

**Reaction of Diazomethane with Platinum(II) Chloride
Complexes of Chelating Olefins. Crystal Structure Analyses of
a-Chloro-*b*-(chloromethyl)-*cd*-
(2,2,*N,N*-tetramethyl-3-buten-1-amine)platinum(II),
a-Chloro-*b*-(chloromethyl)-*dc*-(2,2,*N,N*-tetramethyl-3-buten-1-
amine)platinum(II), *a*-Chloro-*b*-(chloromethyl)-*dc*-
(2,2-dimethyl-3-buten-1-yl methyl sulfide)platinum(II), and
Dichloro[(2,2-dimethyl-4-penten-1-yl)methyl-
sulfonium methylide-*C,C,C*]platinum(II)**

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Reaction of dichloro(2,2,*N,N*-tetramethyl-3-buten-1-amine)platinum(II) (1), dichloro(2,2-dimethyl-3-buten-1-yl methyl sulfide)platinum(II) (2), or dichloro(2,2-dimethyl-2-silabut-3-enyl methyl sulfide)platinum(II) (4), with diazomethane leads to the carbene insertion products *a*-chloro-*b*-(chloromethyl)-*cd*-(2,2,*N,N*-tetramethyl-3-buten-1-amine)platinum(II) (8), *a*-chloro-*b*-(chloromethyl)-*dc*-(2,2-dimethyl-3-buten-1-yl methyl sulfide)platinum(II) (10), and *a*-chloro-*b*-(chloromethyl)-*dc*-(2,2-dimethyl-2-silabut-3-enyl methyl sulfide)platinum(II) (11), respectively. Similar treatment of dichloro(2,2-dimethyl-4-penten-1-yl methyl sulfide)platinum(II) (7) gives an unstable chloromethyl complex which decomposes to a sulfur ylide complex, dichloro[(2,2-dimethyl-4-penten-1-yl)methylsulfonium methylide]platinum(II) (13). In solution, 8 isomerizes at ambient temperature to *a*-chloro-*b*-(chloromethyl)-*dc*-(2,2,*N,N*-tetramethyl-3-buten-1-amine)platinum(II) (9). X-ray crystal structure analyses have been completed on 8, two forms of 9, 10, and 13. Crystals of 8, C₉H₁₉Cl₂NPt, are monoclinic, space group *P*₂₁/*c*, with *a* = 8.464 (2) Å, *b* = 9.563 (2) Å, *c* = 15.112 (3) Å, β = 94.68 (2)°, and *Z* = 4. Crystals of both forms of 9, C₉H₁₉Cl₂NPt, are monoclinic, space group *P*₂₁/*n*. Form 1 has *a* = 6.575 (2) Å, *b* = 12.141 (2) Å, *c* = 16.129 (3) Å, β = 101.10 (2)°, and *Z* = 4. Form 2 has *a* = 7.578 (1) Å, *b* = 15.950 (3) Å, *c* = 10.885 (2) Å, β = 107.26 (2)°, and *Z* = 4. Crystals of 10, C₈H₁₆Cl₂PtS, are monoclinic, space group *P*₂₁/*c*, with *a* = 6.775 (1) Å, *b* = 16.345 (2) Å, *c* = 11.469 (1) Å, β = 105.51 (1)°, and *Z* = 4. Crystals of 13, C₉H₁₈Cl₂PtS, are monoclinic, space group *P*₂₁/*c*, with *a* = 12.851 (2) Å, *b* = 12.950 (1) Å, *c* = 16.206 (2) Å, β = 108.14 (1)°, and *Z* = 8.

Introduction

We have carried out an extensive series of studies¹ on the reactions of palladium(II) complexes of chelating olefinic ligands including 2,2-dimethyl-3-buten-1-yl methyl sulfide and 2,2,*N,N*-tetramethyl-3-buten-1-amine. Our interest has centered particularly on reactions involving the olefin. The ligands used were chosen¹ because (i) ¹H NMR spectra of the original complexes, and of products derived from them, are readily interpretable and (ii) the structures of the ligands restrict the reaction pathways available. Both amine and sulfide ligands were examined to determine the influence of the nature of the accompanying ligand atom on the course of reaction. Indeed, contrary to what one might have anticipated, the nature of the products obtained changes on substituting amine for sulfide and/or six-membered chelate ring for five-membered ring.

Recently we reported^{1b} the results of the reaction of diazomethane with the PdCl₂ complexes of the two ligands mentioned above. We were interested in generating either the cyclopropane analogues (in the expectation that these might give characterizable, chelated complexes) or related complexes, for example, π-allyl or palladiocyclobutane species. Indeed in the case of the sulfide ligand, products

containing cyclopropyl^{1b} and π-allyl² moieties have been obtained. However, the major products from the complexes of both ligands derive from methylene insertion into a Pd-Cl bond. This type of insertion, although well-known for main-group halides, is rather rare for the transition-metal analogues.³ α-Haloalkyl complexes have attracted recent interest⁴ as potential sources of carbenes and as precursors to a wide range of functionalized alkyl derivatives of transition metals. We have now turned to an investigation of the reaction of diazomethane with the platinum(II) analogues for several reasons. First, products of insertion, if formed, were expected to be more stable than the corresponding palladium derivatives. Second, it was hoped that the lower kinetic reactivity of platinum(II) might provide information about steps in the insertion process. Third, any (halomethyl)platinum olefin products might serve as precursor to platinacyclobutanes.

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Table I. Analytical and Physical Data for the Complexes

complex	mp, °C	anal. found (calcd)		
		C	H	N
1	220 ^a	24.41 (24.44)	4.29 (4.36)	3.50 (3.56)
2	199–200	21.15 (21.22)	3.56 (3.56)	
4	151–153 ^a	17.42 (17.48)	3.55 (3.42)	
7	130–132	23.56 (23.42)	3.80 (3.93)	
8 ^b	158–160	26.67 (26.54)	4.68 (4.70)	3.38 (3.44)
9 ^b	154–155			
10 ^b	79–81	23.90 (23.42)	3.86 (3.93)	
13 ^b	158–165			

^aDecomposition. ^bX-ray structure determination done on single crystal.

Experimental Section

Melting points were determined on the Kofler block and are uncorrected. ¹H NMR and ¹³C NMR spectra were recorded on Bruker WH-400 (Southwestern Ontario NMR Centre) or AM-250 spectrometers for solutions in deuteriochloroform with tetramethylsilane as internal standard. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. TLC plates were spread with Kieselgel G (Merck) and run in dichloromethane/methanol (49:1 or 99:1). Diazomethane was prepared by reacting *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide with potassium hydroxide in aqueous 2-(2-ethoxyethoxy)ethanol and was distilled and then trapped in diethyl ether (at 0 °C). Table I contains physical and analytical data for the complexes while Tables II and III contain relevant ¹H NMR data and Table IV contains ¹³C NMR data.

Synthesis of the Dichloroplatinum(II) Complexes. Platinum dichloride was stirred with a slight excess of the appropriate free ligand in dichloromethane (30 mL) at room temperature. When the reaction was complete (no further dissolution of PtCl₂), the solution was filtered and the resulting product crystallized, in some cases after chromatography.

Dichloro(2,2, *N,N*-tetramethyl-3-buten-1-amine)platinum(II) (1). Platinum dichloride (399 mg, 1.50 mmol) and 2,2, *N,N*-tetramethyl-3-buten-1-amine⁵ were allowed to react for 7 days, and then the products were chromatographed to give 1 (200 mg, 34%). Crystallization from chloroform/hexane afforded pale yellow needles.

Dichloro(2,2-dimethyl-3-buten-1-yl methyl sulfide)platinum(II) (2). Platinum dichloride (532 mg, 2.00 mmol) and 2,2-dimethyl-3-buten-1-yl methyl sulfide (3)⁵ were stirred together for 4 days to give 2. Crystallization from dichloromethane/hexane afforded pale yellow rods (720 mg, 90%).

Dichloro(2,2-dimethyl-2-silabut-3-enyl methyl sulfide)platinum(II) (4). Platinum dichloride (441 mg, 1.66 mmol) and 2,2-dimethyl-2-silabut-3-enyl methyl sulfide (5)⁵ upon reaction for 3 days gave 4 (470 mg, 73%) as pale yellow prisms when crystallized from dichloromethane.

Dichloro(2,2-dimethyl-4-penten-1-yl methyl sulfide)platinum(II) (7). Platinum dichloride (381 mg, 1.43 mmol) and 2,2-dimethyl-4-penten-1-yl methyl sulfide (6)⁶ (225 mg, 1.56 mmol) were stirred together for 4 days to give 7 (434 mg, 74%) as rosettes of fine yellow needles when crystallized from acetone/hexane.

Reaction of the Dichloroplatinum(II) Complexes with Diazomethane. Unless otherwise stated, the dichloroplatinum(II) complexes were dissolved in dichloromethane (25 mL) and were treated at 0 °C under an atmosphere of air with aliquots of ethereal diazomethane until analytical TLC showed that all of the substrate had reacted.

Reaction of 1 with Diazomethane. (i) Reaction of 1 (80 mg, 0.203 mmol) gave essentially one less polar product (on TLC evidence). The resulting solution was evaporated, giving *a*-chloro-*b*-(chloromethyl)-*cd*-(2,2, *N,N*-tetramethyl-3-buten-1-amine)platinum(II) (8) as a residual oil (88 mg), which upon crystallization from dichloromethane/hexane yielded air-stable, near colorless needles (62 mg, 75%). (ii) When the above ex-

periment was repeated under an atmosphere of dinitrogen, only 8 was detected by TLC even after the addition of excess diazomethane. Preparative TLC of the reaction product gave 8 (91%). (iii) Upon dissolution in deuteriochloroform (0.5 mL), 8 (44 mg) slowly isomerized to *a*-chloro-*b*-(chloromethyl)-*dc*-(2,2, *N,N*-tetramethyl-3-buten-1-amine)platinum(II) (9). After 24 h at ambient temperature the extent of conversion (¹H NMR, TLC evidence) was substantial (>90%). Heating the solution at 53 °C for a further 24 h pushed the isomerization to near completion, leaving only trace amounts of 8 (<1%). Preparative TLC of this solution gave 9 (43 mg), which crystallized from dichloromethane/hexane as near colorless needles. (iv) When 9 was treated with excess diazomethane at ambient temperature, no reaction was detected by analytical TLC and the starting material was recovered in 95% yield.

Reaction of 2 with Diazomethane. (i) Preparative TLC of the product obtained from reaction of 2 (100 mg, 0.252 mmol) with diazomethane gave *a*-chloro-*b*-(chloromethyl)-*dc*-(2,2-dimethyl-3-buten-1-yl methyl sulfide)platinum(II) (10) (80 mg) as an oil. On standing in deuteriochloroform this material deposited a highly insoluble white solid (3 mg). The residual oil after rechromatography was induced to crystallize from chloroform/hexane, giving air-stable, near colorless rosettes of 10 (65 mg, 63%). This compound survived heating at 53 °C in deuteriochloroform for 48 h. (ii) When the above experiment was repeated by using excess diazomethane under an atmosphere of dinitrogen, only 10 was detected by TLC. This product (90%) was recovered as an oil by preparative TLC.

Reaction of 4 with Diazomethane. Preparative TLC of the product obtained from reaction of 4 (40 mg, 0.098 mmol) with diazomethane gave *a*-chloro-*b*-(chloromethyl)-*dc*-(2,2-dimethyl-2-silabut-3-enyl methyl sulfide)platinum(II) (11) as an oil (38 mg, 91%). Small amounts of a very insoluble pale yellow solid slowly precipitated when this oil was left to stand in deuteriochloroform. The oil obtained from the mother liquors could not be induced to crystallize even after rechromatography.

Reaction of 7 with Diazomethane. (i) Reaction of 7 with diazomethane was performed at -60 °C. As soon as all the substrates had reacted (TLC evidence), the solvent was removed and the oily residue was dissolved in deuteriochloroform. A ¹H NMR spectrum of this solution revealed the presence of two major products, *a*-chloro-*b*-(chloromethyl)-*dc*-(2,2-dimethyl-4-penten-1-yl methyl sulfide)platinum(II) (12) and dichloro(2,2-dimethyl-4-penten-1-yl)methylsulfonium methylide]platinum(II) (13). (ii) When the above experiment was repeated under an atmosphere of dinitrogen, TLC showed that mainly 12 and some 13 had formed. The solvent was removed and the residue dissolved in deuteriochloroform. Monitoring the composition of this solution by TLC and ¹H NMR revealed that during 3 days 12 was largely converted into 13. (iii) Experiment (i) was repeated at 0 °C, and, when the substrate had all reacted, TLC indicated that 12 was the major compound with small amounts of 13 present. This reaction mixture was submitted to preparative TLC, giving mainly 13 and some 12. The former crystallized from dichloromethane/hexane as pale yellow rods. Compound 12 could not be induced to crystallize and gradually converted into 13.

Crystal Structure Analyses. Crystal structure analyses were performed on 8, two forms of 9, 10, and 13. Crystal data, data collection parameters, and refinement results are summarized in Table V.

Intensities were measured⁷ on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromatized Mo K α radiation and the ω -2 θ method. The crystal of form I of 9 had been coated with epoxy adhesive, and as we could not index the "faces" unambiguously, we decided to collect another data set with a fresh crystal. This new crystal had a totally different cell from form I of 9 but proved to have the same molecular structure. Subsequent attempts to produce form I of 9 led only to the production of form II. The diffraction data were corrected⁸ for Lorentz, polarization, and, except for form I of 9, absorption effects.⁹

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Table II. ¹H NMR Data for the Olefinic Protons in the Complexes in CDCl₃

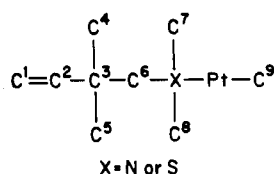
compd	δ			J ₁₋₂ , Hz	J ₁₋₃ , Hz	J ₂₋₃ , Hz
	H ₁	H ₂	H ₃			
1		4.75 ^a	4.00 ^b		12.2	
8	5.13 ^c	4.58 ^c	4.22 ^c	8.8	15.4	
9	4.21 ^b	3.84 ^b	3.44 ^b	7.2	13.3	
2 ^d		4.7-4.9 ^a	3.92		12.5	
2 ^e	4.85	4.46	3.79 ^a	8.0	13.8	
10 ^{d,f}	4.25	3.98 ^b	3.49 ^b	7.7	13.5	
10 ^{e,f}	4.25	3.70	3.34 ^b		13.5	
4 ^d	4.44	4.98 ^b	4.27 ^c	11.0	16.0	1.6
4 ^e	4.53	4.81	4.23	11.4	15.6	1.0
11	4.12 ^b	3.80 ^b	3.79	4.7	6.8	
7 ^d	5.35 ^b	4.79 ^b	4.32 ^c	8.4	14.2	
7 ^e	5.35 ^b	4.69 ^b	4.10 ^c	8.8	14.6	
12	5.1	3.96 ^b	3.89 ^b	8.0	13.7	
13	4.87	4.51	3.65	7.8	12.9	

^aOverlapping multiplet. ^bJ_{Pt-H} range 65-85 Hz. ^cJ_{Pt-H} range 40-65 Hz. ^dMajor isomer. ^eMinor isomer. ^fRun at 243 K.

Table III. ¹H NMR Data for the Nonolefinic Protons in the Complexes in CDCl₃

compd	δ(CMe)		δ(N(S)Me)		δ(N(S)CH ₂)		δ(PtCH ₂ X)		δ(CH ₂ CH=)	
1	1.73	1.22	3.07 ^a	2.96 ^a	2.92 ^b	2.42 ^{a,b}				
8	1.69	1.15		3.03 ^a	3.07 ^b	2.62 ^b	4.03 ^{c,d}	3.93 ^{c,d}		
9	1.60	1.16	2.63 ^e	2.82 ^e	2.70 ^{e,f}	2.43 ^{e,f}	3.77 ^{e,g}	3.71 ^{e,g}		
2 ^h	1.50	1.42		2.65 ^a	2.79 ⁱ	2.61 ⁱ				
2 ^j	1.77	1.41		2.81	2.97 ^k	2.43 ^{a,k}				
10 ^{h,l}	1.41	1.39		2.49 ^e	3.02 ^{e,m}	2.47	3.77 ^{c,n}	3.70 ⁿ		
10 ^{h,l}	1.64	1.36		2.68 ^e	2.78 ^{e,o}	2.47	3.73 ^{c,p}	3.68 ^p		
4 ^h	0.51	0.42		2.73 ^a	1.93 ^{a,b}	1.79				
4 ^j	0.70	0.41		2.78 ^a	2.17 ^r	1.51				
11	0.50	0.36		2.58 ^e		1.84 ^e	3.78 ^{c,p}	3.63 ^{c,p}		
7 ^h	1.46	1.23		2.55 ^a	2.87 ^t	2.80 ^t			2.19 ^u	2.06 ^u
7 ⁱ	1.24	1.21		2.71 ^a	2.81 ⁱ	2.61 ⁱ			2.57 ^v	2.24 ^v
12	1.31	1.20		2.50 ^e	2.73 ^w	2.84 ^w	3.69 ^{c,x}	3.59 ^{c,x}		2.1-2.4 ^y
13	1.40	1.19		3.09	3.25 ^a	2.62 ^z	4.47 ^d	2.94 ^d	1.77 ^{aa}	1.45 ^{aa}

^aJ_{Pt-H} range 40-65 Hz. ^bd (J = 13.3 Hz). ^cJ_{Pt-H} range 65-85 Hz. ^dd (J = 7.9 Hz). ^eJ_{Pt-H} range 10-35 Hz. ^fd (J = 13.8 Hz). ^gd (J = 7.2 Hz). ^hMajor isomer. ⁱd (J = 12.9 Hz). ^jMinor isomer. ^kd (J = 14.6 Hz). ^lRun at 243 K. ^md (J = 11.9 Hz). ⁿd (J = 7.3 Hz). ^od (J = 15.0 Hz). ^pd (J = 6.9 Hz). ^qd (J = 13.1 Hz). ^rd (J = 15.2 Hz). ^sbr q. ^td (J = 12.1 Hz). ^udd (J = 6.4 and 16.5 Hz). ^vdd (J = 3.9 and 18.3 Hz). ^wd (J = 12.4 Hz). ^xd (J = 6.7 Hz). ^yMultiplet. ^zd (11.4 Hz). ^{aa}dd (J = 16.7 Hz).

Table IV. Carbon-13 NMR Data for Complexes in CDCl₃ at Ambient Temperature

compd	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)
1 ^a	65.2	96.2	42.3	26.4	27.5	75.1	55.1	56.2	
8	82.4 ^b	115.1 ^c	40.6		27.5	77.4	56.6	54.7	36.4 ^d
9	59.6 ^e	92.7 ^f	41.4 ^g	27.2 ^h	28.0	70.6	51.5	52.7	19.1 ⁱ
3	111.2	146.8	38.3		26.2	48.4	18.0		
2 ^j	65.5 ^k	102.4 ^l	43.6	27.7 ^m	22.9 ^m	46.2	27.7 ^m		
10 ^j	60.7 ⁿ	97.0 ^o	42.4	27.5	26.9	43.3	20.3		31.4 ^p
10 ^q	57.4 ^r	96.8 ^o	45.5	28.3	27.7	41.2	21.0		s
5	132.7 ^t	137.5 ^u			-3.5 ^v	20.3 ^w	20.3 ^x		
11	71.0 ^c	y		-3.0	-1.9	23.0	15.7		30.8 ^z
11 ^{aa}	72.2 ^c	78.9 ^{bb}		-3.3	-2.3	22.7	14.8		cc
6	117.2	134.8	35.2		26.4	47.9 ^m	17.8		
7 ^j	70.1 ^{dd}	88.7 ^{ee}	36.2	31.4	29.7	51.0	20.0		45.5 ^m
7 ^{aa,q}	70.1	88.4	33	31.1	29.7	43.7	23.7		40.1
13	68.0 ^{ff}	78.2 ^{gg}	35.5	29.7 ^m	25.9 ^m	60.1	27.2 ^m		16.8 ^{hh}
									42.5

^aToo weak to see J_{Pt-C}. ^bJ_{Pt-C} = 58 Hz. ^cJ_{Pt-C} = 71 Hz. ^dJ_{Pt-C} = 930 Hz. ^eJ_{Pt-C} = 260 Hz. ^fJ_{Pt-C} = 252 Hz. ^gJ_{Pt-C} = 25 Hz. ^hJ_{Pt-C} = 47 Hz. ⁱJ_{Pt-C} = 778 Hz. ^jMajor isomer. ^kJ_{Pt-C} = 190 Hz. ^lJ_{Pt-C} = 195 Hz. ^mAssignment uncertain. ⁿJ_{Pt-C} = 237 Hz. ^oJ_{Pt-C} = 240 Hz. ^pJ_{Pt-C} not seen. ^qMinor isomer. ^rJ_{Pt-C} = 234 Hz. ^sNot seen. ^t(J_{C-H} = 151 Hz). ^ud (J_{C-H} = 135 Hz). ^vq (J_{C-H} = 120 Hz). ^wt (J_{C-H} = 130 Hz). ^xq (J_{C-H} = 138 Hz). ^yHidden under CDCl₃ resonances. ^zJ_{Pt-C} = 763 Hz. ^{aa}In acetone-d₆. ^{bb}J_{Pt-C} = 210 Hz. ^{cc}Hidden under acetone-d₆ resonances. ^{dd}J_{Pt-C} = 170 Hz. ^{ee}J_{Pt-C} = 175 Hz. ^{ff}J_{Pt-C} = 215 Hz. ^{gg}J_{Pt-C} = 203 Hz. ^{hh}J_{Pt-C} = 889 Hz.

All the structures were solved⁸ via the heavy-atom method and refined by full-matrix least-squares calculations with anisotropic thermal parameters for the non-hydrogen atoms except for molecule 13. Difference maps computed at intermediate stages

showed peaks consistent with most of the anticipated hydrogen atom sites, and in the final round of calculations allowance was made for hydrogen atoms, where appropriate, in geometrically idealized positions (C-H = 0.95 Å). For compound 13 there are

Table V. Crystal Data, Data Collection Parameters, and Refinement Results for the Complexes

	9				
	8	form I	form II	10	13
formula	C ₉ H ₁₉ Cl ₂ NPt	C ₉ H ₁₉ Cl ₂ NPt		C ₈ H ₁₆ Cl ₂ PtS	C ₉ H ₁₈ Cl ₂ PtS
fw	407.25	407.25		410.28	424.30
space group	P2 ₁ /c	P2 ₁ /n		P2 ₁ /c	P2 ₁ /c
a, Å	8.464 (2)	6.575 (2)	7.578 (1)	6.775 (1)	12.851 (2)
b, Å	9.563 (2)	12.141 (2)	15.950 (3)	16.345 (2)	12.950 (1)
c, Å	15.112 (3)	16.129 (3)	10.885 (2)	11.469 (1)	16.206 (2)
β, deg	94.68 (2)	101.10 (2)	107.26 (2)	105.51 (1)	108.14 (1)
V, Å ³	1219	1263	1256	1224	2563
Z	4	4	4	4	8
D _{calcd.} , g/cm ³	2.22	2.14	2.15	2.23	2.20
F(000)	768	768		768	1600
cryst dimens, mm	0.20 × 0.15 × 0.05	0.10 × 0.10 × 0.20	0.18 × 0.08 × 0.25	0.10 × 0.23 × 0.25	0.06 × 0.10 × 0.20
transmiss factors	0.5658–0.3211, 0.5044 (av)	0.4353–0.1973, 0.3571 (av)		0.5580–0.2767, 0.4710 (av)	0.5462–0.3251, 0.4480 (av)
μ(Mo Kα), cm ⁻¹	120.3	116.2	116.7	121.4	116.0
2θ _{max} , deg	54	54	54	54	40
unique reflctns	3001	2534	2491	2593	2386
I > 3σ(I)	1584	2251	1600	2004	1474
R	0.045	0.095	0.030	0.026	0.037
R _w	0.054	0.118	0.037	0.038	0.041

Table VI. Final Fractional Coordinates for Molecule 8 with Estimated Standard Deviations in Parentheses^a

atom	x	y	z	B, Å ²
Pt	0.01991 (7)	0.14817 (6)	0.35892 (4)	2.482 (8)
Cl1	-0.2252 (4)	0.0516 (5)	0.3210 (3)	3.80 (8)
Cl2	-0.1981 (9)	0.3051 (6)	0.4879 (4)	8.1 (2)
N	0.250 (1)	0.218 (1)	0.393 (1)	2.5 (2)
C1	0.348 (2)	0.198 (2)	0.317 (1)	3.2 (3)
C2	0.302 (2)	0.068 (2)	0.261 (1)	2.8 (3)
C3	0.127 (2)	0.069 (2)	0.236 (1)	3.4 (3)
C4	0.044 (2)	0.187 (2)	0.214 (1)	3.8 (4)
C5	0.387 (2)	0.079 (2)	0.176 (1)	4.2 (4)
C6	0.348 (2)	-0.071 (2)	0.305 (1)	3.9 (4)
C7	0.329 (2)	0.143 (2)	0.472 (1)	4.0 (3)
C8	0.250 (2)	0.371 (2)	0.415 (1)	3.7 (3)
C9	-0.052 (2)	0.184 (2)	0.484 (1)	3.4 (3)

^aAnisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \delta)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

Table VII. Final Fractional Coordinates for Molecule 9 (Form I) with Estimated Standard Deviations in Parentheses^a

atom	x	y	z	B, Å ²
Pt	0.11647 (9)	0.15312 (5)	0.07660 (3)	2.58 (1)
Cl1	0.4064 (7)	0.0531 (4)	0.1387 (4)	4.7 (1)
Cl2	0.250 (1)	0.2393 (6)	-0.0920 (4)	7.3 (2)
N	0.033 (2)	0.189 (1)	0.1980 (9)	3.1 (3)
C1	-0.127 (3)	0.275 (2)	0.185 (1)	4.0 (4)
C2	-0.129 (3)	0.350 (1)	0.109 (1)	3.5 (4)
C3	-0.103 (3)	0.279 (1)	0.033 (1)	3.4 (3)
C4	-0.198 (3)	0.181 (2)	0.016 (1)	4.3 (4)
C5	-0.347 (4)	0.402 (2)	0.088 (2)	6.9 (6)
C6	0.039 (4)	0.438 (2)	0.125 (1)	5.2 (5)
C7	0.228 (3)	0.241 (2)	0.257 (1)	5.0 (4)
C8	-0.024 (3)	0.094 (2)	0.239 (1)	5.3 (5)
C9	0.199 (3)	0.123 (2)	-0.036 (1)	4.0 (4)

^aAnisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \delta)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

two independent molecules in the asymmetric unit. All of the atoms refined normally with anisotropic thermal parameters except for the ethylenic carbon atoms C1B and C2B of molecule B, which always yielded nonpositive definite anisotropic thermal parameters. In the final rounds of calculations for 13, atoms C1B and C2B were constrained to isotropic motion. In refinement cycles a weighting scheme of the form $w = 1/[\sigma^2(F) + p(F)^2]$ was em-

Table VIII. Final Fractional Coordinates for Molecular 9 (Form II) with Estimated Standard Deviations in Parentheses

atom	x	y	z	B, Å ²
Pt	0.08372 (4)	0.21964 (2)	0.18136 (3)	3.609 (6)
Cl1	0.3167 (4)	0.1495 (2)	0.1272 (3)	7.34 (7)
Cl2	0.0762 (4)	0.0886 (2)	0.3998 (3)	6.58 (7)
N	0.1688 (8)	0.3399 (5)	0.1233 (6)	4.0 (2)
C1	0.0640 (10)	0.4065 (6)	0.1666 (7)	3.6 (2)
C2	0.0165 (10)	0.3859 (5)	0.2899 (7)	3.3 (2)
C3	-0.0605 (12)	0.2980 (6)	0.2785 (8)	4.1 (2)
C4	-0.1830 (11)	0.2677 (6)	0.1644 (9)	4.5 (2)
C5	-0.1320 (12)	0.4462 (7)	0.3015 (9)	5.1 (2)
C6	0.1825 (14)	0.3927 (7)	0.4102 (10)	5.6 (3)
C7	0.3693 (12)	0.3544 (8)	0.1761 (11)	6.5 (3)
C8	0.1195 (14)	0.3412 (9)	-0.0199 (9)	6.5 (3)
C9	0.0047 (16)	0.1079 (7)	0.2337 (10)	6.2 (3)

^aAnisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

Table IX. Final Fractional Coordinates for Molecule 10 with Estimated Standard Deviations in Parentheses

atom	x	y	z	B, Å ²
Pt	0.11452 (4)	0.21780 (1)	0.20628 (2)	3.033 (5)
Cl1	-0.1801 (3)	0.1394 (1)	0.1626 (2)	5.67 (5)
Cl2	0.2951 (4)	0.0783 (1)	0.4009 (2)	5.45 (5)
S	-0.0838 (3)	0.3392 (1)	0.1621 (2)	4.21 (4)
C1	0.121 (1)	0.4155 (4)	0.2014 (5)	3.8 (1)
C2	0.285 (1)	0.3842 (4)	0.3115 (6)	3.7 (1)
C3	0.357 (1)	0.2994 (4)	0.2900 (6)	3.7 (2)
C4	0.381 (1)	0.2751 (4)	0.1784 (7)	4.1 (2)
C5	0.468 (1)	0.4411 (5)	0.3319 (7)	5.3 (2)
C6	0.201 (1)	0.3836 (6)	0.4242 (7)	6.3 (2)
C7	0.165 (1)	0.6467 (7)	0.0017 (8)	6.7 (2)
C8	0.283 (1)	0.1144 (4)	0.2532 (7)	4.4 (2)

^aAnisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

ployed. Scattering factors were taken from ref 10, and allowance was made for anomalous scattering.¹¹ Final difference maps

(10) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2B.

(11) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* 1964, 17, 781; Cromer, D. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

Table X. Final Fractional Coordinates for Molecule 13 with Estimated Standard Deviations in Parentheses^a

atom	x	y	z	B, Å ²
PtA	0.57013 (7)	0.27721 (8)	0.18832 (5)	3.19 (2)
Cl1A	0.3880 (5)	0.3423 (6)	0.1550 (4)	4.8 (2)
C12A	0.5046 (6)	0.1126 (6)	0.1597 (5)	7.4 (2)
SA	0.7970 (5)	0.1867 (5)	0.3251 (4)	4.3 (2)
C1A	0.618 (2)	0.429 (2)	0.168 (1)	5.5 (7)
C2A	0.625 (2)	0.422 (2)	0.252 (1)	4.7 (6)
C3A	0.734 (2)	0.421 (2)	0.326 (1)	4.5 (6)
C4A	0.745 (2)	0.354 (2)	0.408 (1)	3.2 (6)
C5A	0.863 (2)	0.372 (2)	0.469 (1)	6.1 (7)
C6A	0.667 (2)	0.400 (2)	0.454 (2)	8.0 (9)
C7A	0.723 (2)	0.243 (2)	0.390 (1)	3.6 (6)
C8A	0.764 (2)	0.054 (2)	0.331 (2)	6.8 (9)
C9A	0.722 (2)	0.226 (2)	0.211 (1)	3.8 (6)
PtB	0.07023 (7)	0.06980 (7)	0.33186 (5)	2.58 (2)
Cl1B	0.1067 (5)	-0.0964 (4)	0.4014 (3)	4.2 (2)
Cl2B	-0.0130 (5)	-0.0072 (5)	0.1981 (3)	4.5 (2)
SB	0.1444 (5)	0.2650 (5)	0.2339 (3)	3.2 (1)
C1B	0.078 (2)	0.129 (2)	0.455 (1)	2.9 (5)*
C2B	0.189 (1)	0.138 (2)	0.446 (1)	2.4 (4)*
C3B	0.237 (2)	0.242 (2)	0.440 (1)	3.2 (6)
C4B	0.318 (2)	0.248 (2)	0.386 (1)	3.2 (6)
C5B	0.348 (2)	0.363 (2)	0.380 (1)	4.3 (6)
C6B	0.421 (2)	0.186 (2)	0.433 (1)	5.2 (7)
C7B	0.268 (2)	0.201 (2)	0.294 (1)	2.8 (5)
C8B	0.126 (2)	0.202 (2)	0.133 (1)	3.9 (6)
C9B	0.040 (1)	0.209 (2)	0.272 (1)	2.8 (5)

^a Atoms with an asterisk were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(\frac{1}{3})[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

Table XI. Interatomic Distances (Å) and Bond Angles (deg) for Molecule 8

(a) Bond Lengths (Å) ^a							
Pt	Cl1	2.301 (3)	N	C7	1.51 (2)		
Pt	N	2.086 (9)	N	C8	1.50 (2)		
Pt	C3	2.264 (13)	C1	C2	1.54 (2)		
Pt	C4	2.247 (15)	C2	C3	1.50 (2)		
Pt	C9	2.057 (13)	C2	C5	1.52 (2)		
Cl2	C9	1.702 (15)	C2	C6	1.52 (2)		
N	C1	1.49 (2)	C3	C4	1.35 (2)		
(b) Bond Angles (deg) ^a							
Cl1	Pt	N	175.1 (3)	C7	N	C8	108 (1)
Cl1	Pt	C3	94.2 (3)	N	C1	C2	114 (1)
Cl1	Pt	C4	88.6 (4)	N	C2	C3	110 (1)
Cl1	Pt	C9	88.1 (4)	C1	C2	C5	107 (1)
N	Pt	C3	83.3 (4)	C1	C2	C6	115 (1)
N	Pt	C4	91.8 (5)	C3	C2	C5	109 (1)
N	Pt	C9	93.5 (5)	C3	C2	C6	109 (1)
C3	Pt	C4	34.9 (5)	C5	C2	C6	108 (1)
C3	Pt	C9	167.4 (5)	Pt	C3	C2	104.6 (9)
C4	Pt	C9	157.6 (5)	Pt	C3	C4	71.9 (9)
Pt	N	C1	109.6 (7)	C2	C3	C4	123 (1)
Pt	N	C7	112.8 (8)	Pt	C4	C3	73.2 (8)
Pt	N	C8	110.4 (8)	Pt	C9	Cl2	114.6 (7)
C1	N	C7	108.4 (9)				
C1	N	C8	108.0 (9)				

^a Numbers in parentheses are estimated standard deviations in the least significant digits.

showed no significant chemical features, and final shift/error ratios¹² were all less than 0.01. Final fractional coordinates are given in Tables VI-X and molecular dimensions in Tables XI-XV. Lists of structure factors, thermal parameters, calculated hydrogen coordinates, torsional angles, and least-square planes have been deposited as supplementary material.

Results and Discussion

Structure and Stereochemistry of 1, 2, 4, and 7. The platinum(II) chloride complexes were prepared by stirring

Table XII. Interatomic Distances (Å) and Bond Angles (deg) for Molecule 9 (Form I)

(a) Bond Lengths (Å) ^a							
Pt	Cl1	2.318 (5)	N	C7	1.58 (3)		
Pt	N	2.18 (1)	N	C8	1.42 (3)		
Pt	C3	2.13 (2)	C1	C2	1.53 (3)		
Pt	C4	2.13 (2)	C2	C3	1.53 (3)		
Pt	C9	2.03 (2)	C2	C5	1.54 (3)		
Cl2	C9	1.75 (2)	C2	C6	1.52 (3)		
N	C1	1.47 (2)	C3	C4	1.35 (3)		
(b) Bond Angles (deg) ^a							
Cl1	Pt	N	92.5 (2)	C7	N	C8	107.4 (8)
Cl1	Pt	C3	165.4 (3)	N	C1	C2	115.7 (8)
Cl1	Pt	C4	157.4 (3)	C1	C2	C3	108.8 (7)
Cl1	Pt	C9	87.2 (3)	C1	C2	C5	106.0 (9)
N	Pt	C3	83.1 (3)	C1	C2	C6	112.7 (8)
N	Pt	C4	89.4 (3)	C3	C2	C5	107.4 (8)
N	Pt	C9	178.7 (3)	C3	C2	C6	110.3 (8)
C3	Pt	C4	37.0 (4)	C5	C2	C6	111.4 (9)
C3	Pt	C9	96.9 (4)	Pt	C3	C2	108.4 (5)
C4	Pt	C9	91.4 (4)	Pt	C3	C4	71.7 (5)
Pt	N	C1	108.1 (5)	C2	C3	C4	122.8 (9)
Pt	N	C7	107.9 (5)	Pt	C4	C3	71.3 (5)
Pt	N	C8	113.4 (8)	Pt	C9	Cl2	115.4 (6)
C1	N	C7	106.0 (8)				
C1	N	C8	113.8 (8)				

^a Numbers in parentheses are estimated standard deviations in the least significant digits.

Table XIII. Interatomic Distances (Å) and Bond Angles (deg) for Molecule 9 (Form II)

(a) Bond Lengths (Å) ^a							
Pt	Cl1	2.310 (3)	C2	C3	1.509 (12)		
Pt	N	2.176 (8)	C2	C5	1.514 (12)		
Pt	C3	2.136 (9)	C2	C6	1.527 (13)		
Pt	C4	2.118 (9)	C3	C4	1.398 (13)		
Pt	C9	2.016 (11)					
Cl2	C9	1.753 (11)					
N	C1	1.485 (11)					
N	C7	1.475 (12)					
N	C8	1.491 (12)					
C1	C2	1.525 (10)					
(b) Bond Angles (deg) ^a							
Cl1	Pt	N	92.2 (2)	C1	C2	C3	108.3 (7)
Cl1	Pt	C3	162.2 (3)	C1	C2	C5	108.2 (7)
Cl1	Pt	C4	159.2 (3)	C1	C2	C6	112.9 (7)
Cl1	Pt	C9	87.6 (4)	C3	C2	C5	108.6 (7)
N	Pt	C3	82.4 (3)	C3	C2	C6	109.6 (8)
N	Pt	C4	90.8 (3)	C5	C2	C6	109.1 (8)
N	Pt	C9	179.5 (4)	Pt	C3	C2	110.0 (6)
C3	Pt	C4	38.4 (4)	Pt	C3	C4	70.1 (5)
C3	Pt	C9	98.0 (4)	C2	C3	C4	122.3 (9)
C4	Pt	C9	89.3 (4)	Pt	C4	C3	71.5 (5)
Pt	N	C1	107.8 (5)	Pt	C9	Cl2	114.8 (6)
Pt	N	C7	112.7 (6)				
Pt	N	C8	108.2 (7)				
C1	N	C7	110.5 (8)				
C1	N	C8	109.3 (8)				
C7	N	C8	108.3 (8)				
N	C1	C2	114.4 (7)				

^a Numbers in parentheses are estimated standard deviations in the least significant digits.

PtCl₂ with a solution of the appropriate ligand, and they were purified by crystallization. The sulfur ligands complex more rapidly than the nitrogen one in accord with the suggestion¹³ that amines are rather poor entering groups for platinum(II) systems.

The NMR spectra of 1, 2, 4, and 7 (see Tables II-IV) clearly demonstrate that in all four, both the olefin and

Table XIV. Interatomic Distances (Å) and Bond Angles (deg) for Molecule 10

(a) Bond Lengths (Å) ^a							
Pt	Cl1	2.314 (2)	S	C7	1.827 (8)		
Pt	S	2.375 (2)	C1	C2	1.533 (9)		
Pt	C3	2.136 (6)	C2	C3	1.513 (9)		
Pt	C4	2.138 (7)	C2	C5	1.518 (10)		
Pt	C8	2.032 (7)	C2	C6	1.545 (10)		
Cl2	C8	1.778 (8)	C3	C4	1.394 (10)		
S	C1	1.830 (7)					
(b) Bond Angles (deg) ^a							
Cl1	Pt	S	90.54 (7)	S	C1	C2	108.1 (4)
Cl1	Pt	C3	163.8 (2)	C1	C2	C3	111.5 (5)
Cl1	Pt	C4	158.1 (2)	C1	C2	C5	107.8 (6)
Cl1	Pt	C8	89.4 (2)	C1	C2	C6	110.1 (6)
S	Pt	C3	84.2 (2)	C3	C2	C5	107.5 (6)
S	Pt	C4	93.2 (2)	C3	C2	C6	109.8 (6)
S	Pt	C8	177.0 (2)	C5	C2	C6	110.0 (6)
C3	Pt	C4	38.1 (3)	Pt	C3	C2	113.7 (5)
C3	Pt	C8	95.1 (3)	Pt	C3	C4	71.1 (4)
C4	Pt	C8	87.9 (3)	C2	C3	C4	122.4 (6)
Pt	S	C1	99.7 (2)	Pt	C4	C3	70.9 (4)
Pt	S	C7	108.9 (4)	Pt	C8	Cl2	114.0 (4)
C1	S	C7	99.6 (4)				

^aNumbers in parentheses are estimated standard deviations in the least significant digits.

the heteroatom are coordinated. Complex 7 is stable, unlike its palladium counterpart in which ready migration of the double bond occurs⁶ to give 14. As expected¹⁴ for platinum(II) complexes, the olefinic resonances suffer upfield shifts upon complexation while downfield shifts are usually observed⁵ upon complexation to palladium(II). The largest upfield shifts are observed for 4, the olefinic protons of which also suffer upfield shifts on complexation to palladium presumably because⁵ metal-to-olefin back-bonding is significantly more important for the vinylsilane than for its carbon analogue. The orientation of the olefinic moiety with respect to the coordination plane for these platinum complexes is probably very similar to that of their palladium analogues.⁵ This conclusion rests mainly on the observation that the signal arising from H² suffers the smallest upfield shift of the olefinic resonances on complexation (because of the proximity of this proton to the cis chloride). The spectra of the sulfur-containing complexes 2, 4, and 7 reveal the presence, in each, of two isomers, which differ in their configurations at sulfur.⁵ The magnitudes of the geminal coupling constants for the SCH₂ groups in the three major isomers suggest⁵ that their S-methyl group has the pseudoequatorial orientation. Integration allows an estimate of the isomer ratios as 2.7:1 for 2, 3.1:1 for 4, and 2.1:1 for 7. The corresponding values for the palladium analogues of 2 and 4 were measured as 3.5:1 and 3:1, respectively.

Synthesis and Structure of 8 and 9. When 1 was treated with diazomethane at 0 °C, only one product, 8, was detected by TLC and ¹H NMR spectroscopy. This compound was purified by crystallization and gave air-stable crystals which analyzed for C₉H₁₉Cl₂NPt. The product yield was not affected either by adding excess diazomethane or by performing the reaction under nitrogen rather than air. The gross structure of 8 was readily deduced from its ¹H NMR spectrum (see Tables II and III) which contains resonances attributable to the chelated olefinic ligand and to the chloromethyl group. Two of the olefinic resonances (H¹ and H³) shift downfield on going from 1 to 8. This is opposite to what was observed for the

Table XV. Interatomic Distances (Å) and Bond Angles (deg) for Molecule 13

(a) Bond Lengths (Å) ^a							
PtA	Cl1A	2.386 (6)	PtB	Cl1B	2.407 (5)		
PtA	Cl2A	2.286 (7)	PtB	Cl2B	2.323 (5)		
PtA	C1A	2.11 (3)	PtB	C1B	2.12 (2)		
PtA	C2A	2.15 (2)	PtB	C2B	2.18 (2)		
PtA	C9A	1.99 (2)	PtB	C9B	2.02 (2)		
SA	C7A	1.78 (2)	SB	C7B	1.79 (2)		
SA	C8A	1.78 (3)	SB	C8B	1.78 (2)		
SA	C9A	1.87 (2)	SB	C9B	1.80 (2)		
C1A	C2A	1.34 (3)	C1B	C2B	1.47 (3)		
C2A	C3A	1.54 (3)	C2B	C3B	1.50 (3)		
C3A	C4A	1.55 (3)	C3B	C4B	1.56 (3)		
C4A	C5A	1.55 (3)	C4B	C5B	1.55 (3)		
C4A	C6A	1.54 (3)	C4B	C6B	1.54 (3)		
C4A	C7A	1.49 (3)	C4B	C7B	1.55 (3)		
(b) Bond Angles (deg) ^a							
Cl1A	PtA	Cl2A	90.6 (3)	C3A	C4A	C5A	106 (2)
Cl1A	PtA	C1A	87.2 (7)	C3A	C4A	C6A	108 (2)
Cl1A	PtA	C2A	87.2 (7)	C3A	C4A	C7A	114 (2)
Cl1A	PtA	C9A	177.3 (6)	C5A	C4A	C6A	107 (2)
Cl2A	PtA	C1A	160.3 (6)	C5A	C4A	C7A	111 (2)
Cl2A	PtA	C2A	162.7 (7)	SA	C4A	C7A	111 (2)
Cl2A	PtA	C9A	90.4 (7)	SA	C7A	C4A	114 (2)
C1A	PtA	C2A	36.7 (7)	PtA	C9A	SA	117 (1)
C1A	PtA	C9A	91 (1)	Cl1B	PtB	Cl2B	91.1 (2)
C2A	PtA	C9A	93 (1)	Cl1B	PtB	C1B	86.3 (6)
C7A	SA	C8A	101 (1)	Cl1B	PtB	C2B	88.9 (6)
C7A	SA	C9A	105 (1)	Cl1B	PtB	C9B	179.4 (6)
C8A	SA	C9A	105 (1)	Cl2B	PtB	C1B	155.8 (6)
PtA	C1A	C2A	73 (2)	Cl2B	PtB	C2B	164.1 (5)
PtA	C2A	C1A	70 (2)	Cl2B	PtB	C9B	88.4 (6)
PtA	C2A	C3A	117 (2)	C1B	PtB	C2B	40.1 (7)
C1A	C2A	C3A	123 (2)	C1B	PtB	C9B	94.3 (8)
C2A	C3A	C4A	119 (2)	C2B	PtB	C9B	91.5 (8)
C7B	SB	C8B	97 (1)	C3B	C4B	C5B	108 (2)
C7B	SB	C9B	105 (1)	C3B	C4B	C6B	108 (2)
C8B	SB	C9B	104 (1)	C3B	C4B	C7B	112 (2)
PtB	C1B	C2B	72 (1)	C5B	C4B	C6B	110 (2)
PtB	C2B	C1B	68 (1)	C5B	C4B	C7B	111 (2)
PtB	C2B	C3B	120 (1)	C6B	C4B	C7B	108 (2)
C1B	C2B	C3B	121 (2)	SB	C7B	C4B	112 (2)
C2B	C3B	C4B	117 (2)	PtB	C9B	SB	118 (1)

^aNumbers in parentheses are estimated standard deviations in the least significant digits.

other reactions (2 → 10, 4 → 11, 15 → 16, and 17 → 18), and thus it was presumed that in 8 the two carbon ligands are mutually trans. After several recrystallizations, a single crystal was picked out for an X-ray crystallographic study which revealed to our surprise that the crystal studied had the carbon ligands cis. However, the ¹H and ¹³C NMR spectra of the remaining crystalline material disclosed that most of the initial complex had been converted into a new product, 9. The proton spectrum of the latter is very similar to that of 8, the only major difference being that the olefinic resonances have suffered appreciable upfield shifts, as would be expected for the cis isomer. The assignment of trans and cis configurations to 8 and 9, respectively, is also supported by comparison of the Pt-H and Pt-C couplings observed for these complexes (Tables II-IV), since couplings to atoms trans to the Pt-CH₂ group should be smaller than those to atoms trans to Pt-Cl because of the greater trans influence of the former.

Because the crystal of what proved to be 9 was coated with adhesive, we were unable to assign faces unambiguously. To allow a new data collection, we prepared a fresh sample by further crystallization. A single crystal was chosen and proved on subsequent analysis to have the trans configuration 8! However, analytical TLC of the remaining crystals revealed the presence of a large proportion of 9 but, significantly, small amounts of 8.

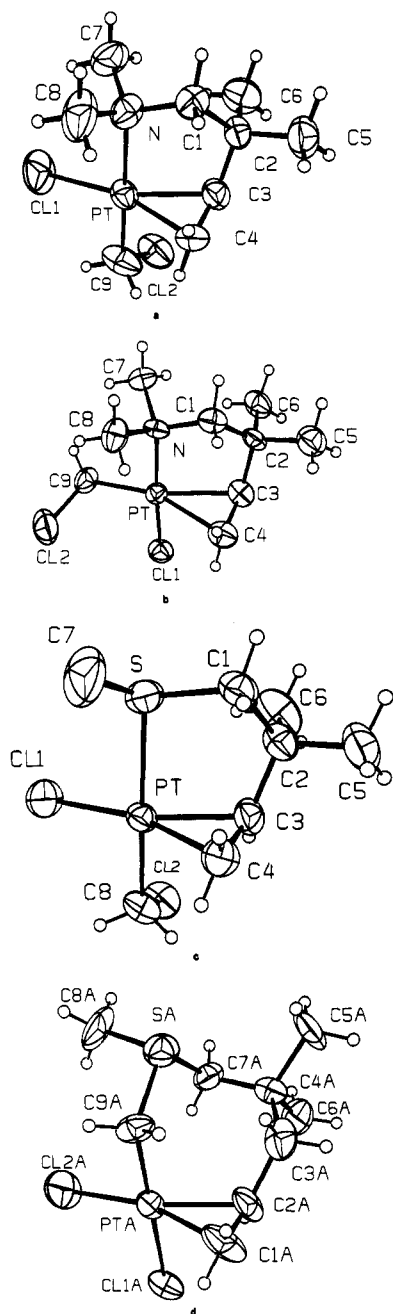


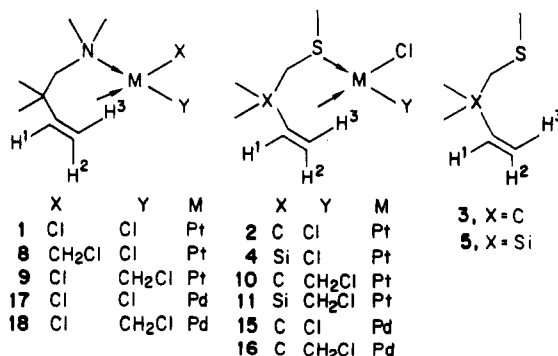
Figure 1. Views of the complexes: form II of 9 (a), 8 (b), 10 (c), and 13, molecule A (d). All diagrams present similar views of the Pt coordination and have ellipsoids at the 50% level.

Therefore, this mixture was kept in warm deuteriochloroform for 48 h, during which time complete isomerization to 9 was achieved (TLC and ^1H NMR evidence). This material was crystallized and a further single crystal chosen for X-ray crystallographic study. This crystal had cell data which conformed to neither 8 nor 9! However, subsequent X-ray analysis of this new material established that it did indeed have the same cis configuration as found for the first form of 9 (9, form I). The new form (9, form II) has essentially the same configuration and conformation as form I; they merely differ in crystal packing.

Views of molecules 9 (form II) and 8 are shown in parts 1a and 1b of Figure 1, respectively. In 8 and both forms of 9, the five-membered ring Pt,N,C(1),C(2),C(3) has a *C*(2) envelope conformation with the Pt,C(3),C(4) plane inclined at 101.4, 98.9, and 102.9° [for 8, 9 (I), and 9 (II), respectively] to the coordination plane Pt,N,Cl(1),C(9). Bond lengths in 8 and 9 are unexceptional; the mean Pt-olefin distances differ by 0.13 Å for 8 and 9, reflecting the trans

effect of CH_2Cl in 8 and Cl in 9.

Synthesis and Structure of 10. Treatment of 2, in dichloromethane at 0 °C, with 1 equiv (or excess) of diazomethane afforded 10 in almost quantitative yield, and no platinum(0) (or polymer) was formed. This contrasts with our results for the Pd analogue 15 which, when treated with diazomethane,³ deposited Pd(0) and gave a variety of products. Reacting 2 with diazomethane under dinitrogen rather than air had no effect¹⁵ on the yield of 10. This product formed air-stable crystals which gave analytical results consistent with the formulation $\text{C}_8\text{H}_{16}\text{Cl}_2\text{PtS}$. The gross structure was readily deduced from its ^1H and ^{13}C NMR spectra (see Tables II–IV). Both spectra show that the olefinic ligand has survived and is still coordinated to platinum via both the sulfur atom and the olefinic function. The ^{13}C NMR spectrum of 10 was determined at 0 °C since at ambient temperature the signals were broad due to sulfur inversion. At 0 °C, the two isomers of 10 are “frozen out”, and comparison of this spectrum with that of 2 reveals the presence, in the former, of two new resonances attributable to PtCH_2Cl (one for each isomer) and upfield shifts for the resonances of the olefinic C's. The ^1H NMR spectrum of 10 at ambient temperature again gave very broad signals due to sulfur inversion. Upon cooling to -30 °C, sharp resonances corresponding to two isomers were observed. In this spectrum, the chloromethyl group in each isomer gives rise to a well-resolved AB quartet. Platinum-hydrogen couplings are observed for the resonances arising from the CH_2SCH_3 moiety, the olefinic protons, and the chloromethyl group. Comparison of the magnitudes of these couplings, and of the Pt-olefinic C couplings with those observed for 8 and 9, indicates that in 10 the two carbon ligands are mutually cis. This cis configuration was first suggested by the shift positions of the resonances attributable to the olefinic protons, which are well upfield of those for 2. The magnitudes of these upfield shifts are comparable to those observed³ on going from 15 to 16, which is known to have a cis configuration. An X-ray crystallographic study firmly established that 10 has this configuration as shown in Figure 1c. The Pt-olefin interaction is symmetric with Pt-C(3) = 2.136 (6) Å and Pt-C(4) = 2.138 (7) Å. The five-membered ring Pt,S,C(1),C(2),C(3) has a *C*(2) envelope conformation. The plane containing the Pt and olefinic C atoms is inclined at 102.6° to the Pt,Cl(1),S,C(8) plane. Similar conformations have been found in the corresponding Pd-nitrogen analogue 16³ and related structures.¹⁶



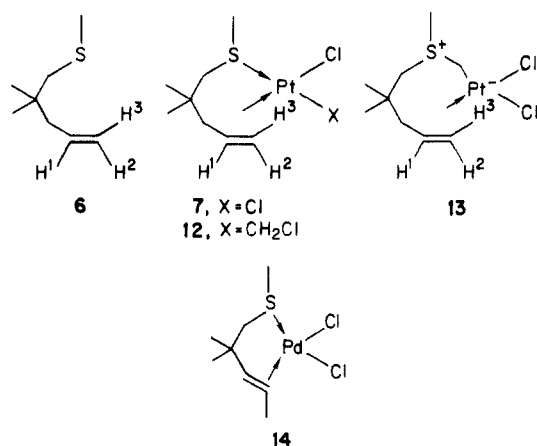
Synthesis and Structure of 11. When 4 was treated with diazomethane at 0 °C, only one product was detected by analytical TLC. This product, 11, was purified by preparative TLC but failed to crystallize. The structure

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is assigned on the basis of its ^1H and ^{13}C NMR spectra, which are very similar to those of 10, although lower temperatures are required to freeze out sulfur inversion in 11.

Synthesis and Structure of 13. When 7 was treated with diazomethane at -60°C , two products, 12 and 13, were detected by TLC and their gross structures were readily deduced from a ^1H NMR spectrum of the mixture (see Tables II and III). The former exhibits resonances attributable to the chelated, olefinic ligand and an AB quartet which arises from the chloromethyl group. The assignment of stereochemistry to 12 is based on the shift positions of the olefinic resonances: the magnitudes of the upfield shifts for these resonances on going from 7 to 12 are very similar to those observed for $2 \rightarrow 10$ and $15 \rightarrow 16$. The configuration assigned is also consistent with the magnitudes of the Pt-H couplings for the olefinic protons and the S-methyl group. Compound 12 was readily converted into 13, for example, by allowing it to remain in solution for several days or upon attempting to isolate it by preparative TLC. A comparison of the ^1H NMR spectra of 12 and 13 shows that for the latter the AB quartet of the chloromethyl group is absent. However, it is replaced by one which shows not only a marked enhancement in the magnetic nonequivalence of the two protons but also an increase in the magnitude of the geminal spin-spin coupling constant. Significantly, the SMe resonances suffers an appreciable shift downfield and the platinum-hydrogen coupling to this group is lost, as expected for the conversion of 12 into 13.



The structure assigned to 13 was confirmed by an X-ray structure analysis. The two independent molecules of 13 in the asymmetric unit of the crystal are separated by normal van der Waals distances, have square-planar coordination at the Pt atoms, and have similar boat-shaped ring conformations. One of the two independent molecules is shown in Figure 1d. The interplanar angles between the Pt,Cl(1),Cl(2),C(9) and Pt,C(1),C(2) planes are 91.1° and 94.1° for molecules A and B, respectively. The Pt-Cl distances show a pronounced trans effect with Pt-Cl(1) (trans to CH_2S) being on average 0.09 \AA longer than Pt-Cl(2) (trans to olefin).

Mechanism of the Insertion. As anticipated, in all four cases investigated, less complex mixtures were obtained than for their palladium analogues. Thus all four substrates gave clean insertion of a methylene unit into a platinum-chlorine bond. The observed rearrangement

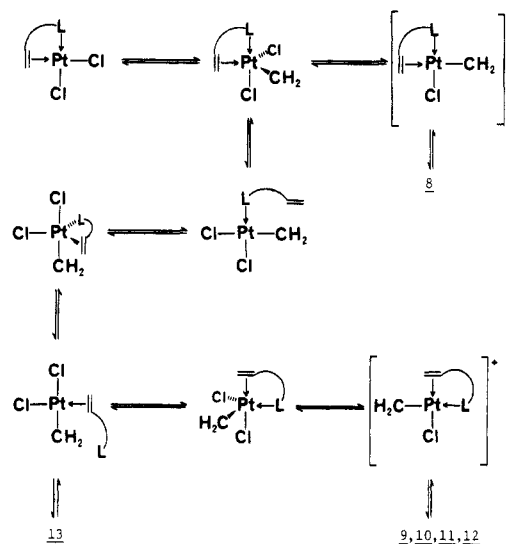


Figure 2. A proposed mechanism for the formation of compounds 8-13.

of 8 into 9 may provide an important clue as to the mechanism of the insertion process. Indeed, it may suggest that 9-12 represent thermodynamic rather than kinetic products. A possible mechanism is outlined in Figure 2. This involves a series of nucleophilic displacement processes which proceed via trigonal-bipyramidal intermediates.¹⁷ The first step is similar to that proposed^{5e} for the reaction of diazomethane with $\text{IrI}(\text{CO})(\text{PPh}_3)_2$: nitrogen could conceivably leave at a later stage. Insertion would be expected to take place preferentially into the Pt-Cl bond which is subject to the higher trans influence;¹⁸ i.e., 8 should be the kinetic product. This scheme would also rationalize the fact that we did not observe the sulfur ligand analogues of 8. Formation of five-coordinate intermediates should be less favorable with the more sterically demanding tertiary amine and a platinum-sulfur bond is expected¹⁹ to be more labile than a platinum-nitrogen bond. This mechanism also accommodates the conversion of 12 into 13. Transformation of a thioether complex into an ylide metal complex is a well-known²⁰ type of reaction, and indeed the reverse process has been reported²¹ for a platinum(II) derivative.

Registry No. 1, 101494-50-2; 2, 101494-51-3; 3, 20025-34-7; 4, 101494-52-4; 5, 101518-24-5; 6, 73411-26-4; 7, 101494-53-5; 8, 101494-54-6; 9, 101627-10-5; 10, 101494-55-7; 11, 101494-56-8; 12, 101494-57-9; 13, 101494-58-0; PtCl_2 , 10025-65-7; 2,2,*N,N*-tetramethyl-3-buten-1-amine, 20166-72-7; diazomethane, 334-88-3.

Supplementary Material Available: Lists of structure factors, thermal parameters, calculated hydrogen coordinates, torsion angles, and least-squares planes for 8, 9 (I), 9 (II), 10, and 13 (141 pages). Ordering information is given on any current masthead page.

(17) Anderson, G. K.; Cross, R. J. *Chem. Soc. Rev.* **1980**, 9, 185-215.

(18) See, for example: Langford, C. H.; Gray, H. B. *Ligand Substitution Processes*; W. A. Benjamin: New York, 1965; p 18. Huheey, J. E. "Inorganic Chemistry, Principles of Structure and Reactivity", 2nd ed.; Harper and Row: New York, 1978; p 490.

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