene complexes, we have explored reactions of metastable silylenes generated in situ with zero-valent platinum compounds. Some of this work has been communicated (10).

Results and discussion

Survey of reactions and observation of (*i*-Pr₃P)₂-Pt=SiMes₂

Silylenes were generated photolytically from linear or cyclic trisilanes, including Mes₂Si: (Mes = mesityl) from Mes₂Si(SiMe₃)₂ (11) or (Mes₂Si)₃ (12), Ph₂Si: (13) from Ph₂Si(SiMe₃)₂, and Me₂Si: from (Me₂Si)₆ (14). The photolyses were carried out using a quartz tube and in hexanes with a 1:1 stoichiometry of silylene precursor to platinum substrate. The first reactions surveyed involved the generation of Mes₂Si: from (Mes₂Si)₃ in the presence of Pt(PEt₃)₃ (15), (C₂H₄)Pt(PPh₃)₂ (15), Pt(P-*i*-Pr₃)₃ (15), Pt(PCy₃)₂ (15), or Pd(PCy₃)₂ (16). While no reaction was observed with Pt(PEt₃)₃, (C₂H₄)Pt(PPh₃)₂, or Pd(PCy₃)₂,

small amounts (<10%) of new products were observed (by ³¹P NMR spectroscopy) with Pt(P-*i*-Pr₃)₃ and Pt(PCy₃)₂. It is notable that in these two cases the reacting platinum species is 2-coordinate, since Pt(P-*i*-Pr₃)₃, unlike Pt(PEt₃)₃, readily dissociates one of its phosphines in solution to give Pt(P-*i*-Pr₃)₂ and an equivalent of free phosphine. Thus, further experiments concentrated on the use of these 2-coordinate species. The generation of Me₂Si: or Ph₂Si: in the presence of Pt(P-*i*-Pr₃)₂ (+ free phosphine) or Pt(PCy₃)₂ gave no new complexes (by ³¹P NMR spectroscopy). However, Mes₂Si: generated from Mes₂Si(SiMe₃)₂ gave >85% of a new, blood-red complex (1) as observed by ³¹P NMR spectroscopy (eq. [3]). Furthermore, use of a slight excess of Mes₂Si(SiMe₃)₂ (1.2 equiv) gave 1 as the only platinum phosphine species observed.



$$Pt(P^{i}Pr_{3})_{3} + Mes_{2}Si SiMe_{3}$$

$$SiMe_{3}$$

$$hv, C_{6}H_{14} P^{i}Pr_{3} + iPr_{3}P_{4}$$

$$Pt=Si$$

$$Pt=Si$$

$$Pt=Si$$

$$Pt=Si$$

$$Pt=Si$$

$$Pt=Si$$

Although there are many examples of silvlene-bridged, dimeric bis(phosphine) platinum complexes (dimeric analogs of 1) (17), the observation of only a single resonance with ¹⁹⁵Pt satellites in the ³¹P NMR spectrum (δ : 82.2 ¹J_{PPt} = 3119 Hz) is consistent with a monomeric structure for 1. Apparently, the steric protection provided by the Mes and *i*-Pr substituents is sufficient to prevent the formation of a more thermodynamically stable 4-coordinate silicon species via dimerization. The ²⁹Si NMR data for 1 are also consistent with the characterization of this complex as monomeric, with an sp^2 -hybridized silicon atom. Silylene complexes exhibit characteristically large downfield chemical shifts, typically in the range of 250 to 340 ppm (8). Significantly, the resonance for **1** (Fig. 1) was observed at δ : 367 (${}^{2}J_{\text{SiP}} = 107 \text{ Hz}$; ${}^{1}J_{\text{SiPt}} = 2973 \text{ Hz}$). For comparison, the only other platinum silylene complexes to be reported have ²⁹Si resonances at δ : 309 for [*trans*-(Cy₃P)₂(H)Pt=Si(SEt)₂][BPh₄] (8c) and δ : 338 for [(*i*-Pr₂PCH₂CH₂P-*i*-Pr₂)(H)Pt=SiMes₂] $[MeB(C_6F_5)_3]$ (8f). Complexes related to 1 include several dimeric analogs of the type $[(R_3P)_2Pt(\mu-SiR'_2)]_2$, which were prepared from reactions of secondary silanes with $Pt(PR_3)_n$ complexes (17), as well as the trimer $[Pt(\mu-SiPh_2)(PMe_3)]_3$, which was derived from loss of Ph₂SiH₂ and PMe₃ from cis- $(Me_{3}P)_{2}Pt(SiHPh_{2})$ (18). While the $[(R_{3}P)_{2}Pt(\mu-SiR'_{2})]_{2}$ complexes exhibit ²⁹Si NMR shifts that are over 400 ppm upfield of that for 1 (in the range of δ : -65 to -95), [Pt(μ -SiPh₂)(PMe₃)]₃ has a ²⁹Si chemical shift of 279 ppm, which is uncharacteristically downfield for a 4-coordinate silicon species.

Repeated attempts to isolate **1** were unsuccessful. Removal of the solvent afforded $Pt(P-i-Pr_3)_3$, along with a variety of unidentified silicon-containing products. When $Pt(P-i-Pr_3)_2$ (19) (without a third equivalent of $P-i-Pr_3$ present) was employed as a trapping reagent, the only platinum product observed upon photolysis was *trans*-H₂Pt(P-*i*-Pr₃)₂ (20) (by ¹H and ³¹P NMR spectroscopy) presumably resulting from C–H activation of the hexanes solvent. When the photolysis reaction was performed in benzene- d_6 , neither solvent activation nor efficient formation of **1** were observed.

Synthesis and structure of (Cy₃P)₂Pt=SiMes₂ (2)

Photolysis of a mixture of Mes₂Si(SiMe₃)₂ and Pt(PCy₃)₂ in hexanes gave a green, supersaturated solution of Me₃SiSiMe₃ (by ¹H and ²⁹Si NMR spectroscopy) and the silylene complex (Cy₃P)₂Pt=SiMes₂ (**2**). Cooling the solution to 0°C, concentrating the solution in vacuo, or allowing the solution to stand for a few hours facilitated precipitation of microcrystalline **2** (54% isolated yield). Complex **2** is completely insoluble in alkane solvents, dichloromethane, fluorobenzene, and tetrahydrofuran (THF) and is only slightly soluble in toluene or benzene. The ¹H NMR spectrum of **2** in benzene-*d*₆ consists of resonances for each of the three types of Mes protons (*o*-Me, *p*-Me, ArH) as well as a group of multiplets for the cyclohexyl protons. Likewise, the ³¹P NMR spectrum contains a single peak with ¹⁹⁵Pt satellites (δ : 71.7, ¹*J*_{PPt} = 3068). Because of its low solubility, a long accumulation time was required to observe the ²⁹Si NMR resonance for **2** at δ : 358 (²*J*_{SiP} = 112 Hz). This large



Fig. 2. ORTEP diagram of 2.



downfield chemical shift is evidence for the presence of an sp^2 -hybridized silicon atom, confirming the assignment of **2** as a silylene complex.

X-ray quality crystals of 2 were grown from dilute (<0.04 M) reaction solutions over a 3-4 h period.³ An ORTEP diagram of 2 is shown in Fig. 2. The Pt-Si bond distance of 2.210(2) Å is the shortest yet reported and is about 6% shorter than typical Pt-Si single bonds (2.30-2.40 Å) (1, 21). For comparison, the Pt-Si distance in $[trans-(Cy_3P)_2(H)PtSi(SEt)_2][BPh_4]$ is 2.270(2) Å, but note that the latter complex was characterized as being somewhat Fischer-like, with both Si—S and Pt—Si π -bonding (8*c*, 22). The summation of angles about Si, 359.8(6)°, confirms the presence of a planar, sp^2 -hybridized silicon atom, and the angles about platinum also sum within experimental error to 360°. The least-squares plane of the silvlene ligand (including Pt, Si, and the two ipso carbons) and the coordination plane of platinum (Si, Pt, P, P) intersect at a dihedral angle of 68.6° (see Fig. 3), which is not optimal for Pt-to-Si π -donation. The ideal dihedral angle for overlap between the HOMO of the L_2 Pt fragment and the empty *p*-orbital on silicon is 90° , which is the

³Supplementary data may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada (http://www.nrc.ca/cisti/irm/unpub_e.shtml for information on ordering electronically).

Fig. 3. ORTEP view of **2** in which most of the cyclohexyl carbon atoms have been removed for clarity. The dihedral angle between the silicon coordination plane and platinum coordination plane is 68.6° .



observed angle of the related germylene and stannylene complexes $(Et_3P)_2PtGe[N(SiMe_3)_2]_2$ (23) and $(i-Pr_2PCH_2CH_2P-i-Pr_2)PdSn[CH(SiMe_3)_2]_2$ (24), respectively. The deviation from 90° for **2** appears to result from steric interactions between the Mes and Cy substituents.

It is interesting that although complexes of the type $(R_3P)_2PtER'_2$ are known for tin, germanium, and now silicon, no such analogs are known with carbon. The complexes with germanium (23) and tin (24) were prepared by reacting a stable, free germylene or stannylene with a platinum complex of the type $(R_3P)_2PtL$, where *L* is a leaving group such as an alkene, alkyne, or oxalate (which forms 2 equiv of CO₂). It is noteworthy that while $(Et_3P)_2PtGe[N(SiMe_3)_2]_2$ decomposes in ambient laboratory light (25), silylene complexes 1 and 2 are generated under intense UV–vis irradiation. Also, no mention has been made of the sensitivity of stannylene complexes to light.

Reactivity of 2

Given that **2** is a member of the $(R'_{3}P)_{2}Pt=SiR_{2}$ class of compounds proposed as intermediates in hydrosilane oligomerization and redistribution, we have searched for similarities between the reactivity of **2** and that of the proposed intermediate species. Alkyne coupling with extruded silylenes is the primary evidence supporting such an intermediate species (vide supra); thus we have examined reactions of **2** with substrates containing unsaturated C—C bonds. Given the high steric congestion surrounding the Pt=Si bond, small substrates, including 2-butyne, propyne, and ethylene, were employed.

Addition of 2-butyne to a benzene- d_6 solution of 2 initially resulted in the formation of an unsymmetrical complex with inequivalent resonances in the ³¹P NMR spectrum. This is consistent with a complex derived from either alkyne addition across the Pt=Si double bond (eq. [4], structure **B**) or coordination of the alkyne to the silylene complex (structure **C**).





This species appears to be an intermediate and is only observed in very small concentrations (<5% by ³¹P NMR spectroscopy), as the silylene complex is converted into the alkyne complex (Cy₃P)₂Pt(η^2 -MeCCMe).⁴ The ³¹P NMR spectrum of the intermediate consists of two doublets with ¹⁹⁵Pt satellites (δ : 41.6, d ²J_{PP} = 34 Hz, ¹J_{PPt} = 3483 Hz; δ : 33.3, d ¹J_{PPt} = 2899 Hz). An analogous process is observed when propyne or ethylene (1 atm (1 atm = 101.325 kPa)) is used as the reactant in place of 2-butyne. In this liganddisplacement reaction the dimesitylsilylene is lost as multiple uncharacterized silicon-containing products. The apparent low stability of the intermediate species is likely due to the steric congestion associated with **2** and its derivatives.

Hydrosilanes do not react cleanly with 2; however, NMR tube reactions indicate that redistribution and, to a small extent, oligomerization processes take place. For example, addition of $PhSiH_3$ (4 equiv) to a green benzene- d_6 solution of 2 resulted in bleaching of the color and formation of Mes₂SiH₂ as the only mesityl-containing product. Redistribution products Ph₂SiH₂, SiH₄, and other Si-H containing products, as well as trace amounts of H₂ (presumably from dehydrocoupling), were also observed (by ¹H NMR spectroscopy). The platinum-containing product from this reaction has equivalent phosphines, as well as a hydride ligand (by NMR spectroscopy). These data are consistent with its formulation as trans-(Cy₃P)₂Pt(H)(SiHPh₂), although this could not be confirmed as it was not isolated. Furthermore, the symmetrical complex trans-(Cy₃P)₂PtH₂ (20) (also consistent with the NMR data) could be ruled out based on comparison of NMR data to an authentic sample.

Complex 2 quantitatively transfers its silylene group to water and alcohols, giving O—H bond insertion products (eq. [5]).

⁴ The alkyne complex, $(Cy_3P)_2Pt(\eta^2-MeCCMe)$, was generated via the addition of 2-butyne to $(Cy_3P)_2Pt$ in order to compare its ³¹P spectrum with the product mentioned here. $(Cy_3P)_2Pt(2-butyne)$ ³¹P NMR (C_6D_6) δ : 36.8, ¹J_{PPt} = 3302 Hz.



Thus, addition of *R*OH (R = H, Me, Et) to **2** resulted in the clean formation of Pt(PCy₃)₂ and the corresponding siloxane Mes₂Si(O*R*)H. No intermediates were observed in the reaction of **1** with ethanol at -60°C (by ¹H and ³¹P NMR spectroscopy in toluene-*d*₈). Related reactivity was previously reported for the base-stabilized silylene complex [Cp*(Me₃P)₂RuSiPh₂(NCMe)]⁺, which was presumed to dissociate acetonitrile prior to reaction with an alcohol (26). This reactivity contrasts with what has been observed for (*i*-Pr₂PCH₂CH₂P-*i*-Pr₂)PdSn[CH(SiMe₃)₂]₂, which reversibly adds H₂O across the Pd—Sn bond to form a palladium hydride species (27).

Many reactions of 2 result in loss of the silylene ligand. For example, O₂ reacts with **2** to give Pt(PCy₃)₂(η^2 -O₂) (28), and the displaced silvlene ligand is observed to decompose to a number of species (but not to significant amounts of the silylene dimerization product, Mes₂Si=SiMes₂). This reactivity is unlike that of the related germylene complex, (Et₃P)₂-PtGe[N(SiMe₃)₂]₂, which cleanly adds O₂ across its double bond (29). Reactions of **2** in benzene- d_6 with an excess amount of i-Pr2PCH2CH2P-i-Pr2, Ph2PCH2CH2PPh2, and PMe₃ led to PCy₃ and Mes₂Si: displacement, with quantitative formation of the corresponding PtL_4 (30) complex (by ³¹P NMR spectroscopy). Addition of 1 equiv of phosphine resulted in partial conversion to PtL_4 , and no other products were observed. These results suggest that the dimesitylsilylene ligand in 2 is rather labile. However, attempts to trap the silvlene by reacting 2 with 2 equiv of 2,3-dimethylbutadiene (which is known to react with free dimesitylsilylene) (31) in benzene- d_6 over 3 days at room temperature failed to give the expected cycloaddition product,

Mes₂Si(CH₂CMeCMeCH₂). Instead, several unidentified mesityl-containing species were observed by ¹H NMR spectroscopy. This suggests that complex decomposition pathways are operative in silylene displacement reactions. Unlike cationic silylene complexes, **2** is stable in the presence of 1 equiv of the nitrogen bases *para*-dimethylaminopyridine and acetonitrile and does not form a base-stabilized silylene complex (32). Formation of the four-coordinate adduct may be disfavored due to the significant steric protection of the electrophilic, *sp*²-hybridized silylene.

Formation of trans-(Cy₃P)₂Pt(H)(SiHMes₂) (3) from 2 and H_2

Hydrogen (1 atm) reacted with a benzene solution of **2** over 2 days to form *trans*-($Cy_3P_2Pt(H)(SiHMes_2)$ (**3**, Scheme 3). With this slow conversion there was competing decomposition of **2** via loss of the silylene ligand to produce

trans-(Cy₃P)₂PtH₂ (20) (ca. 50%; *without* formation of Mes₂SiH₂). At higher temperatures (refluxing benzene- d_6), **3** was hydrogenated to give *trans*-(Cy₃P)₂PtH₂ and Mes₂SiH₂. In contrast to the germylene complex (Et₃P)₂PtGe[N-(SiMe₃)₂]₂ (33), the addition of hydrogen to **2** is irreversible.

Complex 3 is fluxional in solution, as observed by variable-temperature ³¹P NMR spectroscopy. At -29°C, two doublets (δ : 26.9, d ${}^{1}J_{PtP}$ = 2632 Hz, ${}^{2}J_{PP}$ = 346 Hz; δ : 33.6, d ${}^{1}J_{PtP}$ = 2715 Hz) are observed, which, upon heating, broaden and coalesce to a singlet (δ : 28.9, ${}^{1}J_{PtP} = 2707$ Hz) at 91°C. This behavior is consistent with restricted rotation about the sterically congested Pt-Si bond; the rotational barrier ($\Delta G_{\rm rot}^{\ddagger}$) was calculated to be 15.8 ± 0.4 kcal mol⁻¹. The mechanism of hydrogen addition to 2 could involve oxidative addition to the platinum center followed by migration of hydride to the silvlene ligand, or direct addition of hydrogen to the Pt=Si double bond. At this point the mechanism is unknown, but it is interesting to note that whereas the *trans* silyl hydride is formed by this reaction, the oxidative addition of Mes₂SiH₂ to Pt(PCy₃)₂ exclusively gives cis-(Cy₃P)₂-Pt(H)(SiHMes₂) (vide infra).

Synthesis and EXSY NMR Studies of *cis*-(Cy₃P)₂Pt-(H)SiHMes₂ (4)

The *cis* isomer of **3** is obtained via the addition of Mes_2SiH_2 to $Pt(PCy_3)_2$ in 48% isolated yield. Competing *cis–trans* isomerization and decomposition took place upon thermolysis (80°C, 6 h) or photolysis (2.5 h) of a benzene solution of **4**.

The Pt–H and Si–H resonances of **4** are broad at room temperature, suggesting that exchange of these protons takes place. Cooling the sample to -70° C (toluene- d_8) only partially resolved the broad peaks. The cyclohexyl resonances prevent observation of the Pt-H–Si-H proton coalescence at high temperatures, and thus exchange NMR spectroscopy (EXSY) was used to study this process. The ¹H EXSY experiment confirms the exchange of the platinum and silicon hydrides. The rate constant for exchange was determined to be 23 ± 4 Hz (27°C).⁵

Given the stability of silylene ligands in this system, it seemed possible that this exchange could occur via an α -H migration process to give a 5-coordinate intermediate (eq. [6]).

[6]



However, a reductive elimination – oxidative addition couple could also account for this observation. An intermolecular mechanism was suggested upon close examina-

⁵EXSY NMR experiments (phase sensitive NOESY) were performed at two different mixing times of 12 and 25 ms, and exchange rate constants were determined using the program D2DNMR.

Scheme 3.



Fig. 4. Pt-H region of ¹H EXSY NMR spectrum of 4 showing exchange cross peaks between different Pt isotopes.



tion of the Pt-H region of the EXSY spectrum, Fig. 4, which contains cross-peaks corresponding to the exchange of ¹⁹⁵Pt–H hydrides with molecules of complex **4** containing other Pt isotopes. More significantly, EXSY experiments revealed the exchange of Pt-H hydrides with the Si-H hydrides of free H₂SiMes₂ (25 equiv) with a rate constant of 23 ± 4 Hz (27°C). Also, addition of D₂SiMes₂ to 4 resulted in concurrent incorporation of deuterium into the Pt-H and Si-H positions of 4. In addition, ³¹P EXSY NMR experiments provided a similar rate constant $(27 \pm 4 \text{ Hz})$ for phosphine exchange. This process was shown to be intramolecular, based on the absence of cross peaks between ¹⁹⁵Pt-P phosphines with those bound to other isotopes of platinum (Fig. 5), as well as the lack of exchange with free phosphine (5 equiv). Coalescence of the phosphorus resonances of 4 into a broad singlet occurred at 135° C (toluene- d_8), yielding an energy of activation of 16.1 ± 0.5 kcal mol⁻¹. Thus, hydrogen exchange in *cis*-(Cy₃P)₂Pt(H)(SiHMes₂) occurs via the rate-determining reductive elimination of dimesitylsilane, which does not require prior phosphine dissociation. These results are consistent with the recent observation that hydrogen appears not to migrate to platinum in 4-coordinate (*i*-Pr₂PCH₂CH₂P-*i*-Pr₂)Pt-(Me)SiHMes₂, whereas the 3-coordinate cation [(*i*-Pr₂PCH₂- $CH_2P-i-Pr_2)PtSiHMes_2^{\dagger}$ rapidly converts to $[(i-Pr_2PCH_2CH_2 P-i-Pr_{2}(H)Pt=SiMes_{2}^{+}(8f)$.

Conclusion

The first examples of neutral, platinum(0) silylene complexes have been synthesized and characterized by ²⁹Si

Fig. 5. ³¹P EXSY NMR spectrum of 4.



NMR specroscopy (1 and 2) as well as by X-ray crystallography and UV-vis, IR, and Raman spectroscopies (2). Their preparation was achieved via a novel route: trapping of a metastable silvlene with electron-rich bis(phosphine)platinum compounds. These are the first silylene complexes to closely resemble proposed catalytic intermediates, in that the L_2 Pt=Si R_2 compounds (1 and 2) resemble species proposed in the redistribution and oligomerization of hydrosilanes by platinum catalysts. Steric protection of the reactive Pt=Si double bond not only stabilizes 1 and 2, thus allowing for their isolation, but apparently also limits their reactivity. Dihydrogen is the only reactant to yield a product with an intact Si-Pt bond (3). Other substrates either displace the silvlene ligand or fail to react with 2. Although no direct analogies can be drawn between the reactivity of the isolated and proposed intermediate silvlenes, the very existence of 1 and 2 lends some credence to mechanisms which invoke this class of compounds. Studies of the closely related and dynamic molecule cis-(Cy₃P)₂Pt(H)SiMes₂H (4) point to a Pt-H-Si-H exchange mechanism that does not involve a silylene intermediate, but rather a reductive elimination oxidative addition couple. This observation is consistent with the notion that a metal center must be unsaturated for

silylene complex formation by α -migration to be favorable (see ref. 8*f*).

Experimental

General information

Unless otherwise noted, all manipulations were performed under an atmosphere of nitrogen using standard Schlenk techniques and (or) in a glovebox. Dry, oxygen-free solvents were employed throughout. Diethyl ether (Et₂O), pentane, hexane, and toluene were distilled from sodium benzophenone ketyl and stored under N₂ prior to use. Benzene- d_6 and toluene-d₈ were purified by vacuum distillation from Na-K alloy. Unless otherwise specified, all reagents were purchased from commercial suppliers and used without further purification. Pyridine was distilled from sodium and stored under N₂. Pt(P-*i*-Pr₃)₃ (15), Pt(PCy₃)₂ (15), Mes₂Si(SiMe₃)₂ (11), and Mes_2SiH_2 (34) were prepared by literature methods. Lithium aluminum hydride was recrystallized from Et₂O and dried in vacuo prior to use. Ethylene (99.9%) was obtained from Airgas, and 2-butyne (Aldrich) was vactransferred and stored over molecular sieves prior to use. Photolysis reactions were carried out in a Rayonet RPR-100 Hg lamp reactor.

NMR spectra were recorded with a Bruker AMX-400 at 400.1 MHz (¹H) and 162.0 MHz (³¹P) or a DRX-500 at 125.8 MHz (¹³C) instrument and at room temperature and in benzene- d_6 unless otherwise noted. ²⁹Si NMR spectra were obtained with the Bruker DRX-500 instrument at 99.4 MHz using 10 mg of Cr(acac)₃ as a relaxation agent. EXSY NMR experiments (phase sensitive NOESY) were performed at two different mixing times of 12 and 25 ms, and exchange rate constants were determined using the program D2DNMR (35). Melting points were taken under N_2 in sealed capillaries and are uncorrected. Elemental analyses were performed by the UCB Microanalytical Laboratory. Infrared (IR) spectra were obtained on a Mattson Galaxy 3000 FT-IR spectrometer, and all absorptions are reported in cm⁻¹. The UVvis spectrum of 2 in toluene were recorded on a Hewlett Packard 8452A Diode Array spectrophotometer, respectively.

$Pt(P-i-Pr_3)_2$

A previous report described the low-yield conversion of $Pt(P-i-Pr_3)_3$ to $Pt(P-i-Pr_3)_2$ in vacuo (19). An improved synthesis is reported here. In a PTFE-sealed vessel, (i-Pr₃P)₂PtCl₂ (1.94 g, 3.30 mmol) was dissolved in 25 mL of THF, and 1% sodium amalgam (55 g, 30 equiv Na) was added. The pale yellow solution turned red over the reaction time of 3 days. The solution was transferred away from the remaining amalgam-NaCl mixture via cannula. The amalgam was washed with 2×5 mL pentane, and the washings were combined with the original supernatant. All solvent was removed in vacuo to give a viscous red oil. To this, 30 mL of pentane were added, giving a red solution and purple precipitate. The solution was filtered and concentrated to dryness to give red crystals of $Pt(P-i-Pr_3)_3$ (1.62 g, 96%). ¹H NMR δ: 1.99 (m, 1H, CH), 1.31 (virtual q ${}^{2}J_{\rm HP} = {}^{1}J_{\rm HH} =$ 7 Hz, 3H, CH₃). 31 P NMR δ: 72.2 (s with 195 Pt satellites, ${}^{1}J_{\rm PPt} = 4179$ Hz).

$(i-\Pr_3P)_2$ Pt=SiMes₂ (1)

Complex 1 was prepared by the same method employed for 2 (vide infra), using Pt(P-*i*-Pr₃)₃. This red compound was observed in solution but was not isolated. ³¹P NMR δ : 82.2 (s with ¹⁹⁵Pt satellites, ¹J_{PPt} = 3119 Hz). ²⁹Si NMR δ : 367 (t with ¹⁹⁵Pt satellites, ²J_{PSi} = 107 Hz, ¹J_{SiPt} = 2973 Hz).

$(Cy_3P)_2Pt=SiMes_2$ (2)

A fused silica Schlenk tube containing a magnetic stir bar was charged with Pt(PCy₃)₂ (314 mg, 0.415 mmol), Mes₂Si(SiMe₃)₂ (212 mg, 0.499 mmol), and 12 mL of hexane. The resulting mixture was stirred rapidly until all solids dissolved (10 min). Within minutes of beginning photolysis, the color of the solution changed from colorless to green. This color persisted and darkened over the photolysis period of 120 min at which time a green precipitate was observed on the sides of the tube. The hexane and hexamethyldisilane byproduct were removed under vacuum. The resulting mixture was washed with 2×5 mL of hexane to remove tetramesityldisilene (the silylene dimerization byproduct) as well as unreacted Pt(PCy₃)₂. The remaining green solid was dried in vacuo to give analytically pure 2 (mp 104°C decomposition (dec)). Yield: 231 mg (54%). X-ray quality crystals of 2 were grown from dilute (<0.04 M) reaction solutions over a 3–4 h period during photolysis. UV–vis (ϵ (M⁻¹ cm⁻¹)): 282 (14 000), 316 (14 000), 392 (2900). IR: 3033 (w), 1601 (w), 1448 (s), 1265 (w), 1173 (w), 1046 (w), 1002 (w), 850 (m), 738 (w), 723 (w), 613 (w), 512 (w), 464 (m). ¹H NMR δ : 6.83 (s, 4H, ArH), 2.72 (s, 12H, ortho-Me), 2.19 (s, 6H, *para*-Me), 0.8–2.1 (br m, Cy). ³¹P NMR δ : 71.7 (s with ¹⁹⁵Pt satellites, ¹J_{PPt} = 3068 Hz). ²⁹Si NMR δ : 358 (t, ²J_{PSi} = 112 Hz). Anal. calcd for C₅₄H₈₈P₂PtSi: C 63.44, H 8.68; found: C 63.35, H 8.87.

Reaction of 2 with 2-butyne

In an NMR tube, **2** (11 mg, 0.01 mmol), 2-butyne (1 μ L, 0.01 mmol), and benzene- d_6 were combined, and the tube was inverted several times to mix the reactants. The reaction was monitored by ³¹P NMR spectroscopy and produced (Cy₃P)₂Pt(η^2 -MeCCMe) via an unsymmetrical intermediate over several hours.⁴ The ³¹P NMR spectrum of the intermediate consists of two doublets with ¹⁹⁵Pt satellites (δ : 41.6, d ²J_{PP} = 34 Hz, ¹J_{PPt} = 3483 Hz; δ : 33.3, d ¹J_{PPt} = 2899 Hz).

Reaction of 2 with ethylene

A sealable PTFE-capped NMR tube containing **2** (10 mg, 0.01 mmol) and benzene- d_6 was degassed via three freezepump-thaw cycles, and 1 atm of ethylene was introduced. The reaction was monitored by ³¹P NMR spectroscopy as it was converted to $(Cy_3P)_2Pt(\eta^2-C_2H_4)$ via an unsymmetrical intermediate over several hours.

Reaction of 2 with PhSiH₃

Compound 2 (11 mg, 0.01 mmol), $PhSiH_3$ (5 µL, 0.04 mmol), and benzene- d_6 were combined in an NMR tube, which was then inverted several times to mix the reactants. The green color of 2 was rapidly bleached, and ¹H NMR spectroscopy revealed the presence of Mes₂SiH₂, Ph₂SiH₂, SiH₄, and trace H₂.

Formation of trans-(Cy₃P)₂Pt(H)SiMes₂H (3) from 2 and H₂

A sealable PTFE-capped NMR tube containing a solution of **2** (7 mg, 6 µmol) and benzene- d_6 was degassed via two freeze-pump-thaw cycles, and 1 atm of H₂ was introduced. (Cy₃P)₂Pt=SiMes₂ dissolved slowly over the reaction period of 2 days. During this time, the solution changed color from green to pale yellow. The formation of **3** and (Cy₃P)₂PtH₂ (ca. 1:1) was observed by NMR spectroscopy. ¹H NMR (for **3**) & 6.66 (s, 4H, ArH), 5.76 (m with ¹⁹⁵Pt satellites, ²J_{HPt} = 319 Hz, 1H, SiH), 2.43 (s, 12H, *ortho*-Me), 2.25 (s, 6H, *para*-Me), 1.0–2.5 (br m, Cy), –3.12 (t with ¹⁹⁵Pt satellites, ²J_{HP} = 17.6 Hz, ¹J_{HPt} = 629 Hz, 1H, PtH). ³¹P NMR (–29°C, toluene- d_8) & 33.58 (d, ²J_{PP} = 346 Hz, ¹J_{PPt} = 2715 Hz), 26.94 (d with ¹⁹⁵Pt satellites, ²J_{PP} = 346 Hz, ¹J_{PPt} = 2632).

cis-(Cy₃P)₂Pt(H)SiMes₂H (4)

A Schlenk tube containing $Pt(PCy_3)_2$ (228 mg, 0.302 mmol), a magnetic stir bar, and 25 mL of hexane was stirred and cooled to 0°C. Simultaneously, another tube containing Mes₂SiH₂ (81 mg, 0.302 mmol) and 10 mL of hexane was likewise cooled and stirred. The dimesitylsilane solution was added to the first vessel dropwise via cannula over 12 min. Stirring at 0°C was continued for another 10 min, and then the solution was allowed to warm to room temperature. After 1.5 h the solvent was removed in vacuo. Recrystallization from diethyl ether afforded 147 mg (48%) of 4 (mp 159°C dec). IR (KBr): 3014 (m), 2932 (m), 2660 (w), 2150 (w), 2064 (m), 1596 (m), 1546 (w), 1446 (s), 1410 (w), 1328 (w), 1260 (m), 1173 (m), 1105 (m), 1011 (m), 928 (w), 887 (m), 846 (s), 737 (m), 710 (w), 599 (w), 519 (m), 496 (m), 432 (w). ¹H NMR & 6.89 (s, 4H, ArH), 5.86 (br, 1H, SiH), 2.85 (s, 12H, ortho-Me), 2.23 (s, 6H, para-Me), 1–2.2 (br m, Cy), –3.98 (br dd with ¹⁹⁵Pt satellites, ${}^{2}J_{\text{HPcis}} =$ 37 Hz, ${}^{2}J_{\text{HPtrans}} = 183$ Hz, ${}^{2}J_{\text{HPt}} = 1050$ Hz, PtH). ${}^{31}\text{P}$ NMR $\delta: 45.1$ (s with ${}^{195}\text{Pt}$ satellites, ${}^{1}J_{\text{PPt}} = 1580$ Hz), 31.6 (s with ${}^{195}\text{Pt}$ satellites, ${}^{1}J_{\text{PPt}} = 2740$ Hz). ${}^{13}\text{C}$ NMR $\delta: 144.2$ (br, ortho-C), 143.1 (br, ipso-C), 136.0 (br, para-C), 129.3 (s, meta-C), 39.6, 37.1, 31.1, 28.6, 28.2, 27.4, 27.2 (br, Cy), 25.4 (br, ortho-Me), 21.6 (s, para-Me). Anal. calcd for C₅₄H₉₀P₂PtSi: C 63.31, H 8.85; found: C 63.84, H 9.28.

Reactions of 1 with ROH (R = H, Me, Et)

In three separate reactions, water (ca. 0.2 μ L, 0.01 mmol), methanol (0.3 μ L, 0.01 mmol), or ethanol (0.6 μ L, 0.01 mmol) was injected into a septum-capped NMR tube containing **1** (10 mg, 0.01 mmol) and benzene- d_6 . The tube was then inverted several times to assure mixing. The resulting colorless solutions were then analyzed by ¹H and ³¹P NMR spectroscopy, which revealed quantitative formation of Pt(PCy₃)₂ and Mes₂Si(OR)H, which were identified by comparison with independently prepared siloxanes (R = H (36), Me (37), Et (38)).

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