Reactions of Diazomethane Derivatives with Platinum(II): A Facile Method for Platinum Ylide Preparation

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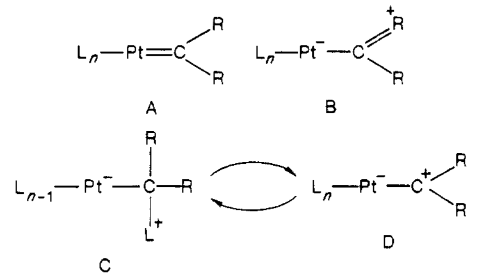
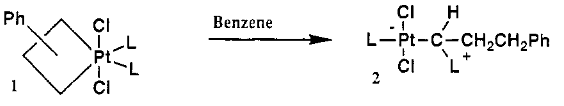
A new and versatile method for the preparation of Pt(II) ylides has been devised by using diazo derivatives and Zeise's dimer. A single-crystal X-ray analysis of the parent complex was performed (orthorhombic, $P2_12_12_1$, a = 5.361 (1) Å, b = 11.805 (2) Å, c = 20.595 (2) Å, Z = 4). Further, X-ray photoelectron spectroscopy results suggest that the platinum methylidene ylide is in the range of values found for various Pt(II) derivatives. An effort to force the system over to a platinum carbene using a carbethoxy group on the carbenoid carbon was not successful.

Introduction

Since the discovery of transition-metal carbene complexes in 1964 and subsequent work showing their importance in olefin metathesis, the area has received considerable attention.[1,2] On this front with platinum complexes, the orbital energy difference between the metal d orbital and carbon p orbital is apparently too large to allow the π-type bonding shown in structure A.[3] Instead one observes complexes and/or derivatives of type B and C. In the type B (Fischer type) carbenes, x is usually oxygen, nitrogen, phosphorus, or an sp^2 carbon. Complexes of type D (R = H or alkyl) which result from the orbital energy difference stated above are not stable and require ligand transfer from the platinum to yield ylides as shown with structure C. In principle, however, a tautomeric equilibrium between C and D might be achieved which would facilitate reactions from structure D.



Although a variety of Pt(II) type C complexes (L = P or S derivatives) have been prepared,[4] similar analogues with pyridine are few.[5-8] This results from the fact that these latter derivatives are prepared from platinacyclobutanes as shown in eq 1.[9,10] Puddephatt has also shown that this reaction proceeds with hydride transfer from the incipient carbene or ylide carbon to the benzylic carbon.



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L= pyridine, 2-methylpyridine

Since this method is obviously restricted to compounds with three or more carbons, a method which would be more versatile in providing simple as well as complex carbon ylides (L = py) was clearly needed. In this paper we wish to report (1) a facile method for platinum ylide preparation (structure C; L = py), (2) an X-ray structure for the parent methylidene derivative, (3) the X-ray photoelectron spectral (XPS) data for the parent methylidene platinum ylide complex, and (4) some interesting results for the diazoacetic ester derivative.

Results and Discussion

Preparation of Pt(II) Ylides. The results of our initial efforts with the substrates diazomethane and diazoethane are shown in Scheme I. NMR data which support the structures for ylides **5** and **6** are listed in Tables I and II. From these data, it is obvious that complex **5**, has two nonequivalent pyridine ligands, platinum, and a single methylene carbon (triplet, 30.1 ppm) which is σ-bonded to platinum as evident by the large coupling constant ($^1J_{\text{Pt-C}}$ = 751 Hz). The platinum resonance at 1852 ppm relative to $K_2Pt(CN)_4$ in D_2O at 25 °C is consistent with a Pt(II) complex.[11] Complex **6** is clearly an analogue from analysis of its NMR spectra. X-ray diffraction analysis of **5** was conducted and will be discussed in the next section. The key to success with these reactions is to have the proper amount of pyridine present at the two stages of the reaction (Scheme I). For example, if 2 equiv of pyridine are added to Zeise's dimer followed by the diazoalkane, a healthy yield of bis(pyridine) platinum dichloride and other derivatives are obtained at the expense of desired product. At the other extreme, an insufficient amount of pyridine will yield dimers of the diazoalkyl groups. Therefore, the most effective synthetic method is to react 1 mol of Zeise's dimer with 2 mol of pyridine to form a solution of the mononuclear complex 4 (not isolated) which is subsequently reacted with a solution

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Table I. Proton NMR Resonances (ppm) for Platinum Complexes

	5	6	7	8	9	10
Py_1 o	8.92	8.86	8.86	8.86	8.86	8.84
py_1 m	7.25	7.15	7.2–7.3	7.2–7.3	7.2–7.3	7.32
py_1 p	7.75	7.5–7.7	7.5–7.7	7.5–7.7	7.5–7.7	7.7–7.9
py_2 o	9.05	8.91	8.52	9.05	8.86	9.11
py_2 m	7.62	7.5–7.7	7.2–7.3	7.5–7.7	7.2–7.3	7.7–7.9
py_2 p	8.02	8.05	7.5–7.7	8.04	7.5–7.7	8.13
CH (ylide	5.45 (100 Hz)[a]	6.01 (116 Hz)[a]	5.62 (118 Hz)[a]	6.59 (119 Hz)[a]	4.90 (123 Hz)[a]	6.58 (114 Hz)[a]
CH_2			3.89	4.18	3.91	4.24
CH_3		1.80	1.90	1.26	1.12	1.34

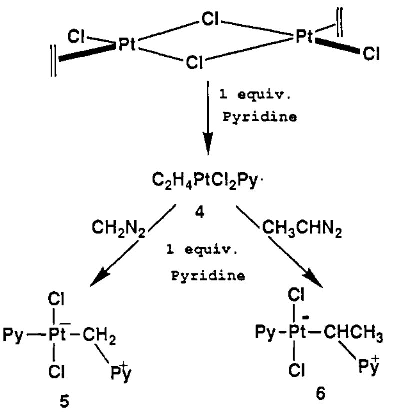
[a] $^2J_{Pt,H}$.

Table II. ^{13}C and ^{195}Pt NMR Resonances (ppm) for Platinum Complexes

	5	6	7	8	9	10
py_1 o	151.7	151.7	153.3	153.6	153.4	NA
py_1 m	126.6	126.0	125.9	126.1	124.6	
py_1 p	139.8	139.8	137.9	138.6	137.8	
py_2 o	143.3	141.9	150.5	151.9	153.4	
py_2 m	124.6	124.5	125.5	125.0	124.6	
py_2 p	137.1	136.8	137.2	137.1	137.8	
CH (ylide)	30.1 (751 Hz)[a]	38.5 (766 Hz)[a]	26.9 (796 Hz)[a]	42.2 (734 Hz)[a]	32.3 (921 Hz)[a]	28.4 (866 Hz)[a]
CH_2			60.2	60.9	60.4	60.8
CH_3		23.9	14.3	14.5	14.2	14.3
C=O			175.9	176.6	...	
^{195}Pt[b]	1852		1817	1984	1966	1983

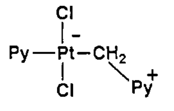
[a] $^1J_{Pt-C}$. [b] Chemical shifts relative to $K_2Pt(CN)_4$ at 25 °C in D_2O.

Scheme I

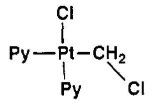


containing both the diazoalkane and 1 mol of pyridine.

X-ray Diffraction Analysis of 5. Although the NMR results were consistent with the proposed structure 5, it would not be possible to unambiguously distinguish 5 from 5′. Moreover, since both would be the parent complex in the series and no previous X-ray structures had been published, an X-ray diffraction analysis was warranted (Figure 1; Tables III and IV). From these data, it is clear that the postulated structure for 5 is correct and that the NMR spectral analyses are valid. It subsequently follows from the similarity in NMR results that complex 6 has the same basic structure.



5



5'

In the crystalline form, complex 5 is chiral. It has selectively crystallized in its two enantiomeric forms, and the absolute configuration is that shown in Figure 1. This is evidenced by the fact that refinement of the mirrored structure leads to significantly higher R values (R = 0.0389 vs. 0.0244 and R_w = 0.0406 vs. 0.0250). Finally, there is the question of π-bonding between platinum and C(6).

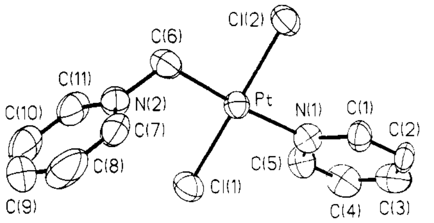


Figure 1. View of the core atoms of $PyPtCl_2CH_2Py$.

Table III. Selected Bond Lengths (Å) and Angles (deg) for 5

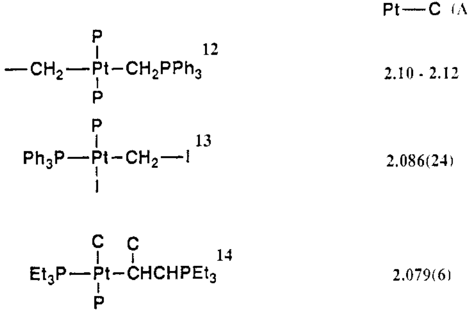
Bond Lengths			
Pt-Cl(1)	2.310 (3)	Pt-C(6)	2.03 (1)
Pt-Cl(2)	2.301 (3)	C(6)-N(2)	1.49 (2)
Pt-N(1)	2.10 (1)		
Bond Angles			
Cl(1)-Pt-Cl(2)	178.9 (3)	Cl(2)-Pt-C(6)	85.7 (3)
Cl(1)-Pt-N(1)	90.6 (3)	N(1)-Pt-C(6)	174.7 (4)
Cl(2)-Pt-N(1)	89.7 (3)	Pt-C(6)-N(2)	117.1 (9)
Cl(1)-Pt-C(6)	93.9 (3)		

Table IV. Atomic Coordinates and Isotropic Thermal Parameters[a] (Å^2) for 5

	x	y	z	U
Pt	0.3750 (1)	0.06488 (4)	0.58413 (2)	0.0402 (2)
Cl(1)	0.4090 (9)	0.0981 (3)	0.6943 (2)	0.059 (1)
Cl(2)	0.3336 (7)	0.0307 (3)	0.4747 (2)	0.054 (1)
N(1)	0.613 (2)	−0.0759 (8)	0.5919 (5)	0.045 (3)
N(2)	0.124 (3)	0.2846 (8)	0.6196 (5)	0.046 (4)
C(1)	0.804 (2)	−0.092 (1)	0.5514 (7)	0.049 (5)
C(2)	0.960 (2)	−0.187 (1)	0.5569 (7)	0.059 (6)
C(3)	0.917 (4)	−0.265 (1)	0.6040 (8)	0.071 (7)
C(4)	0.728 (4)	−0.248 (1)	0.6466 (8)	0.071 (7)
C(5)	0.579 (3)	−0.152 (1)	0.6399 (7)	0.059 (6)
C(6)	0.130 (3)	0.193 (1)	0.5698 (5)	0.051 (5)
C(7)	0.300 (3)	0.362 (1)	0.6191 (7)	0.057 (6)
C(8)	0.303 (3)	0.443 (1)	0.6639 (10)	0.098 (8)
C(9)	0.130 (3)	0.450 (1)	0.7066 (8)	0.107 (8)
C(10)	−0.052 (3)	0.370 (2)	0.7102 (7)	0.091 (8)
C(11)	−0.051 (3)	0.285 (1)	0.6635 (6)	0.067 (6)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Chart I



This is not an easy question to answer in this case with the limited data in hand. However, previous investigators reported the Pt–C bond distances listed in Chart I for the partial structures shown. Considering the diversity of these structures and comparing these data with that for **5**, 2.03 (1) Å, a single bond is indicated. One must also take into account that the position of the carbon is difficult to determine due to the size of the platinum atom.

A more reasonable argument against double-bond character between platinum and C(6) in **5** comes from the fact that N(2) is not in the square-planar plane. π-Bonding would occur with either the d_{xy} or d_{xz} orbitals which would require the N(2) atom to be either in the plane or at 90° to it. The fact that it is 21° out of the plane strongly suggests that there cannot be an effective overlap between the platinum d orbitals and C(6).

XPS Spectroscopy of Complex 5. In order to further characterize **5**, it was desirable to establish the platinum oxidation state. Thus an X-ray photoelectron spectroscopic analysis (XPS) was conducted. The results are listed in Table V along with those for some model compounds. Crystalline samples of **5** were mounted on pure Sn foil which enabled us to use the Sn($3d_{5/2}$) and C(1s) lines for correcting for surface charging effects. From these data, it is apparent that *Pt(IV)* complexes fall in the binding energy range of 76.1–75.9 eV, *Pt(II)* complexes occur in the range 74–72.4 eV, and *Pt(0)* exhibits a value of 71.6 eV when the Pt ($4f_{7/2}$) orbital energy level is compared.[15] Thus, for ylide **5**, the measured value of 72.8 eV places **5** in the lower part of the range for Pt(II) complexes which further suggests that there is no π-bonding to C(6).

Reaction of Diazoacetic Ester with Zeise's Dimer. From the literature and the results with complexes **5** and **6**, it is clear that Pt(II) prefers structure type C when R is an alkyl group or hydrogen. This also means that the overlap between the platinum orbital and the carbon p orbital is small resulting in little or no π-bonding. Further, since the electrons in this orbital system appear to be located on the platinum, the metal orbital must be much lower in energy than the carbon component. Thus, if the carbon orbital could be lowered and/or the Pt(II) orbital energy raised, it might be possible to achieve a platinum–carbon double bond. In this section, we will elaborate on the results of lowering the carbon orbital energy.

By placing electron-withdrawing groups on the carbenoid carbon, not only would the carbon orbital energy be reduced but also there would be an inductive force pulling on the platinum electrons. Thus, ethyl diazoacetate was reacted with Zeise's dimer at reduced temperature (eq 2).

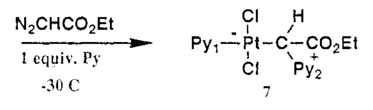


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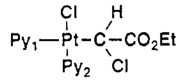
Table V. XPS Data on Representative Pt Complexes

complex	formal ox. state	E_b, eV			
		Pt($4f_{7/2}$)	C(1s)	N(1s)	Cl(2p)
$[(C_2H_5)_3P]_2PtCl_4$	4+	76.1	285.0[b]		199.4
K_2PtCl_6	4+	75.9			199.4
K_2PtCN_4	2+	74.0	285.0[b]	399.3	
$C_6H_{12}PtCl_2$	2+	74.0	285.0[b]		198.7
cis$[(C_2H_5)_3P]_2Pt(CN)_2$	2+	73.9	285.0[b]	398.5	
K_2PtCl_4	2+	73.4			199.4
cis-$[(C_2H_5)_3P]_2Pt(CH_3)$-Cl	2+	72.8	285.0[b]		198.2
$[(C_2H_5)_3P]_2PtHCl$	2+	72.8	285.0[b]		198.2
$Cl_2pyPtCH_2py$ (**5**)[a]	2+	72.8	285.8[b]	401.0	197.6
$[(C_2H_5)_3P]_2Pt(C_6H_5)_2$	2+	72.7	285.0[b]		
cis-$[(C_2H_5)_3P]_2Pt(CH_3)_2$	2+	72.4	285.0[b]		
$(Ph_3P)_3Pt$	0	71.6	285.0[b]		
$(Ph_3P)_4Pt$	0	71.6	285.0[b]		

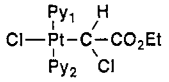
[a] This work (relative to Sn(0) at 486.4 eV). [b] All shifts were corrected for sample charging by normalization of C(1s) to 285.0, and all the data, save the last entry, are from ref 11.

As with complexes **5** and **6**, the NMR data of the product is consistent with structure **7**. Most notable is the fact that there are two different sets of pyridine resonances, one of which shows coupling between the ortho protons and ^{195}Pt. Further, the platinum and ylide carbon resonances are similar to those of complex **5**. The coupling constant of 796 Hz is clearly indicative of a σ-bond to platinum. Finally, the carbon, hydrogen, and chlorine elemental analyses were also correct.

When the solution containing **7** was warmed to room temperature or the original reaction was ran at room temperature, a mixture of complexes **8** and **9** was obtained



8



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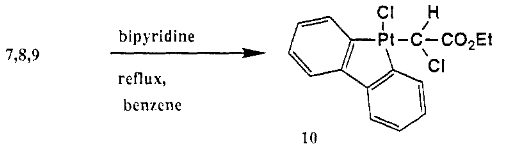
in a ratio of 3:1. NMR data for these two compounds is also listed in Tables I and II. There are several points to note in these data. First, the ^{195}Pt resonances for complexes **8** and **9** are similar to one another and significantly shifted by >100 ppm from that of complexes **5** and **7** (see bottom of table II). Second, in one isomer, the two sets of pyridine resonances are equivalent which is consistent with structure **9**. Finally, the ylide CH chemical shifts for all of the complexes vary over a narrow range, as one would expect with each of the ylide carbon resonances showing *doublet multiplicity* in the gated spectra except **5** which is a triplet.

To add evidence in support of structure **8**, it was reasoned that a bipyridyl analogue would perhaps show similar NMR spectral characteristics. Thus, bipyridine was added to a mixture of **7**, **8**, and **9** and refluxed. The ylide proton NMR resonance for these compounds was monitored by NMR spectroscopy and was observed to be replaced by a single peak at 6.58 ppm (Table I) as the reaction proceeded (eq 3). It is clear from Tables I and II



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(3)

that the ^1H and ^{195}Pt NMR data for **10** are very similar to complex **8**. However, the ylide carbon is shifted upfield significantly. While there does not appear to be a resonable explanation for this result, the authors believe the structures for **8** and **10** are reasonable on the basis of the

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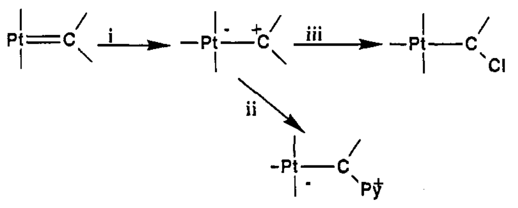
[15] Riggs, W. M. *Anal. Chem.* **1972**, *44*, 830.

other data. Incidentally, elemental analyses for **10** (C, H, Cl) were correct.

In summary, the diazoacetic ester substrate reacts very rapidly with Zeise's dimer to form the typical platinum ylide complex which readily isomerizes to the dipyridyl platinum chloromethyl derivatives **8** and **9**. These compounds are highly significant in that they are platinum derivatives of acetic esters. Exploratory work with regard to their use in carbon–carbon bond formation, the pK_a of the acid, and other electronic effects is underway.

Further, in the hypothetical Pt^{-}—C^{+} moiety, the cationic carbon has three alternatives to satisfy its electron demand: path i, ii, or iii. It is clear that the product of path i is



not viable even with an electronegative functionality such as the carbethoxy group. The kinetically stabilized products are apparently achieved by pyridine coordination, path ii, while the thermodynamic product resulting from equilibration at room temperature requires a chlorine transfer, path iii. All three of these complexes are neutral, but the last has less charge separation.

Summary. A new and facile method for the preparation of Pt(II) ylides has been elaborated. The key features involve the use of diazo derivatives and careful control of the pyridine concentration. Carbethoxy substitution on the carbenoid carbon will yield the analogous platinum ylide exclusively at low temperature, but, at room temperature in solution, it isomerizes to yield the chloromethyl analogues **8** and **9**. Finally, X-ray photoelectron spectroscopy and X-ray crystallography demonstrate that the parent methylidene ylide **5** is indeed a four-coordinate Pt(II) complex.

Experimental Section

General Data. NMR spectra were acquired on a Bruker WM250 MHz spectrometer with $CDCl_3$ as the solvent and shift reference in the ^{13}C and ^{1}H spectra. The ^{195}Pt spectra were standardized with $K_2Pt(CN)_4$ in D_2O at 25 °C as an external standard. K_2PtCl_6 was obtained from Strem Chemicals, and K_2PtCl_4 was obtained via the Johnson Matthey Inc. precious metals loan program. The diazo derivative precursors were obtained from Aldrich and used without purification. Finally, Zeise's dimer was prepared by the method of Littlecott.[16] All reactions were run in ambient air conditions, and all products reported were stable to air. Analyses were performed by Galbraith.

Preparation of Ylides 5 and 6. To an ether solution of 200 mg (0.68 eq) of Zeise's dimer was added 0.54 mL (0.68 mmol) of pyridine with stirring. A second ether solution of the diazo compound (CH_2N_2 or $CH_3CH_2N_2$) in threefold excess (2.04 mmol) was prepared by standard methods (generated from Diazald and *N*-ethyl-*N'*-nitro-*N*-nitrosoguanidine, respectively). To the latter solution, was added a second equivalent of pyridine. The two solutions were then mixed rapidly at room temperature with vigorous stirring. After gas evolution was complete (20 s), the ether was removed from the resulting yellow solids by rotoevaporation. SiO_2 chromatography with chloroform elution gave greater than 95% yield of the ylides. See Tables I and II for NMR spectra data.

Preparation of Ylide 7. To a chloroform solution of 200 mg (0.68 equiv) of Zeise's dimer was added 0.537 mL (0.68 mmol) pyridine with stirring. The yellow mixture was then cooled to −30 °C in a temperature-controlled NMR cavity. A second equivalent of pyridine and 0.11 mL (0.68 mmol) of ethyl diazoacetate were injected into the cooled solution and analyzed. The mixture was brought to room temperature over the course of 30 min. Pouring the yellow solution into triple its volume of rapidly stirred pentane resulted in isolation of ylide **7** in 76% yield. See text for NMR spectral data. Anal. Calcd for $C_{14}H_{16}O_2N_2Cl_2Pt$: C, 32.94; H, 3.14; Cl, 13.92. Found: C, 32.64; H, 3.27; Cl, 14.13.

Table VI. Summary of Crystallographic Data for 5 at 25 °C

mol formula: $C_{11}H_{12}N_2Cl_2Pt$
cryst system: orthorhombic
space group: $P2_12_12_1$ (D_2^4)
a = 5.361 (1) Å
b = 11.805 (2) Å
c = 20.595 (2) Å
V = 1303.4 Å^3
Z = 4
mol wt = 438.23
$F(000)$ = 816
p(calcd) = 2.23 g/cm^3

radiation: Mo Kα (λ = 0.710 69 Å)
reflctns measd: $\pm h,+k,+l$
20 range: 3–40°
scan type: ω
total reflctns measd: 1477
reflctns obsd ($I > 2\sigma(I)$): 1120[a]
abs coeff: 117 cm^{-1}
transmissn factor range: 0.326–0.375
R = 0.0244
R_w = 0.0250
goodness of fit: 1.15
no. of parameters: 146

[a] Crystal system and space group were uncertain at the time of data collection, so data were taken for negative and positive *h* indices. Since the data set was small, the extra data were retained for structure refinement. Thus, 39% of the observed data are redundant.

Preparation of Ylides 8 and 9. Ylides **8** and **9** are formed slowly (~6 h for 5% conversion) by room-temperature isomerization of ylide **7**. This process may be forced to completion by refluxing in benzene for 2 h. Ylides **8** and **9** were formed in a 3:1 ratio (based on NMR integration) and isolated by precipitation with pentane in an overall yield of 90%. See text for NMR spectral data. Anal. Cald for $C_{14}H_{16}O_2N_2Cl_2Pt$ (mixture **8** and **9**): C, 32.94; H, 3.14; Cl, 13.92. Found: C, 32.99; H, 3.24; Cl; 13.59.

Preparation of Complex 10. A benzene solution containing 200 mg (0.59 mmol) of a mixture of **7**, **8**, and **9** was prepared. To this solution was added 95 mg of 2,2'-bipyridine, and the mixture was refluxed for 4 h. Complex **10** was isolated in 74% yield by reducing the solvent volume to 2 mL and precipitation in 10 mL of rapidly stirred pentane. See text for NMR spectral data. Anal. Calcd for $C_{14}H_{14}O_2N_2Cl_2Pt$: C, 33.07; H, 2.76; Cl, 13.98. Found: C, 32.95; H, 2.99; Cl, 13.83.

X-ray Structure Determination of 5. A suitable crystal (0.6 × 0.1 × 0.1 mm) of **5** was grown from $CHCl_3$ by slow diffusion of heptane and mounted on a glass fiber. X-ray data collection was carried out on a Nicolet R3m/e automated four-circle diffractometer with graphite-monochromatized Mo Kα radiation. Three check reflections were measured every 100 scans which revealed a uniform crystal decomposition of 11% during data collection. Laue symmetry was *mmm*, orthorhombic symmetry, and the extinctions indicated space group $P2_12_12_1$ (D_2^4). Unit-cell parameters were obtained by least-squares refinement using 25 centered reflections for which 7° < 2θ < 36° (λ = 0.710 69 Å) by the method of Campana.[17] Crystal data and details of intensity data collection and structure refinement are given in Table VI.

Data reduction, including Lorentz and polarization corrections, and structure solution and refinement were done by using the SHELXTL program package.[16] A Patterson synthesis gave the platinum position, and positions of the remaining non-hydrogen atoms were located by $F_o - F_c$ difference maps. These positions were refined with anisotropic thermal parameters by block cascade least-squares minimizing $\sum w\Delta^2$, with $w = [\sigma^2(F_o) + 0.0003F_o^{\ 2}]^{-1}$. Atomic scattering factors, including anomalous scattering, were taken from Cromer and Waber.[18] Absorption corrections were calculated by Gaussian integration by using measured distances between indexed crystal faces. No corrections were made for extinction. Refinement of a parameter, *n*, multipyling $\Delta F''$ terms[19]

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(17) All crystallographic calculations were performed on a Data General Eclipse computer using the SHELXTL program package by G. M. Sheldrick, Nicolet Analytical Instruments Madison, WI, 1983.

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indicated absolute configuration to be that shown in Figure 1 (n = 1.04 (4)). Refinement of the inverted structure leads to significantly higher R values (R = 0.0389 vs. 0.0244 and R_w = 0.0406 vs. 0.0250), confirming the absolute configuration. Reasonable positions for all hydrogen atoms were located on difference maps, but calculated hydrogen positions were used in structure refinement. The largest peaks of the final difference map were 0.5 to 0.7 e Å^{-3} and were less than 1.5 Å from the platinum position.

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Registry No. **5**, 98772-92-0; **6**, 105280-91-9; **7**, 105280-92-0; **8**, 105280-93-1; **9**, 105369-27-5; **10**, 105280-94-2; CH_2N_2, 334-88-3; CH_3CHN_2, 1117-96-0; Zeise's dimer, 12073-36-8; ethyl diazoacetate, 623-73-4.

Supplementary Material Available: Listings of anisotropic thermal parameters, calculated hydrogen positions, and least-squares planes and atomic deviations therefrom (2 pages); a listing of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

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Structure of the Stable Silaethene $Me_2Si{=}C(SiMe_3)(SiMe\text{-}t\text{-}Bu_2)$[†]

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The structure of the stable, solid silaethene $Me_2Si{=}C(SiMe_3)(SiMe\text{-}t\text{-}Bu_2)$ (**4**) has been determined by X-ray crystallography (orthorhombic, $P2_12_12_1$, a = 8.109 (1) Å, b = 14.886 (2) Å, c = 16.470 (2) Å, V = 1988.10 Å^3, D_{calcd} = 1.005 g cm^{-3} for Z = 4 at -35 °C; R_w = 0.053, $w = 1/\sigma^2(F_o)$ for 163 refined parameters and 2447 observables with $I \geq 2.0\sigma(I)$). The double-bond geometry in **4** is essentially planar, with a twist about Si=C of only 1.6°. The silicon-carbon double-bond length (1.702 (5) Å) is substantially shorter than that in the previously reported sila enol ether $(Me_3Si)_2Si{=}C(OSiMe_3)$(1-adamantyl) (**3**) (1.764 (3) Å) but in excellent agreement with theoretical figures based on ab initio calculations. The difference must be attributed mainly to the different polarity of the double bonds in **3** and **4**, caused by the $-OSiMe_3$ substituent, and to the generally larger bulk of the substituents in **3**.

Introduction

The recent synthesis of stable compounds containing multiple bonds of the $p_\pi-p_\pi$ type to heavier main-group elements demonstrated that the kinetic stability of such compounds may be dramatically improved, provided sufficiently bulky substituents are used.[1,2] This is especially true for unsaturated phosphorus where a great variety of compounds could recently be synthesized for the first time and shown to be stable in condensed phase under ordinary conditions.[3]

Far less is known about multiple bonds involving silicon.[4] Their greater instability, as compared to phosphorus, has been attributed to the smaller gap between their π and π^* orbitals and, in the case of silicon-carbon double bonds, to their greater polarity.[5] Nevertheless, compounds with silicon-silicon,[4a,c,6] silicon-carbon,[4c,7] and silicon-nitrogen[8] double bonds could be successfully synthesized and structurally characterized.[9] The latter studies[6g-i,7b,c,e,8b] showed double bonds involving silicon to be closely related structurally to their carbon analogues. In particular, they were found to be significantly shorter than the respective single bonds, and three-coordinate silicon showed only small[6g,i] deviations from planarity, indicative of substantial p orbital overlap mandatory for "real" π bonds.[10]

In addition to laying the experimental ground for a description of the bonding, structure determinations may

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[†] Unsaturated Silicon Compounds. 18. Compounds of Silicon. 70. Parts 17 and 69: Wiberg, N.; Schurz, K.; Fischer, G. *Chem. Ber.* **1986**, *119*, 3498.

[‡] Universität München.

[§] Technische Universität München.

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