

Platinum η^2 -Disilene Complexes: Syntheses, Reactivity, and Structures

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Stable bis(phosphine)platinum η^2 -disilene complexes analogous to olefin π -complexes have been prepared by various methods. Tetramesityldisilene reacts with bis(tertiary phosphine)platinum oxalates under UV irradiation and with bis(triphenylphosphine)platinum(0) ethylene thermally to produce η^2 -complexes **2a,b**. The reaction of tetrasubstituted 1,2-dihydridodisilanes (R_2SiH)₂ with bis(phosphine)platinum equivalents, e.g., (diphos)PtCl₂/Li or (diphos)Pt(CH₂=CH₂) also yielded platinum η^2 -disilene complexes **6a** (R = *i*-Pr), **6b** (R = Me), and **6c** (R = Ph). Reaction of **6a** (R = *i*-Pr) with H₂ yielded a bis(R_2SiH) platinum complex **8**, which was characterized by X-ray crystallography: monoclinic, $P2_1/n$, $a = 10.679$ (1) Å, $b = 16.564$ (4) Å, $c = 21.854$ (3) Å, $\beta = 97.91$ (1)°. Reactions of **6a,b** with O₂ and NH₃ afforded new four-membered heterocycles arising from addition across the Si-Si bond. The crystal structure of the oxygen adduct **9b** is triclinic, $P\bar{1}$, $a = 9.727$ (1) Å, $b = 11.834$ (2) Å, $c = 14.867$ (2) Å, $\alpha = 88.89$ (1)°, $\beta = 83.19$ (1)°, $\gamma = 66.62$ (1)°. This compound exhibits a short Si-Si distance (2.549 Å), reflecting possible cross-ring bonding between silicon atoms.

Olefin complexes of metals date back to the historic preparation of Zeise's salt in 1827.¹ In recent years several η^2 complexes of diphosphenes, diarsenes, and distibines with transition metals have been described, and the coordination chemistry of these unsaturated ligands is now fairly well established.^{2,3}

Reactive organosilicon species can sometimes be stabilized by coordination to a transition metal. Examples are the adduct/donor stabilized silylene complexes of ruthenium,^{4a} iron,^{4b} and chromium^{4b} and the recent report of stable η^2 -silene complexes of ruthenium.⁵ In addition, Tessier-Youngs and co-workers have prepared several Pt₂Si₂ ring compounds whose structural features have been discussed in terms of a bonding model involving the coordination of a planar R₂SiSiR₂ fragment to two metal moieties.⁶ However, disilene-metal complexes of the η^2 type analogous to metal-olefin complexes were unknown until quite recently. Platinum η^2 -disilene complexes were the subject of a recent communication from our laboratories,⁷ and disilene complexes of molybdenum and tungsten have been reported recently by Berry and co-workers.⁸

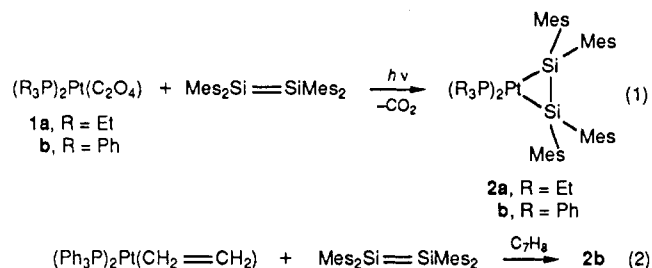
In this paper we describe detailed results on the syntheses of η^2 -disilene-platinum complexes and their reactivities toward small molecules, including the crystal

structures of two new derivatives. One of these is a four-membered ring compound resulting from the oxidation of a platinum-disilene complex. The structural features of this compound will be discussed in relation to the 1,3-cyclodisiloxanes which have been extensively studied in our laboratories.⁹

Results and Discussion

In approaching the task of preparing these heretofore elusive metal complexes of disilenes, two reactive functionalities in silicon chemistry were allowed to react with coordinatively unsaturated platinum substrates: the Si=Si double bond now readily available in our laboratories, and the Si-H bond. Oxidative addition of the silicon-hydrogen bond is one of the simplest methods of forming transition metal-silicon bonds.¹⁰

Coordination Chemistry of Tetramesityldisilene. The ultraviolet irradiation of (oxalato)bis(phosphine) complexes of platinum(II) results in the reductive elimination of the oxalate ligand as CO₂ and the formation of the 14-electron intermediate [(R₃P)₂Pt].¹¹ When the platinum oxalate complex **1a** or **1b** (eq 1, Mes = mesityl)



was irradiated with 254-nm light in the presence of an equimolar amount of tetramesityldisilene, a bright orange solution was produced. After 2 h of photolysis, at which time the oxalate bands (ν_{CO}) of **1a,b** had disappeared in

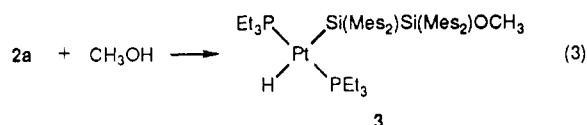
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the IR, the reaction mixture was worked up to afford **2a,b** as air-sensitive, yellow-to-orange solid powders. Alternatively, **2b** was also obtained in less than 20% yield from the reaction of tetramesityldisilene and an equimolar amount of $(\text{Ph}_3\text{P})_2\text{Pt}(\text{CH}_2=\text{CH}_2)$.

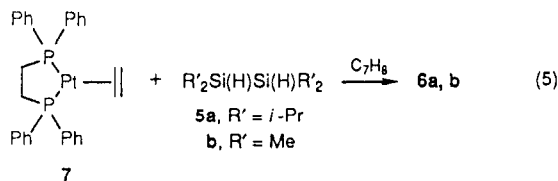
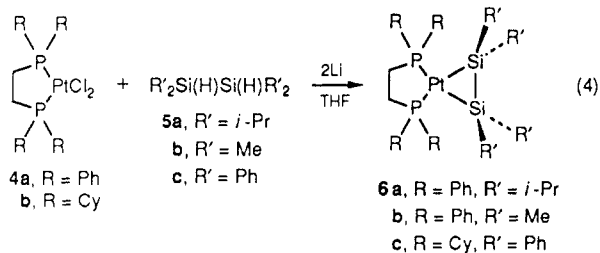
The NMR and mass spectra of **2a,b** are consistent with their formulation as platinum–disilene complexes. The ^{31}P chemical shifts observed (**2a**, 23.3 ppm; **2b**, 19.5 ppm) are in the range of those for known η^2 complexes of ethylene, e.g., $(\text{R}_3\text{P})_2\text{Pt}(\text{CH}_2=\text{CH}_2)$ (20.4 ppm, R = Et; 32.0 ppm, R = Ph).¹² The $^1J_{\text{Pt-P}}$ coupling constants for **2a,b** are significantly lower than in **1a,b** or in olefin–Pt complexes, indicating that in **2a,b**, the Pt–P bond is made less covalent by a ligand of relatively high trans influence.¹³ Silyl groups have been shown to reduce coupling constants ($^1J_{\text{Pt-P}}$) in trans bonds very markedly.¹⁴ The ^{29}Si NMR resonances for **2a** and **2b**, –23.1 and –29.1 ppm, are considerably upfield of that for free tetramesityldisilene (63.6 ppm), consistent with the previous observation that ^{31}P chemical shifts of diphosphenes are shifted markedly upfield in their η^2 transition metal complexes.² Upfield ^{13}C NMR chemical shifts also occur when alkenes are η^2 bonded to transition metals.¹⁵

The formulation of **2a** as an η^2 complex of tetramesityldisilene was further supported by its reaction with methanol. Cleavage of the Pt–Si bond occurred to provide **3**, a σ -bonded disilane complex of platinum containing a



Pt–H bond. The trans geometry is assigned to **3** since it shows only one ^{31}P NMR resonance. Consistent with this assignment, the ^1H NMR spectrum in the hydride region exhibits a 1:2:1 triplet ($^2J_{\text{P-H}}$) flanked by ^{195}Pt satellites.

Reaction of $\text{R}_2\text{Si}(\text{H})\text{Si}(\text{H})\text{R}_2$ with Pt Complexes. Oxidative additions of monomeric silanes to platinum complexes are well-known,^{6,16} and we find that similar reactions take place with 1,2-dihydridodisilanes. As illustrated in eqs 4 and 5, the reaction of disilanes **5** with

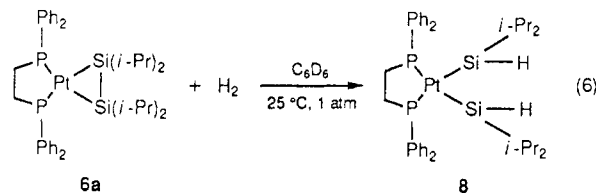


bis(phosphine)platinum equivalents **4** or **7** also afforded platinum η^2 -disilene complexes **6a–c** as yellow microcrystals, which were characterized by ^1H , ^{31}P , and ^{29}Si NMR, FAB-MS, and elemental analyses. To account for the formation of **6a–c**, we have proposed a mechanism involving a tandem oxidative insertion into Si–H bonds followed by reductive elimination of hydrogen.⁷ These results clearly demonstrate that sterically unencumbered disilenes can be stabilized in the coordination sphere of transition metals. Similar stabilization of otherwise unstable molecules is seen in diphosphene–metal complexes, a classic example being $(\eta^2\text{-HP}=\text{PH})\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2$.¹⁷

The yields in the reactions shown in eq 4 are low (10–20%); the reaction mixtures contain significant quantities of oligomeric or polymeric silane byproducts that were not identified. The ^{29}Si NMR spectrum also provided evidence for the formation of small amounts of Si–H complexes such as **8** (vide infra). The second pathway (eq 5) gave cleaner reaction mixtures and higher yields.

Unlike **2a**, **6a** did not react in a simple fashion with methanol. The reaction appeared to proceed with both Si–Pt and Si–Si bond breaking, to give a complex mixture of products. Compound **6a** was, however, derivatized successfully by reaction with dihydrogen or dioxygen.

Hydrogenolysis. Platinum–silicon bonds are generally cleaved by reaction with dihydrogen, often under mild conditions.¹⁸ However, when **6a** was reacted with H_2 at room temperature, the Si–Si bond was cleaved instead of the Pt–Si bonds, producing **8** in nearly quantitative yield (eq 6). The new compound was characterized by standard NMR techniques and elemental analysis.



It is possible that the presence of the chelating diphosphine hinders the hydrogenolysis of Pt–Si bonds in **6a**. Analogous cases are known in the literature.¹⁹ Although it is plausible to envisage the formation of **8** proceeding through an intermediate octahedral platinum(IV) complex, no such Pt–H species were detected by ^1H NMR or IR, even at low temperatures (–60 °C). In this reaction, the silicon moiety behaves like an activated disilene. Free disilenes, e.g., tetramesityldisilene, fail to react with H_2 , even in the presence of a Pt catalyst.²⁰

An X-ray crystal structure of **8** was determined; details of the crystallographic data are summarized in Table I, and significant bond distances and angles are listed in Table II. As shown in the thermal ellipsoid drawing of **8** (Figure 1) the coordination geometries of the platinum- and metal-bound silicons are close to idealized square planar and tetrahedral, respectively. The five Si, P, and Pt atoms comprising the central skeleton of the molecule are all nearly coplanar with a dihedral angle of 2° between the two planes defined by Si(2), Pt(1), P(2) and Si(1), Pt(1), P(1). The Pt–Si bond lengths (Pt–Si(2) = 2.355 (3) Å and

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Table I. Crystal and Refinement Data for 8 and 9b

	8	9b
empirical formula	C ₃₈ H ₅₄ P ₂ Si ₂ Pt	C ₃₀ H ₃₆ OSi ₂ P ₁ Pt
color, habit	yellow prisms	Colorless blocks
cryst size, mm	0.31 × 0.35 × 0.25	0.35 × 0.4 × 0.43
cryst syst	monoclinic	triclinic
space group	P2 ₁ /n	P1
a, Å	10.697 (1)	9.727 (1)
b, Å	16.564 (4)	11.834 (2)
c, Å	21.845 (3)	14.867 (2)
α, deg	90	88.89 (1)
β, deg	97.91 (1)	83.19 (1)
γ, deg	90	66.62 (1)
V, Å ³	3833.73 (2)	1560 (1)
Z	4	2
FW	824.04	725.81
D(calc), g/cm ³	1.428	1.546
abs coeff, mm ⁻¹	3.86	4.74
diffractometer	Nicolet P-1	Nicolet P3/F
radiation	Nicolet P-1	Nicolet P3/F
radiation	graphite monochromated	Mo Kα (0.710 73 Å)
2θ range, deg	3.5–50	3.5–50
scan type	Wyckoff	θ–2θ
scan speed	var, 4–29	var, 4–29
std rflctns	3 std/97 rflctns	3 std/97 rflctns
no. of rflctns cllctd	10 605	6068
abs corr	empirical, ψ scans	
min, max transmissn	0.342, 0.886	0.462, 0.964
indpdnt rflctns	6822	5526
obsd rflctns (F _o > 3σ(F _o))	4156	4939
data/param	10.7/1	15.2/1
final R(F), R(wF)	0.048, 0.067	0.026, 0.037
weighting scheme	1/w = σ ² (F) + 0.00146F ²	1/w = σ ² (F) + 0.00082F ²
final GOF	1.376	1.106
Δ/σ	0.03	0.003
highest peak in final diff map, e/Å ³	1.98 ^a	1.32 ^b

^aThe final difference map had no peaks of significance. There were seven residual peaks of 1.06–1.98 e/Å³ in the vicinity of the platinum, and all others were less than 1 e/Å³. ^bLikewise, in 9b, there were two residual peaks of 1.01 and 1.32 e/Å³ near the Pt, and all others were less than 1 e/Å³.

Table II. Selected Bond Lengths (Å) and Angles (deg) for 8

Distances			
Pt(1)–Si(1)	2.378 (4)	Pt(1)–Si(2)	2.355 (3)
Pt(1)–P(1)	2.306 (3)	Pt(1)–P(2)	2.302 (3)
Si(1)–H(1A)	1.555	Si(1)–C(27)	1.926 (13)
Si(1)–C(30)	1.918 (13)	Si(2)–H(1B)	1.551
Si(2)–C(33)	1.895 (18)	Si(2)–C(36)	1.769 (22)
Angles			
Si(1)–Pt(1)–Si(2)	88.6 (1)	Si(1)–Pt(1)–P(1)	96.3 (1)
Si(2)–Pt(1)–P(1)	175.1 (1)	Si(1)–Pt(1)–P(2)	177.7 (1)
Si(2)–Pt(1)–P(2)	90.3 (1)	Ptn(1)–Pt(1)–P(2)	84.8 (1)
Pt(1)–Si(1)–H(1A)	113.2 (1)	Pt(1)–Si(1)–C(27)	113.3 (4)
H(1A)–Si(1)–C(27)	105.6 (3)	Pt(1)–Si(1)–C(30)	112.6 (4)
H(1A)–Si(1)–C(30)	104.6 (4)	C(27)–Si(1)–C(30)	106.9 (6)
Pt(1)–Si(2)–H(1B)	92.2 (1)	Pt(1)–Si(2)–C(33)	115.9 (7)
H(1B)–Si(2)–C(33)	109.1 (6)	Pt(1)–Si(2)–C(36)	117.7 (7)
H(1B)–Si(2)–C(36)	109.4 (8)	C(33)–Si(2)–C(36)	110.7 (11)

Pt–Si(1) = 2.378 (4) Å are relatively long when compared to other Pt–Si bonds in similarly crowded environments.^{6,21} The discrepancy in the two bond lengths is a consequence of the proximity of Si(1) to one of the phenyl rings attached to P(1). This is reflected in the relatively smaller bond angles around Si(1) when compared to those around Si(2). There is no interaction between the two silicons, as they are separated by 3.306 Å, which is well outside the range of known single Si–Si bonds (2.33–2.70 Å).²²

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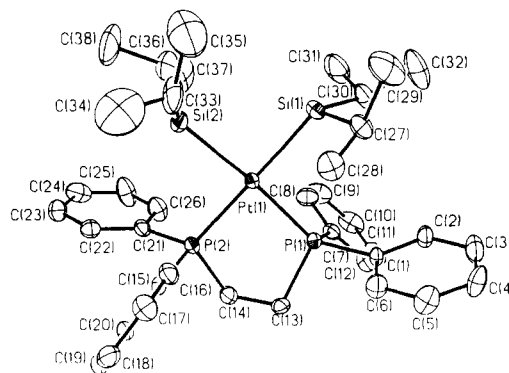
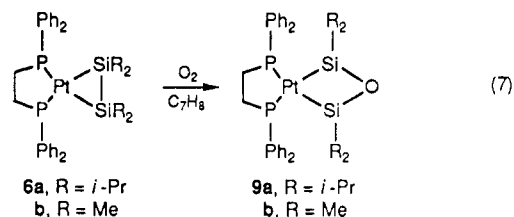


Figure 1. Thermal ellipsoid plot for 8 (30% probability). Hydrogen atoms omitted for clarity.

The silyl hydrides could not be located from the difference Fourier map. Their positions were instead calculated to fit the tetrahedral environment of the respective silicons to which they are bonded, assuming a fixed Si–H bond distance of 1.5 Å. Since numerous compounds with Pt–H–Si bridging are known, the possibility of hydrogen bridging in 8 should be considered. The IR and NMR spectra of 8 in solution indicate that the silane hydrogens are not bridged to the platinum atom. An IR absorption assignable to the Si–H stretch is found at 1968 cm⁻¹ in the usual region for terminal silanes, and the ¹J_{Si–H} coupling constant of 150 Hz is also normal for terminal Si–H. Hydrogen bridging might nevertheless occur in the solid state, but the essentially square-planar arrangement at Pt, as well as the coplanarity of the five atoms, P, P, Pt, Si, and Si,²³ are more consistent with an unbridged structure.

Oxidation. In view of the well-documented oxidation chemistry of free disilenes,⁹ it was natural for us to explore the reactivity of platinum- η^2 -disilene complexes toward O₂. When oxygen was bubbled through solutions of 6a,b, the novel oxygen adducts 9a,b were isolated in relatively good yields (60–75%).



The spectroscopic and analytical data are consistent with the formulation of 9a,b as four-membered ring compounds. Of particular interest are the ²⁹Si{¹H} NMR data, which show significantly smaller ¹J_{Pt–Si} values (990–1000 Hz) relative to those observed in the platinum- η^2 -disilene complexes. This, coupled with the upfield shift in the observed ²⁹Si resonances for 6a,b, indicates a decrease in s-character in the Pt–Si bonds upon oxidation and may reflect further loss of π -character in the Pt–Si bonding network.

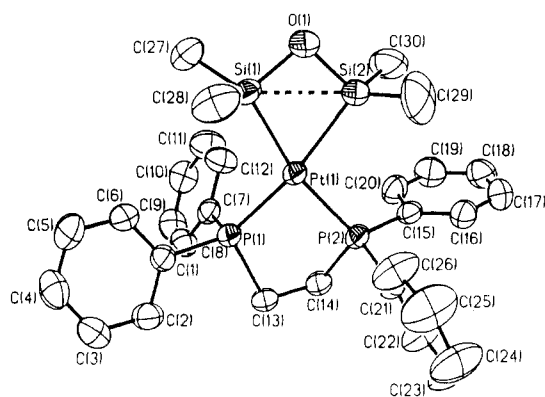
The structure of 9b was unequivocally established by an X-ray structural determination (Tables I and III and Figure 2). The structure consists of a nearly planar Pt/Si/O four-membered ring with a dihedral angle of 7.2° between the Si(1), O(1), Si(2) and Si(1), Pt, Si(2) planes.

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Table III. Selected Bond Lengths (Å) and Angles (deg) for 9b

Distances			
Pt(1)-P(1)	2.332 (1)	Pt(1)-P(2)	2.315 (1)
Pt(1)-Si(1)	2.374 (2)	Pt(1)-Si(2)	2.373 (1)
P(1)-C(1)	1.828 (4)	P(1)-C(7)	1.832 (5)
P(1)-C(13)	1.855 (6)	P(2)-C(14)	1.856 (5)
P(2)-C(15)	1.824 (4)	P(2)-C(21)	1.818 (5)
Si(1)-Si(2)	2.549 (2)	Si(1)-O(1)	1.693 (3)
Si(1)-C(27)	1.878 (6)	Si(1)-C(28)	1.884 (6)
Si(2)-O(1)	1.689 (5)	Si(2)-C(29)	1.881 (9)
Si(2)-C(30)	1.874 (8)		
Angles			
P(1)-Pt(1)-P(2)	84.5 (1)	P(1)-Pt(1)-Si(1)	109.2 (1)
P(2)-Pt(1)-Si(1)	166.2 (1)	P(1)-Pt(1)-Si(2)	168.5 (1)
P(2)-Pt(1)-Si(2)	101.8 (1)	Si(1)-Pt(1)-Si(2)	65.0 (1)
Pt(1)-P(1)-C(1)	125.3 (2)	Pt(1)-P(1)-C(7)	111.1 (1)
C(1)-P(1)-C(7)	103.5 (2)	Pt(1)-P(1)-C(13)	107.8 (1)
C(1)-P(1)-C(13)	104.4 (2)	C(7)-P(1)-C(13)	102.3 (2)
Pt(1)-P(2)-C(14)	108.2 (2)	Pt(1)-P(2)-C(15)	120.3 (2)
C(14)-P(2)-C(15)	103.3 (2)	Pt(1)-P(2)-C(21)	114.4 (2)
C(14)-P(2)-C(21)	103.8 (2)	C(15)-P(2)-C(21)	105.2 (2)
Pt(1)-Si(1)-Si(2)	57.5 (1)	Pt(1)-Si(1)-O(1)	98.3 (2)
Si(2)-Si(1)-O(1)	41.0 (2)	Pt(1)-Si(1)-C(27)	121.8 (2)
Si(2)-Si(1)-C(27)	129.9 (2)	O(1)-Si(1)-C(27)	106.4 (2)
Pt(1)-Si(1)-C(28)	114.6 (3)	Si(2)-Si(1)-C(28)	119.1 (2)
O(1)-Si(1)-C(28)	108.5 (3)	C(27)-Si(1)-C(28)	106.1 (3)
Pt(1)-Si(2)-Si(1)	57.6 (1)	Pt(1)-Si(2)-O(1)	98.4 (1)
Si(1)-Si(2)-O(1)	41.1 (1)	Pt(1)-Si(2)-C(29)	119.9 (3)
Si(1)-Si(2)-C(29)	123.6 (3)	O(1)-Si(2)-C(29)	109.1 (4)
Pt(1)-Si(2)-C(30)	113.9 (3)	Si(1)-Si(2)-C(30)	127.4 (2)
O(1)-Si(2)-C(30)	109.3 (3)	C(29)-Si(2)-C(30)	105.8 (3)
Si(1)-O(1)-Si(2)	97.8 (2)		

**Figure 2.** Thermal ellipsoid plot for **9b** (50% probability). Hydrogen atoms omitted for clarity.

The silicon atoms and their substituents lie in a plane perpendicular to the two planes making up the ring. As in **8**, the Pt-Si bonds (2.373 (1), 2.374 (2) Å) are relatively long compared to Pt-Si bonds in environments of comparable steric demands.^{6,21} The Si-Si separation of 2.549 (2) Å in **9b** is within the range of known Si-Si single bonds (2.33–2.70 Å).²² The Si-O bonds (1.689 (5), 1.693 (3) Å) are slightly longer than the bond lengths found for other cyclic siloxanes (1.61–1.65 Å),²⁴ while the Pt-O separation of 3.108 Å is within the 3.2–3.3-Å distance predicted from the van der Waals' radii for Pt and O.²⁵ There is an acute deviation of the angle at the "square planar" platinum (Si-Pt-Si = 65.0 (0)°), while the angles at the two silicons, although still obtuse, are smaller than the 109° predicted for a tetrahedral environment (Pt-Si(1)-O = 98.3 (2)°,

Pt-Si(2)-O = 98.4 (1)°). The endocyclic Si-O-Si angle is 97.8 (2)°, compared to normal siloxane bond angles of about 145°.

Discussion of Structure. Compound **9b** is structurally similar to the cyclometaladisiloxane (Ph₃P)₂(CO)(H)Ir-(Me₂SiOSiMe₂) reported by Curtis,²⁶ in which the Si-Si distribution is 2.53 Å. The structural features of **9b** are intermediate between those of Tessier-Youngs Pt/Si dimers,⁶ which have Si...Si distances of 2.57–2.65 Å, and the 1,3-cyclodisiloxanes studied in our laboratories, with Si...Si 2.31–2.39 Å.⁹ These features are in marked contrast to those of other metal-silicon four-membered rings which show large cross-ring Si-Si separations (3.852–4.225 Å), acute M-Si-M angles (69.6–75.0°), and short M-M distances (2.708–3.183 Å).²⁷ Among such compounds only (Cp₂TiSiH₂)₂ has a similarly short cross-ring Si-Si distances (2.69 Å) and M-Si-M angle (103°).²⁸

The structural results obtained for **9b** can be discussed in terms of three qualitative bonding models, involving (1) electron repulsions between the Pt and O, (2) unsupported Si-Si π -bonds,^{29a} and (3) bent bonds resulting from ring strain. According to the first model, strong repulsions between the Pt and O atoms force the silicon atoms close to each other, but there is no bonding between them. This would be consistent with recent ab initio calculations on H₂Si₂O₂ which describe the 1,3-cyclodisiloxane ring as consisting of four equivalent, localized Si-O bonds with no appreciable σ -bonding between the silicons.^{9,28} Furthermore, the ¹J_{Pt-Si} value (991 Hz) for **9b** is similar to reported values (851–878 Hz) for other Pt-Si σ -bonded complexes³⁰ and is therefore consistent with the localized σ -bond description for the Pt-Si bonds in **9b**.

The second model, which is an extension of the Dewar-Chatt-Duncanson model, has been invoked to describe the bonding in the Pt/Si dimers^{6,31} and the cyclodisiloxanes [(R₂SiO)₂].^{29a} In **9b**, the Pt, Si and P atoms are approximately coplanar with a dihedral angle of 11.4° between the two planes defined by Si(1), Pt, Si(2) and P(1), P(2). This, coupled with the likewise nearly planar geometry of the central Pt-Si-O-Si four-membered ring and the acute distortion of the angle at the platinum are all features that would be consistent with a η^2, η^2 -disilene bonding description in which Me₂Si=SiMe₂ is π -coordinated to both Pt and O.³¹ The Si-Si distance in **9b** is about 19% longer than that in free disilenes (~2.14 Å). This compares with the 21–24% lengthening of the Si-Si bond distance in the Tessier-Youngs Pt-Si dimers and the increase of 12% or 27% in the C-C distance in ethylene when π -complexed to two zirconium centers in Zr₂X₆-(PEt₃)₄(CH₂=CH₂) (X = Br or Cl, respectively).³³ In the

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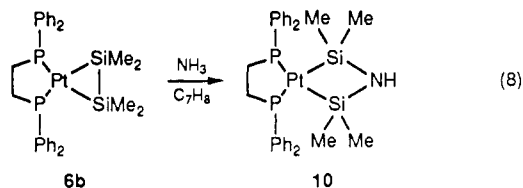
(24) (a) Bokii, N. G.; Zakharova, G. N.; Struchkov, Y. T. *Z. Strukt. Khim.* **1972**, *13*, 291. (b) Steinfink, H.; Post, B.; Fankuchen, I. *Acta Crystallogr.* **1955**, *8*, 420. (c) Kiss, J.; Mencez, G. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1975**, *B31*, 1214. (d) Hossain, M. A.; Hursthouse, M. D.; Malik, K. M. A. *Ibid.* **1979**, *B35*, 522.

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third model, invoked by Curtis,²⁶ the strain present in the four-membered metallacycle would cause the Pt-Si bonds to be "bent", so that the maximum electron density lies outside the Pt-Si vector. In **9b** the considerable decrease (by over 40°) of the endocyclic Si-O-Si angle relative to those for unstrained siloxanes is expected to lead to some weakening and lengthening of the Si-O bonds, as is observed.

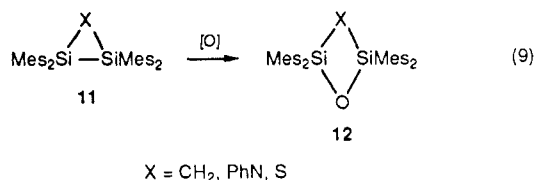
Reactivity toward σ -Donors. In light of the evidence presented thus far for platinum- η^2 -disilene complexes with appreciable residual Si-Si π -bonding, it was anticipated that reaction with σ -donor ligands, such as diphos, might displace the disilene fragment thus affording a new, low-temperature route to disilenes. However, when **6a** was reacted with an equimolar amount of diphos in benzene at room temperature, then under reflux, the expected products (diphos)₂Pt and (*i*-Pr₂Si)₄ (from dimerization of thermally unstable *i*-Pr₂Si=Si-*i*-Pr₂)³⁴ were not detected. Only starting materials, diphos, and unidentifiable brown-black decomposition products were recovered. Thus, it appears that disintegration of the Pt-Si ring occurred upon reaction with the diphosphine. Similar fragmentation of Pt-Si rings has been observed in reactions with π -acceptor ligands such as CO and *t*-BuNC, yielding Pt complexes containing no silicon.^{16a} The experiment shows that the disilene fragment is not as loosely bound to the platinum center as, for example, ethylene in analogous metal- η^2 -alkene complexes.

Preliminary investigations into the reactivity of **6b** toward tertiary and secondary amines, e.g., Et₃N, Et₂NH, and Me₂NH, suggested no reaction or led also to disintegration of the Pt-Si ring resulting in unidentifiable products. However when ammonia was bubbled through a toluene solution of **6b**, the novel complex **10** was isolated



in nearly quantitative yield. Compound **10** crystallizes as mildly air-sensitive colorless rods that melt to an orange liquid at ca. 160 °C. The spectroscopic and analytical data are consistent with the formulation of **10** as a four-membered heterocycle. The ³¹P and ²⁹Si NMR data for **10** are very similar to those obtained for **9b**, the oxygen-containing four-membered ring analogue.

In summary, our initial studies into the reactivity of platinum- η^2 -disilene complexes with small molecules, e.g., H₂, O₂, and NH₃, have led to the formation of new products arising from addition across the Si-Si bond rather than from cleavage of Pt-Si bonds. The findings are consistent with earlier results from disilacyclopropane chemistry. As shown in eq 9, the three-membered ring compounds **11** undergo Si-Si rather than Si-X bond cleavage with oxidants, e.g., MCPBA, to afford four-membered heterocycles **12**.³⁵



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Experimental Section

General Procedures. All reactions were performed under an atmosphere of nitrogen or argon. Air-sensitive materials were handled by using standard Schlenck techniques or in a drybox maintained under a positive pressure of nitrogen and equipped with a Vacuum Atmospheres HE-493 purification unit and HE-63-P automatic pressure controller.

Materials. All solvents were distilled from appropriate drying agents. Lecture bottles of hydrogen (99.999%), ethylene, and anhydrous ammonia (99.999%) were purchased from Matheson and Aldrich Chemical Companies. The phosphine ligands 1,2-bis(diphenylphosphino)ethane (diphos) and 1,2-bis(dicyclohexylphosphino)ethane (dcpe) were obtained from Strem. Lithium powder containing 2% Na (Fluka) and potassium sticks (Aldrich) were used. (R₃P)₂Pt(C₂O₄)¹¹ (R = Et, Ph), (Ph₃P)₂Pt(CH₂=CH₂),³⁶ Mes₂Si=SiMes₂,³⁷ (*i*-Pr₂SiH)₂,³⁸ (Me₂SiH)₂,³⁹ (Ph₂SiH)₂,⁴⁰ (diphos)PtCl₂,⁴¹ (dcpe)PtCl₂,⁴² (diphos)Pt(C₂H₄),¹² and (dcpe)Pt(C₂H₄)¹² were prepared as described in the literature.

Spectra. IR spectra were recorded on a Beckman 4230 spectrophotometer or a Mattson Instruments FT-IR, Model NU-10000. Solution spectra were recorded in matched 0.1-mm NaCl cells. Proton spectra were recorded on a Bruker WP-200, WP-270, or AM-500 spectrometer (often through the decoupler coils on the AM-500); ¹³C{¹H}, ³¹P{¹H} and ²⁹Si{¹H} spectra were acquired on the Bruker AM-500 instrument at 125, 202.5, and 100 MHz, respectively. The notation {¹H} indicates broad-band noise decoupling of the hydrogen nuclei.

¹H chemical shifts were measured by using the solvent resonance (arising from incomplete deuteration) relative to Me₄Si at 0 ppm; ³¹P chemical shifts were measured relative to external 85% H₃PO₄; ²⁹Si chemical shifts were referenced to external Me₄Si in the same solvent; and ¹³C shifts to the signal from the solvent. The ²⁹Si spectra were acquired using INEPT pulse sequences. All chemical shifts reported are in ppm units.

High-resolution mass spectral data were obtained on a Kratos MS-80 or AEI MS-9; fast atom bombardment mass spectra (FAB-MS) were obtained from the Midwest Center for Mass Spectrometry, Lincoln, NE, and from the Department of Biochemistry, UW-Madison.

Irradiations at 254 nm were performed in a Rayonet RPR-208 or RPR-100 photochemical reactor. Melting points are uncorrected. Microanalyses were done by Galbraith Laboratories, Knoxville, TN, or Desert Analytics, Tucson, AZ.

Photolysis of (R₃P)₂Pt(C₂O₄) (1a, R = Et; 1b, R = Ph) with Tetramesityldisilene. In a typical experiment, a quartz Schlenck tube containing tetramesityldisilene (0.1 g, 0.2 mmol) and an equimolar amount of **1a,b** in degassed acetonitrile/benzene (40 mL) was irradiated in a Rayonet reactor ($\lambda = 254$ nm) at 0–5 °C under argon. The reaction was monitored by IR and ³¹P{¹H} NMR spectroscopies; gradual disappearance of the oxalate bands ($\nu_{C=O}$ 1703 (**1a**), 1710 cm⁻¹ (**1b**)) in the IR and growth of a new resonance at the expense of the one corresponding to **1a,b** in the ³¹P{¹H} NMR spectrum indicated near completion of the reaction after 2 h. Extraction with hexane and slow evaporation of solvent precipitated yellow-orange solid powders **2a,b** in low yields (ca. 10–15%). **2a**: ¹H NMR (C₆D₆) 6.7 (s, 8 H), 2.4 (s, 24 H), 2.1 (s, 12 H), 1.7 (m, 12 H), 1.0 (m, 18 H); ³¹P{¹H} NMR (C₆D₆) 23.3 (s, ¹J_{Pt-P} = 2730 Hz); ²⁹Si{¹H} NMR (C₆D₆) -23.9; HRMS (FAB) calcd for C₄₈H₇₄P₂PtSi₂ 964.3211, found 964.3281. **2b**: ¹H NMR (C₆D₆) 7.8 (m, 12 H), 7.5 (m, 18 H), 6.6 (s, 8 H), 2.5 (s, 24 H), 2.1 (s, 12

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H); $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6) 19.5 (s, $^1J_{\text{Pt-P}} = 1725$ Hz); $^{29}\text{Si}\{^1\text{H}\}$ NMR (C_6D_6) -29.1; HRMS (FAB) calcd for $\text{C}_{72}\text{H}_{74}\text{P}_2\text{PtSi}_2$ 1252.5851, found 1252.5924.

Reaction of $(\text{Ph}_3\text{P})_2\text{Pt}(\text{CH}_2=\text{CH}_2)$ with Tetramesityldisilene. In a drybox atmosphere, a 25-mL round-bottom Schlenk flask was charged with tetramesityldisilene (0.1 g, 0.2 mmol) and $(\text{Ph}_3\text{P})_2\text{Pt}(\text{CH}_2=\text{CH}_2)$ (0.15 g, 0.2 mmol). Toluene was vacuum transferred in, and the resulting orange solution was allowed to stir overnight under argon. Solvent removal followed by workup in hexane afforded a yellow-orange solid powder in 18% yield. The ^1H , $^{31}\text{P}\{^1\text{H}\}$, and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra for the compound are identical with those for **2b**.

Reaction of **2a with MeOH.** Freshly distilled MeOH (5 mL) was vacuum transferred into a Schlenk flask containing a C_6D_6 solution of **2a** (0.05 g, 0.1 mmol). The resulting pale yellow mixture was allowed to stir overnight under argon. Examination by ^1H NMR indicated that the major product contained a Pt-H and two different mesityl groups. Selected spectroscopic data of interest for **3**: ^1H NMR (C_6D_6) -17.1 (t, $^2J_{\text{P-H}} = 15.25$ Hz, $^1J_{\text{Pt-H}} = 1288$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6) 10.4 (s, $^1J_{\text{Pt-P}} = 2722$ Hz); $^{29}\text{Si}\{^1\text{H}\}$ NMR (C_6D_6) -22.0, -34.1; HRMS (FAB) calcd for $\text{C}_{49}\text{H}_{78}\text{OP}_2\text{PtSi}_2$ 996.3631, found 996.3713.

(diphos)Pt(Si_2 -*i*-Pr₄O), **6a. Method A.** In a typical preparation, a 100-mL round-bottom Schlenk flask was charged with equivalent amounts of (diphos)PtCl₂ (0.265 g, 0.4 mmol) and (*i*-Pr₂SiH)₂ (0.092 g, 0.4 mmol) in a drybox. Lithium powder (2% Na, 0.006 g, 0.9 mmol) was then added, followed by vacuum transfer of THF (20 mL). The reaction mixture eventually turned orange-red with noticeable evolution of gas, presumably H₂. After overnight stirring under argon, THF was evaporated, and the residue was extracted into toluene (10 mL). Filtration under argon followed by cooling to -20 °C of a concentrated toluene solution afforded yellow microcrystals of **6a** in 20% yield. ^1H NMR (CD_2Cl_2) 7.61 (m, 8 H), 7.43 (m, 12 H), 2.14 (dt, $^2J_{\text{P-H}} = 17.6$ Hz, $^3J_{\text{H-H}} = 6.3$ Hz, 2 H), 2.05 (dt, $^2J_{\text{P-H}} = 17.6$ Hz, $^3J_{\text{H-H}} = 6.3$ Hz, 2 H), 1.55 (m, 4 H), 0.85 (d, $^3J_{\text{H-H}} = 10.4$ Hz, 24 H); $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6) 56.21 (s, $^1J_{\text{Pt-P}} = 1344$ Hz, $^2J_{\text{P-Si}} = 12.5$ Hz, $^2J_{\text{P-trans-Si}} = 138$ Hz); $^{29}\text{Si}\{^1\text{H}\}$ NMR (C_7D_8) 19.60 (dd, $^1J_{\text{Pt-Si}} = 1128$ Hz, $^2J_{\text{P-cis-Si}} = 12.5$, $^2J_{\text{P-trans-Si}} = 138$ Hz); FAB-MS 822 (M^+ , 100% rel intensity), 751 ($\text{M}^+ - i\text{-PrSi}$, 20%), 708 ($\text{M}^+ - i\text{-Pr}_2\text{Si}$, 38%), 594 ($\text{M}^+ - \text{Si}_2$ -*i*-Pr₄, 70%). Anal. Calcd for $\text{C}_{38}\text{H}_{52}\text{P}_2\text{PtSi}_2$: C, 55.52; H, 6.38. Found: C, 55.69; H, 6.36.

Method B. In a drybox atmosphere, a 50-mL round-bottom Schlenk flask was charged with (diphos)Pt(C_2H_4), **7a** (0.16 g, 0.3 mmol), and **5a** (0.07 g, 0.3 mmol). Toluene was vacuum transferred in, and bubbling was observed from gas evolution. The yellow solution was heated to reflux for 1 h, after which it was concentrated under vacuum and cooled to 20 °C. The precipitated yellow solid was collected on a Schlenk frit and dried under vacuum, yield 135 mg (55%). The compound had spectroscopic data (NMR, FAB-MS) identical with those for **6a**.

(diphos)Pt(Si_2Me_4), **6b. Method A.** Compound **6b** was prepared as an extremely air-sensitive yellow solid in ca. 25% yield from **4a** and **5b** under conditions described above for **6a**. ^1H NMR (C_7D_8) 7.68 (m, 8 H), 7.52 (m, 12 H), 2.20 (dt, $^2J_{\text{P-H}} = 15.8$ Hz, $^3J_{\text{H-H}} = 5.8$ Hz, 2 H), 2.12 (dt, $^2J_{\text{P-H}} = 15.8$ Hz, $^3J_{\text{H-H}} = 5.8$ Hz, 2 H) 0.18 (s, 12 H); $^{31}\text{P}\{^1\text{H}\}$ NMR (C_7D_8) 59.52 (s, $^1J_{\text{Pt-P}} = 1371$ Hz); $^{29}\text{Si}\{^1\text{H}\}$ NMR (C_7D_8) 23.47 (dd, $^2J_{\text{P-cis-Si}} = 13.2$ Hz, $^2J_{\text{P-trans-Si}} = 150.5$ Hz, $^1J_{\text{Pt-Si}} = 1252$ Hz); FAB-MS 709 (M^+ , 100% rel intensity), 651 ($\text{M}^+ - \text{SiMe}_2$, 43%); C, H analyses were unsatisfactory.

Method B. By a procedure analogous to that described for **6a**, **6b** was prepared in ca. 45% yield from **7a** and **5b**.

(dcpe)Pt(Si_2Ph_4), **6c. Method A.** By a procedure analogous to that described for **6a**, **6c** was prepared in 12% yield. ^1H NMR ($\text{C}_6\text{D}_6/\text{CD}_2\text{Cl}_2$) 7.42 (m, 8 H), 7.1 (m, 12 H), 2.3 (m, 4 H), 1.7-1.4 (m, 44 H); $^{31}\text{P}\{^1\text{H}\}$ NMR (C_7D_8) 73.47 (s, $^1J_{\text{Pt-P}} = 1545$ Hz, $^2J_{\text{P-cis-Si}} = 13.5$ Hz, $^2J_{\text{P-trans-Si}} = 148$ Hz); $^{29}\text{Si}\{^1\text{H}\}$ NMR (C_7D_8) -7.84 (dd, $^2J_{\text{P-cis-Si}} = 13.5$ Hz, $^2J_{\text{P-trans-Si}} = 148$ Hz, $^1J_{\text{Pt-Si}} = 1125$ Hz); FAB-MS 982 (M^+ , 100% rel intensity), 906 ($\text{M}^+ - \text{Ph}$, 77%), 877 ($\text{M}^+ - \text{SiPh}$, 46%), 800 ($\text{M}^+ - \text{SiPh}_2$, 52%). Anal. Calcd for $\text{C}_{50}\text{H}_{68}\text{P}_2\text{PtSi}_2$: C, 61.1; H, 6.93. Found: C, 58.7; H, 6.94.

(diphos)Pt(Si_2 -*i*-Pr₄H₂), **8.** Through a solution of **6a** (0.1 mmol) in C_7D_8 (2 mL) at 25 °C in a Schlenk tube was bubbled H₂ (1 atm) for 15 min. The solution eventually turned from yellow to nearly colorless, and a sample was removed for ^1H NMR. No

Pt-H resonances were observed. Surprisingly a well-defined doublet of doublets with Pt satellites was seen in the Si-H region at 4.38 ppm. IR (C_7D_8) ν_{SiH} 1968 cm^{-1} ; ^1H NMR (C_7D_8) 7.66 (m, 8 H), 7.24 (m, 12 H), 4.38 (dd, $^3J_{\text{P-H}} = 12.14$ Hz, $^3J_{\text{P-trans-H}} = 21.95$ Hz, $^2J_{\text{Pt-H}} = 120$ Hz), 1.89 (m, 2 H), 1.81 (m, 2 H), 1.46 (m, 4 H), 1.22 (d, $^3J_{\text{H-H}} = 9.2$ Hz, 24 H); $^{31}\text{P}\{^1\text{H}\}$ NMR (C_7D_8) 59.36 (s, $^1J_{\text{Pt-P}} = 1213$ Hz); $^{29}\text{Si}\{^1\text{H}\}$ NMR (C_7D_8) 24.32 (dd, $^2J_{\text{P-cis-Si}} = 13.6$ Hz, $^2J_{\text{P-trans-Si}} = 149$ Hz, $^1J_{\text{Pt-Si}} = 1315$ Hz); the ^1H -coupled ^{29}Si NMR spectrum showed a triplet owing to the nearly equal values for $^1J_{\text{Si-H}}$ and $^1J_{\text{P-trans-Si}}$ (149 Hz); mp 170-172 °C. Anal. Calcd for $\text{C}_{38}\text{H}_{54}\text{P}_2\text{PtSi}_2$: C, 55.39; H, 6.60. Found: C, 55.59; H, 6.56.

(diphos)Pt(Si_2 -*i*-Pr₄O), **9a.** Oxygen was bubbled through a toluene solution (15 mL) of **6a** (0.1 mmol) for 1 h. The now colorless solution was concentrated under vacuum and then cooled at -20 °C to afford colorless microcrystals of **9a** in 60% yield; mp 251-253 °C; ^1H NMR (C_7D_8) 7.49 (m, 8 H), 7.34 (m, 12 H), 1.60 (m, 2 H), 1.37 (m, 2 H), 1.15 (m, 4 H), 0.7 (m, 24 H); $^{29}\text{Si}\{^1\text{H}\}$ NMR (C_7D_8) 11.2 (dd, $^2J_{\text{P-cis-Si}} = 9.3$ Hz, $^2J_{\text{P-trans-Si}} = 115$ Hz, $^1J_{\text{Pt-Si}} = 1001$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (C_7D_8) 41.61 (s, $^1J_{\text{Pt-P}} = 1671$ Hz). Anal. Calcd for $\text{C}_{38}\text{H}_{52}\text{OP}_2\text{PtSi}_2$: C, 55.42; H, 6.21. Found: C, 55.34; H, 6.19.

(diphos)Pt($\text{Si}_2\text{Me}_4\text{O}$), **9b.** Analogously, **9b** was prepared in ca. 75% yield from **6b** and oxygen; mp 232-234 °C; ^1H NMR (C_7D_8) 7.55 (m, 8 H), 7.43 (m, 12 H), 1.57 (m, 2 H), 1.43 (m, 2 H), 0.08 (s, 12 H); $^{31}\text{P}\{^1\text{H}\}$ NMR ($\text{C}_6\text{D}_6/\text{CD}_2\text{Cl}_2$) 61.51 (s, $^1J_{\text{Pt-P}} = 1405$ Hz); $^{29}\text{Si}\{^1\text{H}\}$ NMR ($\text{C}_6\text{D}_6/\text{CD}_2\text{Cl}_2$) 13.25 (dd, $^2J_{\text{P-cis-Si}} = 6.5$ Hz, $^2J_{\text{P-trans-Si}} = 131$ Hz, $^1J_{\text{Pt-Si}} = 991$ Hz). Anal. Calcd for $\text{C}_{30}\text{H}_{36}\text{OP}_2\text{PtSi}_2$: C, 49.66; H, 4.97. Found: C, 49.49; H, 4.94.

Reaction of **6a with diphos.** To a Schlenk flask containing a benzene-*d*₆ solution of **6a** (0.05 g, 0.1 mmol), a C_6D_6 solution of diphos (0.025 g, 0.1 mmol) was added dropwise. The yellow-orange mixture was allowed to stir overnight at ambient temperature. A sample was removed and examined by $^{31}\text{P}\{^1\text{H}\}$ NMR. Only starting materials were present [δ 56.2 (**6a**), δ -14.1 (diphos)]. The reaction mixture was then heated under reflux to afford a brown-black solution after 1 h. Examination by $^{31}\text{P}\{^1\text{H}\}$ NMR revealed less diphos present along with a new peak at 19.5 ppm with no Pt satellites [lit.⁴² Pt(diphos)₂, 30.2 ppm ($^1J_{\text{Pt-P}} = 3728$ Hz)]. No peaks corresponding to (*i*-Pr₂Si)₄⁴³ were observed in the $^{29}\text{Si}\{^1\text{H}\}$ NMR and HRMS spectra.

(diphos)Pt($\text{Si}_2\text{Me}_4\text{NH}$), **10.** In a drybox a 50-mL round-bottom Schlenk flask was charged with **6b** (0.20 g, 0.30 mmol). Toluene (20 mL) was vacuum transferred in. Anhydrous ammonia was bubbled into the stirred yellow solution. Within 15 min the yellow color of the mixture was discharged, yielding a clear, nearly colorless solution. Addition of ammonia was halted after 0.5 h. Solvent evaporation followed by washing of the residue with hexane (3 × 10 mL) afforded **10** (0.20 g, 91%) as a mildly air-sensitive white solid. Analytically pure **10** can be obtained as colorless, crystalline rods by slow cooling (0 to -10 °C) of a saturated toluene solution; mp 158-160 °C (orange liquid); IR (KBr) ν_{NH} 3150 cm^{-1} ; ^1H NMR (C_7D_8) δ 7.48 (m, 8 H), 7.37 (m, 12 H), 5.13 (br m, 1 H), 1.48 (m, 2 H), 1.35 (m, 2 H), 0.05 (s, 12 H); $^{31}\text{P}\{^1\text{H}\}$ NMR (C_7D_8) 60.63 (s, $^1J_{\text{Pt-P}} = 1440$ Hz); $^{29}\text{Si}\{^1\text{H}\}$ NMR (C_7D_8) δ -12.13 (dd, $^2J_{\text{P-cis-Si}} = 7.4$ Hz, $^2J_{\text{P-trans-Si}} = 134$ Hz, $^1J_{\text{Pt-Si}} = 1000.6$ Hz); FAB-MS 725 ($\text{M}^+ + 1$, 95% rel. intensity), 710 ($[\text{M} + 1] - \text{NH}$, 100%), 651 ($[\text{M}^+ + 1] - \text{SiMe}_2\text{NH}$, 31%). Anal. Calcd for $\text{C}_{30}\text{N}_3\text{NP}_2\text{PtSi}_2$: C, 49.72; H, 5.11. Found: C, 49.58; H, 5.09.

Crystallographic Studies. Suitably sized crystals of **8** and **9b** were mounted on glass fibers and protected from air with a coating of epoxy cement. The initial orientation matrix was calculated from 12 machine-centered reflections obtained from a rotation photograph. These data were used to determine the crystal system. Final unit cell parameters were subsequently determined from the least-squares fit of the angular settings of 25 reflections ($25^\circ < 2\theta < 30^\circ$). No significant decrease in the intensity of the standard reflections was observed during the course of data collection for both compounds. Details of crystal data and intensity collection are summarized in Table I. The data were processed by using the SHELXTL PLUS software package on a Microvax II. An empirical ellipsoidal correction was applied to both data sets. The structures were solved by standard Patterson and difference Fourier techniques. Only those reflections

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with $I_o > 3\sigma(I_o)$ were used in the full-matrix, least-squares refinements. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in idealized positions (C-H = 0.96 Å; H-C-H = 109.5°), allowed to ride with the carbons to which they are attached, and their individual isotropic thermal motion was fixed at 0.08. The exception was the silyl hydrides in **8**, which were allowed to ride with the Si atoms but refined isotropically.

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Supplementary Material Available: Tables of atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for **8** and **9b** (10 pages); listings of structure factors for **8** and **9b** (45 pages). Ordering information is given on any current masthead page.

Clusters Containing Carbene Ligands. 8. Formation of Ligands Containing (Dialkylamino)carbene Centers by a Novel 1,1-Hydrogenation of Ynamine Ligands

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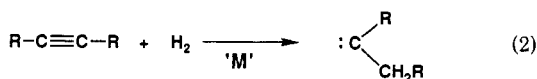
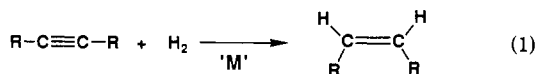
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The reaction of the complex $\text{Os}_3(\text{CO})_9(\mu_3\text{-MeC}_2\text{NMe}_2)(\mu_3\text{-S})$ (**1**) with hydrogen at 125 °C and 1 atm yielded the two new compounds $\text{Os}_3(\text{CO})_7[\mu\text{-C}(\text{Et})\text{N}(\text{Me})\text{CH}_2](\mu_3\text{-S})(\mu\text{-H})_3$ (**3**; 7%) and $\text{Os}_3(\text{CO})_8[\text{C}(\text{Et})\text{NMe}_2](\mu_3\text{-S})(\mu\text{-H})_2$ (**4**; 9%). At 125 °C and 10 atm of H_2 pressure the yield of **4** was increased to 33%, the yield of **3** decreased to essentially zero, and the two new compounds $\text{Os}_3(\text{CO})_8[\text{C}(\text{Et})\text{N}(\text{Me})\text{CH}_2](\mu_3\text{-S})(\mu\text{-H})$ (**5**) and $\text{Os}_3(\text{CO})_8[\eta\text{-H}_2\text{CC}(\text{H})\text{C}(\text{H})\text{NMe}_2](\mu_3\text{-S})(\mu\text{-H})$ (**6**) were formed in very low yield. Compounds **3** and **4** can be interconverted by the addition and elimination of CO. Compounds **3-6** were characterized by IR, NMR, and single-crystal X-ray diffraction analyses. Each compound consists of a sulfur-bridged triangular triosmium cluster. Compound **3** contains a bridging $\text{EtCN}(\text{Me})\text{CH}_2$ ligand. The ethyl-substituted carbon is a carbene center. Compound **4** contains a terminally coordinated carbene, $\text{EtC}(\text{NMe}_2)$. Compound **5** contains a chelating $\text{EtCN}(\text{Me})\text{CH}_2$. The ethyl-substituted carbon is a carbene center. Compound **6** contains a $\eta^2\text{-H}_2\text{CC}(\text{H})\text{C}(\text{H})\text{NMe}_2$ ligand. The carbene centers in compounds **3-5** were formed by 1,1-hydrogenations at the methyl-substituted carbon atom of the ynamine ligand in **1**. In compounds **3** and **5** one of the *N*-methyl groups was metalated. The (dimethylamino)allyl ligand in **6** was formed by a 1,2-dihydrogenation of the ynamine ligand in **1** plus a CH activation on the methyl group on the carbon atom. Crystal data: for **3**, space group *Pbca*, $a = 12.884$ (3) Å, $b = 23.897$ (5) Å, $c = 12.522$ (3) Å, 1858 reflections, $R = 0.034$, $R_w = 0.033$; for **4**, space group $\text{P}\bar{1}$, $a = 9.955$ (1) Å, $b = 13.971$ (2) Å, $c = 8.227$ (1) Å, $\alpha = 102.91$ (1)°, $\beta = 113.134$ (9)°, $\gamma = 92.06$ (1)°, 2606 reflections, $R = 0.027$, $R_w = 0.031$; for **5**, space group $\text{P}2_1/n$, $a = 9.260$ (2) Å, $b = 12.784$ (3) Å, $c = 16.734$ (3) Å, $\beta = 90.60$ (2)°, 2163 reflections, $R = 0.025$, $R_w = 0.026$; for **6**, space group $\text{P}2_1/n$, $a = 10.226$ (3) Å, $b = 12.589$ (5) Å, $c = 15.990$ (7) Å, $\beta = 106.88$ (3)°, 2129 reflections, $R = 0.036$, $R_w = 0.039$.

Introduction

The hydrogenation of alkynes by metal complexes invariably proceeds to yield alkenes, usually with a cis stereochemistry, by the 1,2-addition of hydrogen to the triple bond (eq 1).^{1,2} To our knowledge, the alternative



1,1-hydrogenation to yield alkylidenes has not yet been

reported (eq 2). For most substituents, eq 2 as written is probably thermodynamically unfavorable. However, in the presence of stabilizing substituents and a metal atom for complexation, eq 2 may become thermodynamically favorable.

Recent studies of the coordination of ynamine ligands in metal cluster complexes have shown that the amine-substituted carbon atom possesses an appreciable carbene-like character.³⁻⁶

We have now investigated the reactions of the complex $\text{Os}_3(\text{CO})_9(\mu_3\text{-MeC}_2\text{NMe}_2)(\mu_3\text{-S})$ (**1**) with H_2 and have observed a preference for the formation of the ethyl(dimethylamino)carbene ligand grouping by the addition of

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