

Organoplatinum(II) and -(IV) and Organopalladium(II) and -(IV) Complexes of a Macrocyclic Thioether: X-ray Crystal Structure of Pt(C₆H₅)₂(9S3), an Example of Exodentate 1,4,7-Trithiacyclononane (9S3)

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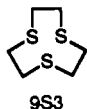
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Displacement of coordinated 1,5-cyclooctadiene or norbornadiene from suitable precursors has given a series of η^1 -C-bonded organoplatinum(II) complexes containing 1,4,7-trithiacyclononane (9S3), i.e. PtRR'(9S3) [R = R' = Me (1), Et (2), CH₂CMe₃ (3), CH₂SiMe₃ (4), Ph (5); R = Me, R' = CH₂SiMe₃ (6); R = Cl, R' = CH₂SiMe₃ (7)]. The dimethylpalladium(II) complex PdMe₂(9S3) (8) has been obtained similarly from PdMe₂(tetramethylethylenediamine), but Pd(CH₂SiMe₃)₂(9S3) (9) could not be isolated in a pure state. Crystals of 5 are orthorhombic, space group *Pbca*, with *a* = 12.047(1) Å, *b* = 17.660(2) Å, *c* = 16.854(2) Å, and *Z* = 8. The structure was solved by heavy-atom methods and refined by least squares analysis to *R* = 0.031 and *R_w* = 0.046 for 2498 unique observed reflections. The platinum atom is bound to two sulfur atoms of bidentate 9S3 and to two cis-phenyl groups in an almost planar array. The macrocyclic thioether adopts an exodentate conformation such that the uncoordinated sulfur atom points away from the metal atom, in contrast to the more usual endodentate conformation found in PdX₂(9S3) (X = Cl, Br). At room temperature, the 9S3 CH₂ resonances in the ¹H and ¹³C{¹H} NMR spectra of 1-7 are broad; variable-temperature NMR studies of 2 and 4 suggest that this is caused by exchange of free and coordinated sulfur atoms. Complexes 3 and 4 react with halogens to give diorganoplatinum(IV) salts [PtXR₂(9S3)]X [R = CH₂SiMe₃, X = I (10), Br (11); R = CH₂CMe₃, X = I (13)], and 1 and 2 oxidatively add methyl or ethyl iodide to give triorganoplatinum(IV) salts [PtR₂R'(9S3)]I [R = R' = Me (14); R = Et, R' = Me (15); R = R' = Et (16)]; in these products 9S3 is probably tridentate. The palladium(II) complex 8 likewise adds methyl iodide to give [PdMe₃(9S3)]I (17), which can be converted into a nitrate salt [PdMe₃(9S3)]NO₃ (18). These compounds show no tendency to reductively eliminate ethane, and they are the first isolable organopalladium(IV) complexes that do not contain a nitrogen donor, thus demonstrating the ability of endodentate 9S3 to stabilize octahedral or pseudooctahedral geometries.

Introduction

The versatile macrocyclic thioether 1,4,7-trithiacyclononane (abbreviated 9S3)² forms a range of transition metal complexes which are generally far more stable than those of acyclic monodentate or bidentate thioethers. X-ray structural analyses have shown that 9S3 usually acts as a facial tridentate or bidentate



ligand, and the stability of its complexes has been attributed to the fact that only a small change in the endodentate conformation of the free ligand is required for coordination.^{3,4} In the nickel triad, the halide complexes PdX₂(9S3) (X = Cl, Br) have a square planar geometry in which 9S3 is bidentate, but there is an additional weaker axial Pd-S interaction [*d*(Pd-S_{ax}) = 3.140(2), 3.125(1) Å for X = Cl,⁵ Br,⁶ respectively, cf. *d*(Pd-S_{eq}) = 2.25-2.27 Å]. The cations [M(9S3)₂]²⁺ (M = Pd, Pt) also possess a basic square planar structure, but they differ in their axial

interactions. For M = Pd, both 9S3 ligands adopt the usual endodentate conformation leading to two weak axial interactions [*d*(Pd-S_{eq}) = 2.32-2.33 Å, *d*(Pd-S_{ax}) = 2.96-3.00 Å]; i.e., the coordination geometry is a tetragonally distorted octahedron.^{6,7} In contrast, for M = Pt, there is one axial interaction from an endodentate 9S3 ligand [*d*(Pt-S_{eq}) = 2.25-2.30 Å; *d*(Pt-S_{ax}) = 2.88-2.93 Å] and the second 9S3 ligand adopts an unusual conformation in which the remaining sulfur atom points away from the metal atom [*d*(Pt-S) = 4.04 Å]; the coordination geometry is, therefore, square-based pyramidal.⁸ These cations can be reversibly oxidized to trivalent metal species [M(9S3)₂]³⁺.^{8,9} Although the platinum(IV) cation [Pt(9S3)₂]⁴⁺ has been mentioned briefly,^{4,10} the only well-characterized metal(IV)-9S3 complex in the nickel triad is the pseudooctahedral species [PtMe₃(9S3)]Cl·2H₂O, obtained by reaction of the ligand with [PtClMe₃]₄.¹¹

Planar dialkyls and diaryls of platinum(II), PtR₂L₂, are well-known to add halogens (X₂) and alkyl halides (R'X) to give octahedral organoplatinum(IV) complexes PtX₂R₂L₂ and PtX-R'R₂L₂, respectively,¹² and more recently, organopalladium(IV)

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- (2) Other abbreviations: cod = 1,5-cyclooctadiene; nbd = norbornadiene; tmeda = *N,N,N',N'*-tetramethylethylenediamine; (pz)₃CH = tris(1-pyrazolyl)methane.
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Table I. Analytical Data for 9S3 Complexes^a

complex	% C	% H	% Hal	% S
PtMe ₂ (9S3) (1) ^b	23.7(23.9)	4.5(4.3)		23.7(22.4)
PtEt ₂ (9S3) (2)	27.7(27.6)	5.1(4.9)		
Pt(CH ₂ SiMe ₃) ₂ (9S3) (4) ^c	30.6(30.5)	6.2(6.2)		17.5(17.1)
PtPh ₂ (9S3) (5)	40.8(41.0)	4.2(4.1)		18.2(18.6)
PtMe(CH ₂ SiMe ₃)(9S3) (6)	27.7(26.7)	5.5(5.1)		
PtCl(CH ₂ SiMe ₃)(9S3) (7) ^d	24.1(24.5)	4.6(4.5)	7.1(7.3)	
PdMe ₂ (9S3) (8)	30.8(29.8)	5.7(5.9)		30.4(30.4)
[PtI(CH ₂ SiMe ₃) ₂ (9S3)]I (10) ^e	20.9(20.0)	4.3(3.8)	31.6(31.4)	12.0(12.0)
[PtI(CH ₂ SiMe ₃) ₂ (9S3)]CF ₃ SO ₃ (12)	21.8(22.2)	4.2(4.3)		
[PtMe ₃ (9S3)]I (14)	19.8(18.9)	3.9(3.4)		17.6(15.8)
[PtMeEt ₂ (9S3)]I (15) ^f	23.0(23.1)	4.4(4.4)	22.1(22.7)	
[PtEt ₃ (9S3)]I (16)	24.4(23.2)	4.6(4.5)	21.5(21.7)	
[PdMe ₃ (9S3)]I (17)	23.6(23.3)	4.6(4.3)	27.7(27.7)	21.0(20.6)
[PdMe ₃ (9S3)]NO ₃ (18) ^g	27.5(26.8)	5.4(4.7)		

^a Found values in parentheses. ^b % Pt: calcd, 48.1; found, 48.1. ^c % Pt: calcd, 35.5; found, 35.7. ^d % Pt: calcd, 39.2; found, 39.2. ^e % Pt: calcd, 24.3; found, 24.0. ^f % Pt: calcd, 33.9; found, 33.1. ^g % N: calcd, 3.6; found, 3.8.

complexes have been isolated from similar reactions.¹³ The most stable representatives of the latter class are those containing tripodal, facially coordinating N-donor ligands.¹⁴ The aim of the work described here was to prepare σ -carbon bonded complexes of platinum(II) and palladium(II) containing 9S3, to establish the mode of binding of the S-donor, and to see if the metal atom in these compounds could be oxidized to the +4 oxidation state.

Experimental Section

All reactions were carried out in a nitrogen atmosphere with use of standard Schlenk techniques and freshly distilled, dry solvents. After preparation, the complexes, which were usually air-stable, were dried in high vacuum to remove traces of solvents. NMR spectra were measured on Varian XL200 (¹H at 200.01 MHz; ¹³C at 50.29 MHz; ¹⁹⁵Pt at 42.94 MHz) and Varian Gemini 300 (¹H at 300.10 MHz; ¹³C at 75.46 MHz) spectrometers and are reported in ppm to high frequency of Me₄Si (¹H, ¹³C) or (external) aqueous Na₂PtCl₆ (¹⁹⁵Pt). Infrared spectra were measured as KBr disks on Perkin Elmer 683 and 1800 spectrometers, conductivities at 20 °C on a WTW LF 550 meter with dip-type platinum electrodes, and mass spectra (EI) on a VG Micromass 7070 F instrument. Analyses were done in-house. Analytical, NMR (¹H, ¹³C), molar conductivity, and selected IR spectroscopic data are collected in Tables I–IV, respectively.

The agreement between found and calculated carbon (and in some cases hydrogen) analyses for complexes **6**, **8**, **10**, **14**, **16**, and **18** is beyond the normal limits of acceptability. The reasons are unknown, and attempts at purification by recrystallization in most cases were unsuccessful. Where possible, analyses for halogen, sulfur, or platinum have also been carried out, and these are usually in fair agreement with the calculated values.

Starting Materials. The reagents 1,4,7-trithiacyclononane (9S3),¹⁵ PtR₂(cod) (R = Me,^{16,17} Ph,¹⁶ CH₂CMe₃,^{16,18} CH₂SiMe₃¹⁶) and PdMe₂(tmeda)¹⁹ were prepared by the appropriate literature methods. The complex Pt(CH₂SiMe₃)₂(nbd) was made in 98% yield by the action of Me₃SiCH₂MgCl on PtCl₂(nbd), and was converted into PtCl(CH₂SiMe₃)(nbd) (73% yield) by reaction with HCl (1 equiv) generated from acetyl chloride and methanol. Similar treatment of Pt(CH₂CMe₃)₂(cod) gave PtCl(CH₂CMe₃)(cod). Addition of CH₃Li to PtCl(CH₂SiMe₃)(nbd) following the procedures of refs 16 and 18 gave PtMe(CH₂SiMe₃)(nbd).

Bis(trimethylsilyl)methyl(*N,N,N',N'*-tetramethylethylenediamine)palladium(II), Pd(CH₂SiMe₃)₂(tmeda). To a stirred suspension of PdCl₂(tmeda) (294 mg, 1.00 mmol) in ether (20 mL) at –30 °C was added dropwise Me₃SiCH₂MgCl (0.81 M solution in ether, 13 mL, 10.5

mmol). The mixture was stirred at 0 °C for 1 h, allowed to come to room temperature, and stirred for a further 3 h. The black solution was treated with aqueous NH₄Cl, and the aqueous phase was washed with ether (2 × 20 mL). The combined ether extracts were dried (MgSO₄) and evaporated to dryness to give a yellow oil which was kept in a vacuum, first at –40 °C for 4 h and then at –30 °C for 12 h, to remove as much residual ether as possible. The oil decomposed at room temperature within ca. 5 min, but solutions in donor solvents, such as MeCN, THF, and acetone, survived for ca. 30 min. ¹H NMR (CD₃CN): δ 3.28 (s, 12H, NMe₂), 2.15 (s, 4H, CH₂N), 0.07 (s, 18H, SiMe₃), 0.03 (s, 4H, CH₂Si). ¹³C{¹H}NMR(CD₃CN): δ 55.3 (s, CH₂N), 27.3 (s, NMe₂), –1.36 (SiMe₃), –3.39 (CH₂Si).

Preparations. Dimethyl(1,4,7-trithiacyclononane)platinum(II), PtMe₂(9S3) (1). A solution containing PtMe₂(cod) (335 mg, 1.00 mmol) and 9S3 (180 mg, 1.00 mmol) in acetonitrile (7 mL) was heated under reflux for 2 h. A small amount of brown solid was removed by centrifugation, and the yellow solution was evaporated to dryness. The resulting yellow solid was washed with ether (3 × 5 mL) and dried in a vacuum. The yield was 230 mg (57%). The compound melts at 120 °C with decomposition and is readily soluble in CH₂Cl₂, CHCl₃, and warm acetonitrile. MS: 405, [M]⁺ (40.5%); 180, [9S3]⁺ (17.4%); 120, [(CH₂CH₂S)₂]⁺ (100%).

Diethyl(1,4,7-trithiacyclononane)platinum(II), PtEt₂(9S3) (2). A solution containing PtEt₂(cod) (196 mg, 0.542 mmol) and 9S3 (96 mg, 0.532 mmol) in acetonitrile (6 mL) was heated to 50 °C. The solution turned orange after 15 min, and a yellow-orange solid began to precipitate after 45 min. It is important not to heat the reaction mixture for more than ca. 45 min, otherwise the only product is the insoluble yellow-orange solid whose constitution is unknown. The supernatant yellow solution was separated by centrifugation and evaporated to dryness in a vacuum. The resulting yellow powder was washed with hexane (3 × 5 mL) and dried in a vacuum to give 160 mg (69%) of product. The compound is moderately soluble in hexane and freely soluble in most other organic solvents.

Dineopentyl(1,4,7-trithiacyclononane)platinum(II), Pt(CH₂CMe₃)₂(9S3) (3). This was prepared similarly to **1** from Pt(CH₂CMe₃)₂(cod) (1.08 g, 2.42 mmol) and 9S3 (0.43 g, 2.42 mmol) in acetonitrile (20 mL). The red-brown oil obtained after removal of solvent was treated with ether until a yellow solid formed; this was then washed with hexane. The yield of **3** was 600 mg (48%). Analytical data were low in C and H, but the compound was identified by its NMR spectra (Table II).

Bis(trimethylsilyl)methyl(1,4,7-trithiacyclononane)platinum(II), Pt(CH₂SiMe₃)₂(9S3) (4). A suspension of Pt(CH₂SiMe₃)₂(cod) (955 mg, 2.00 mmol) and 9S3 (403 mg, 2.23 mmol) in acetonitrile (20 mL) was heated under reflux for 4 h to give a yellow solution. Evaporation to dryness at 80 °C gave a yellow solid from which the excess of 9S3 was removed by vacuum sublimation at 100 °C (10^{–4} mmHg) for 16 h. The residue was dissolved in benzene (10 mL), and after centrifugation to remove a small amount of brown solid, the solution was evaporated to give a yellow or pale-orange solid. After the solid was dried in a vacuum at room temperature for 16 h, the yield of **4** was 86 mg (78%). MS: 549, [M]⁺ (4.3%); 534, [M – CH₃]⁺ (3.8%); 462, [M – CH₂SiMe₃]⁺ (1.5%); 180, [9S3]⁺ (6.4%); 73, [SiMe₃]⁺ (100%). δ (¹⁹⁵Pt): –4246 (C₆D₆), –4239 (CD₃CN).

Diphenyl(1,4,7-trithiacyclononane)platinum(II), PtPh₂(9S3) (5). A suspension of PtPh₂(cod) (250 mg, 0.546 mmol) and 9S3 (100 mg, 0.554

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Table II. NMR (¹H, ¹³C) Spectra of Organoplatinum and Organopalladium Complexes Containing 9S3^{a,b}

complex	¹ H		¹³ C{ ¹ H}	
	9S3	M-R	9S3	M-R
1	4.0–2.5 (v br)	0.58 (s, 86.0)	39.0 (s)	–11.1 (751.3)
2	4.0–2.5 (v br)	1.48 (q, CH ₂), 1.33 (t, CH ₃) ³ J _{HH} = 7, ³ J _{PH} = 42.4	38.9 (s)	19.2 (CH ₂ CH ₃ , 7.4), 7.0 (CH ₂ CH ₃ , 823)
3 ^c	3.7–2.6 (v br)	1.80 (s, CH ₂ , 91.8), 1.02 (s, Me)	37.7 (br s)	36.3 (CMe ₃), 35.0 (Me, 53.1), 32.3 (CH ₂ , 870)
4 ^d	3.7–1.5 (4 br m)	1.03 (s, CH ₂ , 97.8), 0.42 (s, Me)	40–38 (v br), 38–36 (v br)	3.6 (Me, ³ J _{PH} = 33.0, ¹ J _{SiC} = 47.5), –1.5 (CH ₂ , ¹ J _{PH} = 697.5, ¹ J _{SiC} = 53.7)
5 ^e	3.5–3.0 (br m)	7.5–7.1 (m, H ^{3,5}), 6.9–6.6 (m, H ^{2,4,6}) (Ph)	37.4 (s)	137.5 (C ^{3,5} , 36.3), 126.7 (C ^{2,6} , 76.6), 121.4 (C ⁴ , 12.2)
6	4.0–2.5 (v br)	0.60 (s, PtMe, 84.7), –0.03 (s, SiMe ₃)	41–37 (br)	2.7 (SiMe ₃ , 33.3), –1.5 (CH ₂ , 705), –10.6 (PtMe, 751)
7 ^f	3.6–3.0 (v br)	0.73 (s, CH ₂ , 76.2), 0.02 (s, Me)	nm	nm
8	3.38–3.14 (m)	0.32 (s, Me)	39.1	–5.9 (Me)
9 ^g	3.3–2.8 (br m)	0.06 (s, SiMe ₃), 0.00 (s, CH ₂)	nm	nm
10 ^h	4.15–3.95 (br m), 3.95–3.75 (br m), 3.75–3.55 (br m), 3.25–3.05 (br m)	1.70 (d, CHH), 1.46 (d, CHH) (² J _{HH} = 12.8, ² J _{PH} = 74.2), 0.15 (s, Me)	43.2, 38.1, 37.3	4.7 (CH ₂ , 485), 2.6 (Me, ³ PtC = 10.7, ¹ J _{SiC} = 50.5)
11 ⁱ	4.3–3.1 (v br)	1.7–1.2 (br, CH ₂), 0.18 (s, Me)	44.6, 37.5, 35.8	8.4 (CH ₂ , 489.3), 2.9 (Me, 10.4)
12 ^j	3.65 (s, 13.2), 3.5 (br m), 3.15 (br m)	1.77 (d, CHH), 1.50 (d, CHH) (² J _{HH} = 12.8, ² J _{PH} = 74.4), 0.17 (s, Me)	42.2, 37.5, 36.8	4.63 (CH ₂ , 491), 2.35 (Me)
13	4.2–3.9 (br m), 3.9–3.6 (br m), 3.5–3.2 (br m)	2.66 (s, CH ₂ , 76.7), 1.14 (s, Me)	44.6 (10.0), 39.1 (9.7), 37.4 (7.8)	40.2 (CH ₂ , 496.4), 37.6 (CMe ₃), 32.6 (Me, 21.1)
14	3.98 (m, CHH), 3.12 (m, CHH)	0.94 (s, Me, 67.5)	36.2	–2.4
15	3.95 (m, CHH), 3.13 (m, CHH)	1.81 (m, CHH), 1.76 (m, CHH), 1.28 (t, CH ₂ CH ₃ , ³ J _{HH} = 7.6, ³ J _{PH} = 56.7), 0.85 (s, PtMe, 68.4)	36.0 (4.5), 35.9 (6.8), 34.7 (4.4)	19.1 (CH ₂ CH ₃ , 31.8), 16.0 (CH ₂ CH ₃ , 607.2), –0.3 (PtMe, 647.1)
16	3.96 (m, CHH), 3.15 (m, CHH)	1.79 (q, CH ₂ , ³ J _{HH} = 7.7, ² J _{PH} = 70.7), 1.30 (t, Me, ³ J _{HH} = 7.7, ² J _{PH} = 56.5)	nm	nm
17	3.99 (m, CHH), 3.12 (m, CHH)	1.51 (s, Me)	35.3	16.6 (Me)
18	3.70 (m, CHH), 3.10 (m, CHH)	1.47 (s, Me)	34.5	16.5 (Me)

^a Measured in CDCl₃, except where stated otherwise. ^b Coupling constants (Hz) in parentheses are J_{PH}, except where stated otherwise; quoted multiplicities do not include ¹⁹⁵Pt satellites. ^c ¹³C NMR in C₆D₆. ^d ¹H, ¹³C NMR in C₆D₆. ^e ¹H, ¹³C NMR in DMSO-*d*₆. ^f In CD₃CN. ^g In CD₂Cl₂. ^h ¹H NMR (acetone-*d*₆): δ 4.0 (m), 3.80 (m), 3.50 (m) (9S3), 1.76 (d, CHH), 1.50 (d, CHH) (²J_{HH} = 12.8, ²J_{PH} = 74.4), 0.17 (s, Me). ⁱ ¹H NMR in CD₂Cl₂; ¹³C NMR in C₆D₆. ^j ¹H, ¹³C NMR in CD₂Cl₂.

Table III. Molar Conductivities Λ_M (S cm² mol^{–1}) of Organoplatinum(IV) and Organopalladium(IV) Complexes (10^{–3} M) in Nitromethane at 20 °C^a

complex	Λ _M
[Pt](CH ₂ SiMe ₃) ₂ (9S3)]I (10)	66 ^b
[PtBr](CH ₂ SiMe ₃) ₂ (9S3)]Br (11)	79
[Pt](CH ₂ SiMe ₃) ₂ (9S3)]CF ₃ SO ₃ (12)	94
[Pt](CH ₂ CMe ₃) ₂ (9S3)]I (13)	72
[PtMe ₃ (9S3)]I (14)	101
[PdMe ₃ (9S3)]I (17)	97
[PdMe ₃ (9S3)]NO ₃ (18)	115

^a Quoted ranges for 1:1 electrolytes: 75–95 S cm² mol^{–1} (MeNO₂); 100–140 S cm² mol^{–1} (acetone) (Geary, W. J. *Coord. Chem. Rev.* 1971, 7, 81). ^b Λ_M (acetone) = 106 S cm² mol^{–1}.

mmol) in acetonitrile (7 mL) was placed in an oil bath kept at 110 °C. White crystals were formed in a clear yellow solution after 10 min, and the reaction was complete after 60 min. The yellow supernatant liquid was decanted, and the colorless crystals were washed with acetonitrile (5 mL) and ether (2 × 10 mL) and then dried in a vacuum for 5 h. The yield of **5** was 200 mg (70%). The complex is almost insoluble in acetonitrile, CHCl₃, and CH₂Cl₂. MS: 180, [9S3]⁺ (23.3%); 154, [C₆H₅C₆H₅]⁺ (100%); 78, [C₆H₆]⁺ (100%).

Methyl((trimethylsilyl)methyl)(1,4,7-trithiacyclononane)platinum(II), PtMe(CH₂SiMe₃)(9S3) (6). This yellow solid was prepared in

a manner similar to that used for **1** from PtMe(CH₂SiMe₃)(cod) and 9S3. The yield was 58%. The complex is readily soluble in acetonitrile and CHCl₃ and moderately soluble in hexane. MS: 477, [M⁺] (0.1%); 462, [M – CH₃]⁺ (0.3%); 391, [M – CH₂SiMe₃]⁺ (0.3%); 180, [9S3]⁺ (16.0%); 73, [SiMe₃]⁺ (90.0%); 61, [CH₂CH₂SH]⁺. δ(¹⁹⁵Pt): –4249 (CDCl₃).

Chloro((trimethylsilyl)methyl)(1,4,7-trithiacyclononane)platinum(II), PtCl(CH₂SiMe₃)(9S3) (7). A solution containing PtCl(CH₂SiMe₃)(nbd) (205 mg, 0.50 mmol) and 9S3 (91 mg, 0.50 mmol) in THF (10 mL) was heated under reflux for 4 h. The usual workup gave a pale yellow powder which was washed with ether (2 × 10 mL). The yield of **7** was 220 mg (88%). MS: 497, [M]⁺ (0.5%); 483, [M – CH₃]⁺ (4.0%); 180, [9S3]⁺ (19.0%); 73, [Me₃Si]⁺ (63.2%); 61, [CH₂CH₂SH]⁺ (100%). IR (KBr): 305 cm^{–1} [ν(PtCl)].

Dimethyl(1,4,7-trithiacyclononane)palladium(II), PdMe₂(9S3) (8). A solution containing PdMe₂(tmeda) (700 mg, 2.77 mmol) and 9S3 (470 mg, 2.61 mmol) in acetonitrile (20 mL) was heated at 50 °C for 1.5 h. Solvent was evaporated under reduced pressure, and the pale yellow solid was washed with hexane (3 × 10 mL). The yield was 780 mg (94%).

Bis((trimethylsilyl)methyl)(1,4,7-trithiacyclononane)palladium(II), Pd(CH₂SiMe₃)₂(9S3) (9). To a sample of Pd(CH₂SiMe₃)₂(tmeda), prepared as above, was added 9S3 (180 mg, 1.00 mmol) dissolved in acetonitrile (20 mL). The mixture was stirred at room temperature for 72 h, and the solvent was pumped off to give **9** as an orange solid admixed with colorless 9S3. It was identified by its ¹H NMR spectrum (Table II) and a FABMS (glycerol matrix): 461, [M – H]⁺; 373, [M – CH₂SiMe₃

Table IV. IR maxima of Methylplatinum and Methylpalladium Complexes of 9S3

complex	bands (KBr), cm ⁻¹
PtMe ₂ (9S3) (1)	2988 w, 2951 m, 2905 vs, 2888 vs, 2855 vs, 2818 s, 2785 vs (C-H str), 1433 m, 1405 vs, 1392 s, 1307 m, 1287 s, 1271 vs, 1217 s, 1196 m, 1150 m, 1131 m, 1024 m, 940 m, 917 m, 831 s, 820 vs, 805 s, 678 m, 660 m, 549 s
PdMe ₂ (9S3) (8)	2990 w, 2910 s, 2890 s, 2850 s, 2760 m (C-H str), 1420 sh, 1400 vs, 1309 m, 1290 vs, 1270 vs, 1162 m, 1150 m, 940 m, 918 m, 835 s, 820 vs, 810 s, 700 m, 670 m, 660 m, 509 s
[PtMe ₃ (9S3)]I (14)	2959 m, 2935 m, 2895 vs, 2808 m (C-H str), 1436 m, 1401 vs, 1296 m, 1263 s, 1225 vs, 1173 w, 1124 m, 1020 w, 936 ms, 901 s, 823 vs, 730 ms, 661 m, 617 m, 552 m, 483 m
[PdMe ₃ (9S3)]I (17)	2986 m, 2962 m, 2932 m, 2904 vs, 2812 m (C-H str), 1437 m, 1402 vs, 1284 m, 1217 s, 1167 vs, 1126 m, 1016 w, 933 s, 898 s, 820 vs, 727 m, 692 m, 663 m, 618 m, 514 m, 478 m

-H]⁺; 281, [M - 9S3 - H]⁺. Attempts to obtain a pure sample of **9**, e.g. by removal of 9S3 at 50 °C in a vacuum, by recrystallization from acetonitrile/hexane or dichloromethane/hexane, or by chromatography on silica gel in 3:1 THF/hexane, were either unsuccessful or caused decomposition.

Bis((trimethylsilyl)methyl)iodo(1,4,7-trithiacyclonane)platinum(IV) Iodide, [Pt(CH₂SiMe₃)₂(9S3)]I (**10**). Iodine (110 mg, 0.433 mmol) in dichloromethane (5 mL) was added dropwise to a stirred solution of **4** (181 mg, 0.329 mmol) in the same solvent (5 mL). The brown solution was stirred for 1 h at room temperature, centrifuged to remove a small amount of black solid, and evaporated to dryness to give a brown powder. Recrystallization from dichloromethane/hexane at 0 °C gave red-brown microcrystals which were washed with cold ether (50 mL). The yield of **10** was 143 mg (54%). δ(¹⁹⁵Pt): -3976 (CD₂Cl₂).

Bis((trimethylsilyl)methyl)bromo(1,4,7-trithiacyclonane)platinum(IV) Bromide, [PtBr(CH₂SiMe₃)₂(9S3)]Br (**11**). A solution of bromine (12 μL, 0.237 mmol) in dichloromethane (5 mL) was added slowly to a solution of **4** (130 mg, 0.236 mmol) in the same solvent (5 mL). After 1 h at room temperature, the suspension was evaporated to dryness and the residue was washed with ether to give **11** as an orange powder (120 mg, 70%).

Bis((trimethylsilyl)methyl)iodo(1,4,7-trithiacyclonane)platinum(IV) Triflate, [Pt(CH₂SiMe₃)₂(9S3)]CF₃SO₃ (**12**). A stirred solution of **10** (50 mg, 0.06 mmol) in acetone (12 mL) was treated with silver triflate (16 mg, 0.06 mmol). The cloudy brown solution was stirred at room temperature for 1 h in the absence of light and filtered through Celite. The filtrate was centrifuged for 1 h to remove traces of AgI and evaporated to give **12** as a tan solid (50 mg, 97%). δ(¹⁹⁵Pt): -3976 (CD₂Cl₂).

Dineopentylido(1,4,7-trithiacyclonane)platinum(IV) Iodide, [Pt(CH₂CMe₃)₂(9S3)]I (**13**). This was prepared similarly to **10** by slow addition of iodine (200 mg, 0.77 mmol) in ether (10 mL) to a solution of **3** (400 mg, 0.77 mmol) in dichloromethane (10 mL). The product was obtained as a brown powder and was identified by its NMR spectra (Table II).

Trimethyl(1,4,7-trithiacyclonane)platinum(IV) Iodide, [PtMe₃(9S3)]I (**14**). Iodomethane (0.45 mL, 7.2 mmol) was added to a stirred suspension of **1** (0.172 g, 0.424 mmol) in dichloromethane (10 mL) at room temperature, and the yellow solution was stirred for 40 min. Evaporation to a ca. 2-mL volume and addition of hexane (6 mL) gave **14** as a pale yellow solid, which was collected by filtration and washed with hexane. The yield was 157 mg (68%).

The complexes [PtMeEt₂(9S3)]I (**15**) and [PtEt₃(9S3)]I (**16**) were obtained similarly as yellow solids in ca. 80% yield by addition of iodomethane and iodoethane, respectively, to **2**. The complex [PdMe₃(9S3)]I (**17**) was obtained similarly to **14** as a pale orange solid in 83% yield by addition of iodomethane to **8**.

Trimethyl(1,4,7-trithiacyclonane)palladium(IV) Nitrate, [PdMe₃(9S3)]NO₃ (**18**). Silver nitrate (12 mg, 0.071 mmol) was added to a solution of **17** (28 mg, 0.061 mmol) in acetone (20 mL). The suspension was stirred at room temperature for 1 h, filtered, and the filtrate was

Table V. Summary of Crystallographic Data for Pt(C₆H₅)₂(9S3) (5)

chem formula	C ₁₈ H ₂₂ PtS ₃	<i>T</i> , °C	25
fw	529.44	ρ _{calc'd} , g cm ⁻³	1.962
space group	orthorhombic, <i>Pbca</i>	μ, mm ⁻¹	18.0
<i>a</i> , Å	12.047(1)	<i>F</i> (000)	2048
<i>b</i> , Å	17.660(2)	<i>R</i> ^a	0.031
<i>c</i> , Å	16.854(2)	<i>R</i> _w ^b	0.046
<i>V</i> , Å ³	3585.7	<i>S</i> ^c	1.54
<i>Z</i>	8		

^a *R* = Σ|*F*_o| - |*F*_c|/Σ|*F*_o|. ^b *R*_w = {Σw(|*F*_o| - |*F*_c|)²/Σ(w*F*_o²)^{1/2}}. ^c *S* = goodness of fit = {Σw(|*F*_o| - *k*|*F*_c|)²/(*m* - *n*)^{1/2}}, where *m* = no. reflections and *n* = number of variables.

evaporated to ca. 1 mL. The pale buff solid that precipitated on addition of ether was collected by filtration and washed with ether. The yield of **18** was 13 mg (54%).

Crystallography. Data were collected on a colorless crystal of PtPh₂(9S3) (**5**) of dimensions 0.34 × 0.12 × 0.20 mm, obtained directly from the reaction mixture. Reflection intensities were recorded on a Philips PW1100/20 diffractometer using graphite-monochromated Cu Kα radiation. Lattice parameters were calculated from a least-squares analysis of setting angles of 25 reflections [51 < 2θ < 60°; λ (Cu Kα) = 1.5418 Å]. A total of 3148 unique reflections, of which 487 with *I* < 3σ(*I*) were regarded as unobserved, was collected by means of θ-2θ scans of width (1.1 + 0.142 tan θ)° in θ at a rate of 4° min⁻¹ with 5-s background counts on each side of every scan; 2θ_{max} = 128° with 0 ≤ *h* ≤ 14, -12 ≤ *k* ≤ 0, and 0 ≤ *l* ≤ 19. Three check reflections measured every 90 min showed a 10% decrease in intensity during data collection, so a decomposition correction was applied to all data.²⁰ Data were corrected for absorption (*A** = 13.28 - 4.39), and the structure was solved by use of heavy-atom techniques (SHELXS-86).²¹ A summary of crystallographic data is given in Table V. Refinement was performed by means of full-matrix least-squares methods with anisotropic displacement factors for non-hydrogen atoms. Hydrogen atoms were positioned geometrically and were not refined. A difference-Fourier map revealed a minor twinned image (ca. 2%) at (0.5 - *x*, *y*, *z*); atoms with fixed positional and displacement parameters were placed at these positions and relative populations refined. Refinement on *F*, 201 parameters, gave the *R* values shown in Table V, with weighting scheme *w* = [σ²(*F*) + (0.0004)*F*²]⁻¹, maximum shift/error ratio = 0.08, and maximum and minimum heights in the final difference map of +0.88 and -0.95 e Å⁻³ near the Pt atom. An extinction correction was applied (final value *g* = 0.45(3) × 10⁴) and three reflections with very poor agreement between *F*_{rel} and *F*_{calc} were deleted. Atomic scattering factors for neutral atoms, and real and imaginary dispersion terms were used,²² and the data reduction and refinement computations were performed with XTAL 3.0.²³ Positional and isotropic displacement parameters of non-hydrogen atoms are listed in Table VI.

Results

Attempts to prepare organoplatinum(II) and organopalladium(II) complexes containing the macrocyclic thioether 9S3 by treatment of MCl₂(9S3) with organolithium or Grignard reagents led only to decomposition. However, the coordinated diene in PtRR'(cod) is readily displaced on heating with 9S3 in acetonitrile to give good yields of the yellow diorganoplatinum(II) complexes PtRR'(9S3) [R = R' = Me (**1**), Et (**2**), CH₂CMe₃ (**3**), CH₂SiMe₃ (**4**), Ph (**5**); R = Me, R' = CH₂SiMe₃ (**6**)]. Similarly, the monoalkyl complex PtCl(CH₂SiMe₃)(9S3) (**7**) is obtained from PtCl(CH₂SiMe₃)(nbd) and 9S3 in refluxing THF. The dimethylpalladium(II) complex PdMe₂(9S3) (**8**) can be isolated as a yellow solid from the reaction of PdMe₂(tmeda) with 9S3 in hot acetonitrile. Unlike the platinum(II) complexes, **8** is moderately

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Table VI. Non-Hydrogen Positional and Isotropic Displacement Parameters for PtPh₂(9S3) (5)^a

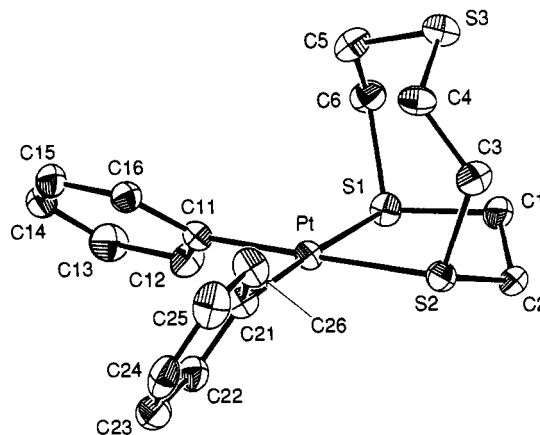
atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{eq} ^b Å ²
Pt	0.15963(2)	0.54921(2)	0.58916(2)	0.0320(1)
S(1)	0.0728(2)	0.6461(1)	0.5171(1)	0.0408(5)
S(2)	0.2130(2)	0.49776(9)	0.4664(1)	0.0397(5)
S(3)	0.3596(2)	0.6959(1)	0.4658(1)	0.0550(7)
C(1)	0.1022(7)	0.6271(4)	0.4127(4)	0.048(3)
C(2)	0.1164(7)	0.5433(4)	0.3986(4)	0.042(2)
C(3)	0.3490(6)	0.5364(5)	0.4358(6)	0.048(3)
C(4)	0.3973(6)	0.5985(5)	0.4889(5)	0.049(3)
C(5)	0.2729(7)	0.7256(4)	0.5483(5)	0.051(3)
C(6)	0.1494(7)	0.7332(4)	0.5338(5)	0.050(3)
C(11)	0.1113(6)	0.5964(4)	0.6923(4)	0.037(2)
C(12)	0.0024(6)	0.6267(4)	0.7013(5)	0.047(2)
C(13)	-0.0277(8)	0.6619(5)	0.7736(5)	0.060(3)
C(14)	0.0463(7)	0.6683(4)	0.8363(5)	0.049(3)
C(15)	0.1474(7)	0.6390(5)	0.8280(5)	0.050(3)
C(16)	0.1814(6)	0.6032(4)	0.7582(4)	0.041(2)
C(21)	0.2269(6)	0.4610(4)	0.6511(4)	0.040(2)
C(22)	0.1642(7)	0.4153(5)	0.6972(5)	0.049(3)
C(23)	0.2069(8)	0.3499(4)	0.7336(5)	0.056(3)
C(24)	0.3154(9)	0.3322(4)	0.7246(5)	0.059(3)
C(25)	0.3796(9)	0.3782(5)	0.6801(6)	0.063(3)
C(26)	0.3376(7)	0.4420(5)	0.6435(6)	0.052(3)

^a Population of all atoms 0.9769(9). ^b $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$.

air-sensitive, decomposing over a period of days, but under nitrogen in the dark it is stable at room temperature for many months. It darkens to orange-tan on exposure to light, but this treatment does not seem to affect the NMR or IR spectra. Thermal decomposition of **8** (ca. 110 °C, 90 min) gave a mixture of ethane (ca. 70%), ethylene (ca. 20%) and methane (ca. 10%), as determined by GC analysis of the vapor. The bis(trimethylsilyl)methyl complex Pd(CH₂SiMe₃)₂(9S3) (**9**) is formed as an orange solid on treatment of Pd(CH₂SiMe₃)₂(tmeda) with an excess of 9S3, but it could not be purified.

The ¹H and ¹³C{¹H} NMR spectra of **1–4** and **6** show clearly that the alkyl groups are σ-bonded to the metal. For example, the CH₃-Pt resonance of **1** appears as a sharp singlet with ¹⁹⁵Pt satellites at δ 0.58 (²J_{PtH} = 86.0 Hz), and there is correspondingly a CH₃-Pt singlet at δ -11.1 (¹J_{PtC} = 751.3 Hz). Similar large values of ¹J_{PtC} are observed for **2, 3, 4** and **6**. The magnitudes of ²J_{PtH} and ¹J_{PtC} in **1** and **3** are similar to those observed in [PtMe₂(SEt₂)₂]₂²⁴ and [Pt(CH₂SiMe₃)₂(SMe₂)₂]₃²⁵ respectively. Moreover, the magnitudes of ²J_{PtH} and ¹J_{PtC} in **1** are similar to those of PtMe₂(cod), thus placing dialkyl sulfides close to alkenes (and halides) in the NMR trans-influence series.²⁶ Whereas the Pt-alkyl signals are sharp, resonances in the region δ 4.0–1.5 due to the 9S3 CH₂ groups of **1–6** appear as one or more broad humps; this feature suggested the possibility of fluxional behavior arising from exchange between free and coordinated sulfur atoms (see later).

A single-crystal X-ray study of PtPh₂(9S3) (**5**) confirmed that the platinum atom is bound to two sulfur atoms of bidentate 9S3 and to two cis-σ-phenyl groups, the coordination geometry being close to planar. The molecular structure is shown in Figure 1, and important bond lengths and angles are given in Table VII. The phenyl rings are oriented at angles of 42.8(2) and 59.5(2)° relative to the coordination plane. The 9S3 ligand adopts an exodentate conformation such that the uncoordinated sulfur atom points away from the metal atom [Pt-S(3) = 4.103(2) Å]. This differs from the more usual endodentate conformation of 9S3 found in PdX₂(9S3) (X = Cl, Br),^{5,6} which gives rise to a weak axial Pd-S interaction, but it is similar to that found for one of

**Figure 1.** Diagram of molecular structure of PtPh₂(9S3) (**5**) showing labeling of the non-hydrogen atoms. Thermal ellipsoids show 30% probability levels and hydrogen atoms are deleted for clarity.**Table VII.** Interatomic Distances (Å) and Angles (deg) for Non-Hydrogen Atoms of PtPh₂(9S3) (**5**)

Pt-S(1)	2.345(2)	Pt-S(2)	2.350(2)
Pt-C(11)	2.014(7)	Pt-C(21)	2.043(7)
S(1)-C(1)	1.826(8)	S(1)-C(6)	1.815(8)
S(2)-C(2)	1.818(8)	S(2)-C(3)	1.848(8)
S(3)-C(4)	1.822(8)	S(3)-C(5)	1.817(9)
C(1)-C(2)	1.51(1)	C(3)-C(4)	1.53(1)
C(5)-C(6)	1.51(1)	C(11)-C(12)	1.42(1)
C(11)-C(16)	1.40(1)	C(12)-C(13)	1.42(1)
C(13)-C(14)	1.39(1)	C(14)-C(15)	1.33(1)
C(15)-C(16)	1.40(1)	C(21)-C(22)	1.35(1)
C(21)-C(26)	1.38(1)	C(22)-C(23)	1.41(1)
C(23)-C(24)	1.35(1)	C(24)-C(25)	1.35(1)
C(25)-C(26)	1.38(1)		
S(1)-Pt-S(2)	87.02(6)	S(1)-Pt-C(11)	90.9(2)
S(1)-Pt-C(21)	176.6(2)	S(2)-Pt-C(11)	177.9(2)
S(2)-Pt-C(21)	92.7(2)	C(11)-Pt-C(21)	89.4(3)
Pt-S(1)-C(1)	106.2(3)	Pt-S(1)-C(6)	108.1(3)
C(1)-S(1)-C(6)	101.9(4)	Pt-S(2)-C(2)	101.9(2)
Pt-S(2)-C(3)	110.2(3)	C(2)-S(2)-C(3)	103.2(4)
C(4)-S(3)-C(5)	104.6(4)	S(1)-C(1)-C(2)	110.7(5)
S(2)-C(2)-C(1)	114.1(5)	S(2)-C(3)-C(4)	116.0(6)
S(3)-C(4)-C(3)	117.2(6)	S(3)-C(5)-C(6)	117.8(6)
S(1)-C(6)-C(5)	116.7(5)	Pt-C(11)-C(12)	120.9(5)
Pt-C(11)-C(16)	123.0(5)	C(12)-C(11)-C(16)	116.0(6)
C(11)-C(12)-C(13)	119.5(7)	C(12)-C(13)-C(14)	121.8(8)
C(13)-C(14)-C(15)	118.4(7)	C(14)-C(15)-C(16)	122.2(8)
C(11)-C(16)-C(15)	122.0(7)	Pt-C(21)-C(22)	121.8(6)
Pt-C(21)-C(26)	121.4(6)	C(22)-C(21)-C(26)	116.7(7)
C(21)-C(22)-C(23)	122.5(8)	C(22)-C(23)-C(24)	119.7(8)
C(23)-C(24)-C(25)	118.5(8)	C(24)-C(25)-C(26)	122.0(9)
C(21)-C(26)-C(25)	120.7(8)		

the 9S3 ligands in [Pt(9S3)₂]²⁺ (⁸ (see Introduction). The Pt-S bond lengths in **5** [2.345(2), 2.350(2) Å] are close to the distance of 2.365(5) Å reported for Pt-S trans to aryl carbon in the cycloplatinated crown thioether [Pt(1,3-C₆H₃CH₂SCH₂-CH₂CH₂SCH₂CH₂CH₂S)]BF₄²⁷ and are significantly greater than the Pt-S distances in [Pt(9S3)₂]²⁺ [2.246(8)–2.305(8) Å].⁷ The Pt-C(phenyl) distances [2.014(7), 2.043(7) Å] are equal within experimental error and within the range found in various monomeric arylplatinum(II) tertiary phosphine complexes, e.g. *cis*-PtPh₂(Ph₂PCH₂PPh₂) [2.05(1) Å],²⁸ *cis*-PtCl(C₆H₄Me-4)(PEt₃)₂ [2.05(3) Å],²⁹ and *cis*-PtPh[Ge(OH)Ph₂](PEt₃)₂ [2.043(13) Å].³⁰

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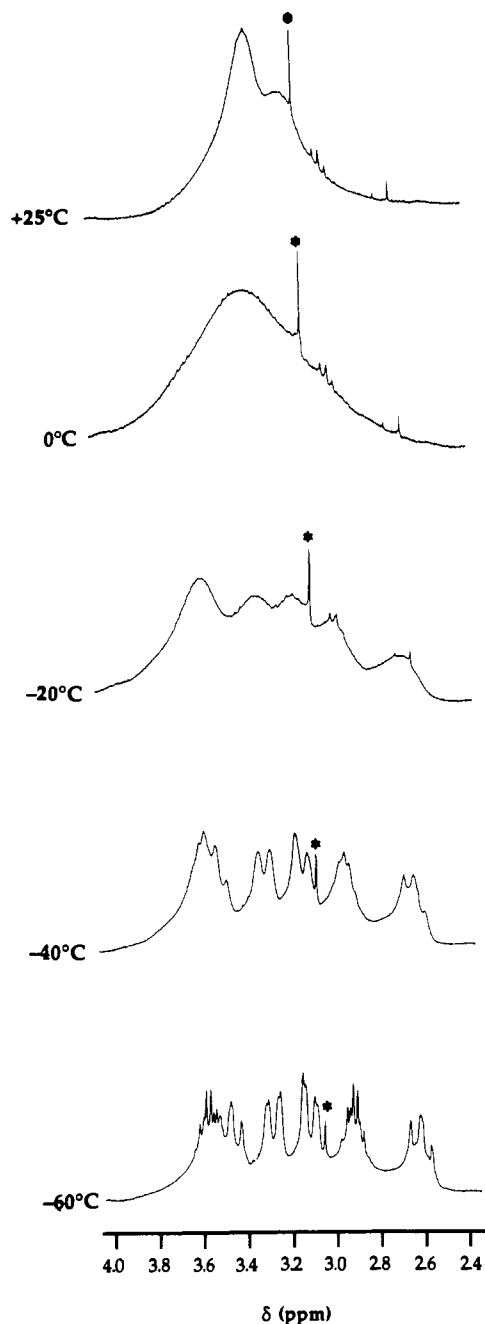


Figure 2. Variable temperature ^1H NMR spectrum of the 9S3 CH_2 protons of $\text{PtEt}_2(9\text{S3})$ (**2**) in CD_2Cl_2 . The peak marked with an asterisk is due to free 9S3.

When a solution of $\text{PtEt}_2(9\text{S3})$ (**2**) in CD_2Cl_2 at 25°C is cooled, the two broad absorptions due to the CH_2 groups of 9S3 broaden, collapse, and separate at -60°C into five well-resolved multiplets in the region δ 3.8–2.6 (Figure 2). Similarly, the four broad multiplets arising from the 9S3 CH_2 groups of the thermally more stable compound $\text{Pt}(\text{CH}_2\text{SiMe}_3)_2(9\text{S3})$ (**4**) in toluene- d_8 at 20°C sharpen at -20°C to give four sharp multiplets in the region δ 3.6–1.6 in the intensity ratio 1:3:1:1 and coalesce to give two broad absorptions at 60°C (Figure 3). Studies of **2** above 25°C were prevented by thermal decomposition. We have not attempted to assign the low-temperature ^1H NMR spectra because of their complexity, but the variable temperature $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **4** (Figure 4) is more informative. At -20°C it consists of three sharp singlets at δ 38.9, 38.6, and 36.5, arising from the three pairs of inequivalent carbon atoms of bidentate 9S3; the resonance at δ 38.9 shows ^{195}Pt satellites ($^2J_{\text{PtC}} = 54.9$ Hz) and is assigned tentatively to the carbon atoms C^1 lying in

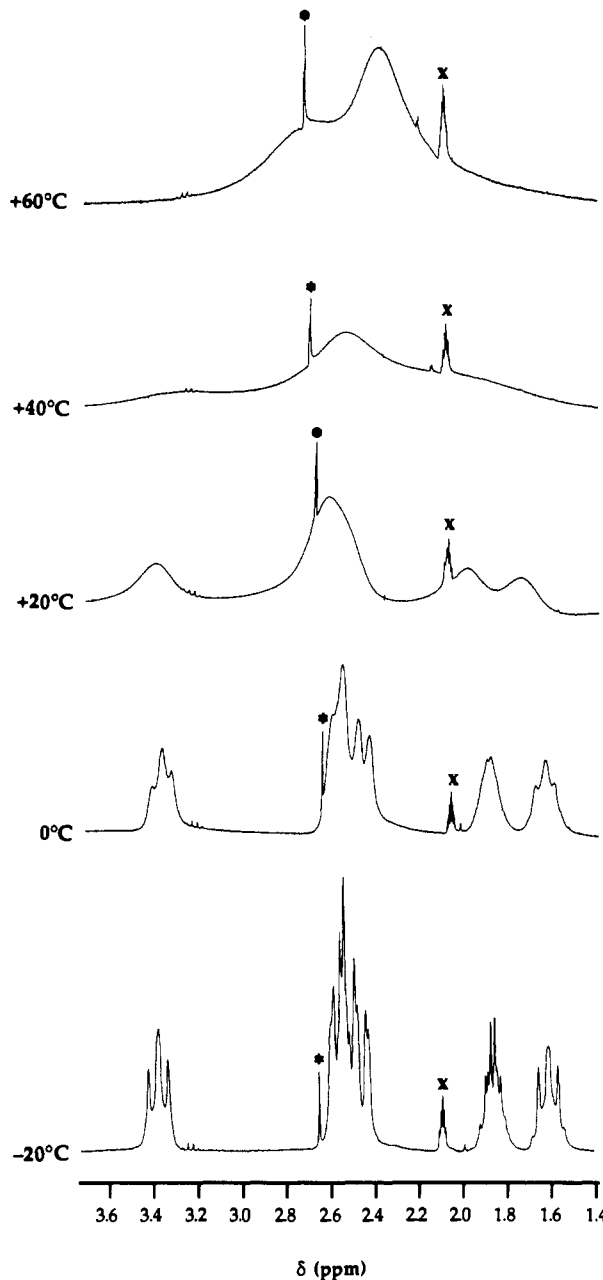


Figure 3. Variable temperature ^1H NMR spectrum of the 9S3 CH_2 protons of $\text{Pt}(\text{CH}_2\text{SiMe}_3)_2(9\text{S3})$ (**4**) in toluene- d_8 . The peaks marked with an asterisk and a cross are due to free 9S3 and to residual protons of the solvent, respectively.

the coordination plane (Figure 5).³¹ As the solution is warmed, the two higher frequency resonances coalesce and the third broadens. At 40°C all three resonances have coalesced, and the resulting singlet sharpens further at 60°C . For both **2** and **4**, the Pt-alkyl resonances and the singlet due to a small amount of free 9S3 remain sharp as the temperature is varied; hence, the variable-temperature NMR behavior is caused by an intramolecular process in coordinated 9S3. The free energy of activation (ΔG^\ddagger) for the process can be estimated as approximately 58 kJ mol^{-1} from the temperature of 2.5°C at which the two lower field, closely spaced ^{13}C resonances coalesce. A more detailed study based on line shape analysis of the spectra is planned.

(31) The basis of this assignment is an assumed analogy with the observed Karplus-type angular dependence of the magnitudes of the coupling constants $^3J_{\text{Pt-N-C-H}}$ and $^4J_{\text{Pt-N-C-H}}$ in amino acid and chelating diamine complexes of platinum(II).^{32,33}

(32) Erikson, L. E.; McDonald, J. W.; Howie, J. K.; Clow, R. P. *J. Am. Chem. Soc.* **1968**, *90*, 6371.

(33) Appleton, T. G.; Hall, J. R. *Inorg. Chem.* **1971**, *10*, 1717.

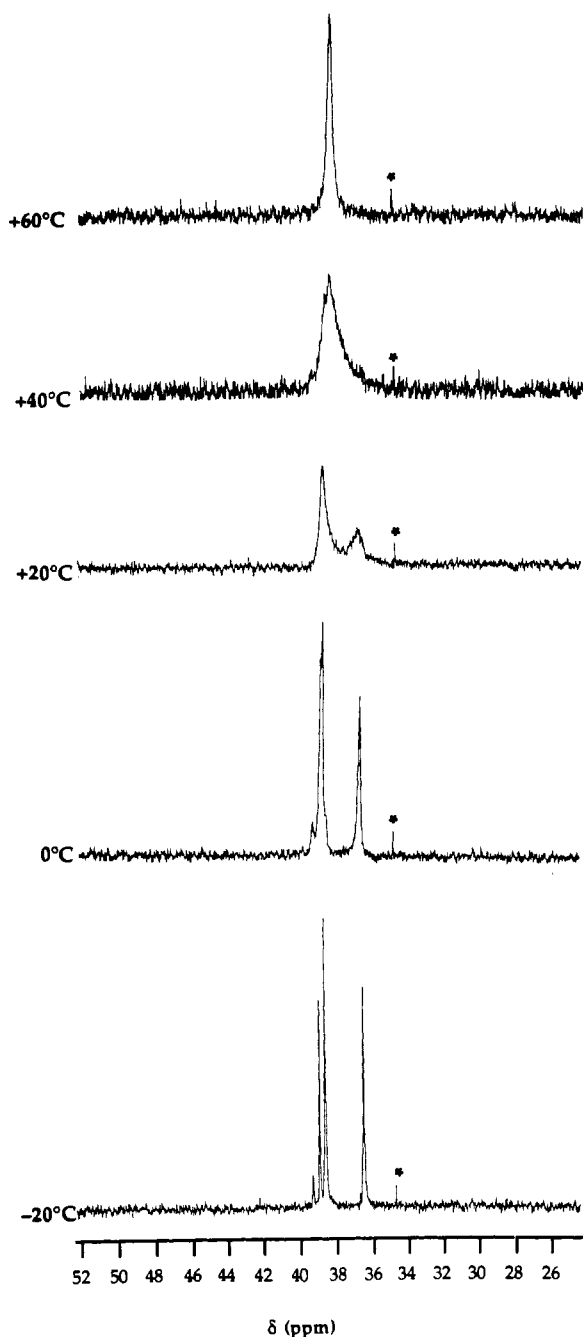


Figure 4. Variable temperature $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the 9S3 CH_2 groups of $\text{Pt}(\text{CH}_2\text{SiMe}_3)_2(9\text{S3})$ (**4**) in $\text{toluene-}d_8$. The peak marked with an asterisk is due to free 9S3.

We assume that complexes **2** and **4** in solution have the same basic structure as found for **5** in the solid state and that the fluxional behavior is a consequence of exchange of the bound and uncoordinated sulfur atoms. As shown in Figure 5, this process could be initiated by a conformational change in the 9S3 ligand from exodentate to endodentate, thus bringing the dangling sulfur atom within the coordination sphere. Exchange could then occur by a series of 1,4-metallotropic shifts induced by pivots of 60° about the Pt–S bonds, similar to those suggested for *fac*-trimethylplatinum(IV) complexes containing various multidentate sulfur donors.^{11,34} We cannot exclude the possibility that there is a ground-state structural change from exodentate- to endodentate-binding of 9S3 in solutions of **2** and **4**, followed by a series of 1,4-metallotropic shifts.

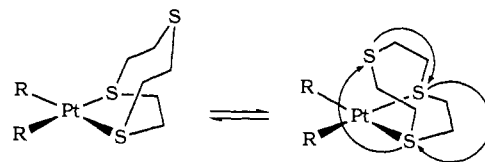
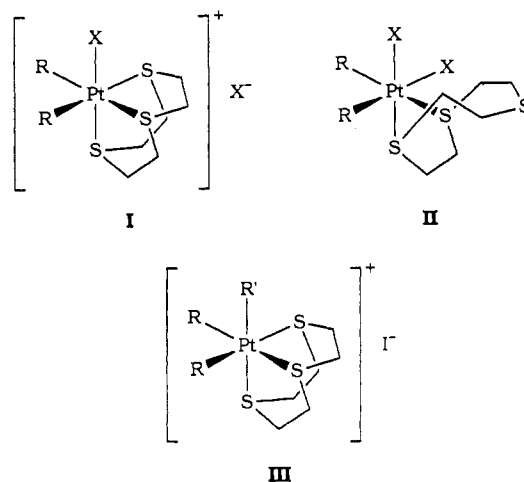


Figure 5. Conformational change and 1,4-metallotropic shifts in $\text{PtR}_2(9\text{S3})$.

The ^1H NMR spectrum of $\text{PdMe}_2(9\text{S3})$ (**8**) at room temperature shows a singlet due to Pd–Me at δ 0.32 and, in contrast to its platinum(II) analogue **1**, a well-resolved AA'BB' multiplet in the region δ 3.38–3.14 due to the six axial and six equatorial protons of coordinated 9S3. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, there is a sharp singlet at δ 39.1, due to apparently equivalent CH_2 groups, and a Pd–Me singlet at δ –5.9. The general similarity of the IR spectra of **1** and **8** (Table IV) implies that the compounds are structurally similar; in particular, strong bands at 549 (**1**) and 509 cm^{-1} (**8**) can be assigned to the Pt–CH₃ and Pd–CH₃ stretching frequencies, respectively.^{35,36} We suggest that **8**, like **1**, contains bidentate 9S3 coordinated to the planar divalent metal atom but that the free and coordinated sulfur atoms in **8** exchange more easily than those in the platinum(II) complexes. Attempts to obtain low-temperature NMR spectra of **8** were frustrated by the poor solubility of the complex.

Oxidative Additions. Treatment of the diorganoplatinum(II) complexes of 9S3 with iodine, bromine, or alkyl iodides gives the corresponding platinum(IV) complexes. The red-brown solids of empirical formula $\text{PtX}_2(\text{CH}_2\text{SiMe}_3)_2(9\text{S3})$ [$\text{X} = \text{I}$ (**10**), Br (**11**)] obtained from **4** and the appropriate halogen show in their $^{13}\text{C}\{^1\text{H}\}$ NMR spectra three singlets in the region δ 45–35 arising from inequivalent CH_2 groups of 9S3, as well as CH_2SiMe_3 resonances in the region δ 2–10. As expected for platinum(IV) complexes, the ^{195}Pt coupling to the directly bound carbon atom (ca. 490 Hz) is about 0.7 of the value of ca. 700 Hz observed for **4**. The molar conductivities of **10** and **11** in nitromethane are close to the values expected for 1:1 electrolytes (Table III). These data are consistent with an ionic formulation $[\text{PtX}(\text{CH}_2\text{SiMe}_3)_2(9\text{S3})]^+\text{X}^-$ (**I**) in which 9S3 functions as a *fac*-tridentate



ligand. The 9S3 CH_2 resonances in the region δ 3–4 of the ^1H NMR spectra of **10** and **11** consist of many overlapping multiplets which undoubtedly arise from the three different pairs of axial and equatorial hydrogen atoms. Apart from some viscosity broadening at the lower temperature, the appearance of these multiplets (in the case of **10**) did not change between $+20^\circ\text{C}$ and -60°C in CD_2Cl_2 , so that there is no fluxional behavior of the type observed in **4**. The triflate salt $[\text{PtI}(\text{CH}_2\text{SiMe}_3)_2(9\text{S3})]^+\text{OTf}^-$

(34) Abel, E. W.; Booth, M.; King, G.; Orrell, K. G.; Pring, G. M.; Šik, V. *J. Chem. Soc., Dalton Trans.* **1981**, 1846. Abel, E. W.; King, G. D.; Orrell, K. G.; Šik, V.; Cameron, T. S.; Jochem, K. *Ibid.* **1984**, 2047.

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(36) Adams, D. M.; Chatt, J.; Shaw, B. L. *J. Chem. Soc.* **1960**, 2047. Adams, D. M. *Ibid.* **1962**, 1220.

CF₃SO₃ (**12**), which is obtained from **10** and silver triflate, is also a 1:1 electrolyte in nitromethane, and its spectroscopic properties are generally similar to those of **10** and **11**: two of the three 9S3 CH₂ resonances, at δ 3.5 and 3.15, are complex multiplets, although the third, at δ 3.65, is a broad triplet ($^3J_{\text{PtH}} = 13.2$ Hz). The chemical shifts $\delta(^{195}\text{Pt})$ of **10** and **12** in CD₂Cl₂ are identical (-3976 ppm relative to Na₂PtCl₆) and are less shielded than those of the platinum(II) complexes **4** and **6** (ca. -4250 ppm), as expected.³⁷

The three singlets in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the dineopentylplatinum(IV) complex PtI₂(CH₂CMe₃)₂(9S3) (**13**) have observable ^{195}Pt satellites [δ 44.6 ($^2J_{\text{PtC}} = 10.0$ Hz), 39.1 ($^2J_{\text{PtC}} = 9.7$ Hz) and 37.4 ($^2J_{\text{PtC}} = 7.8$ Hz)], and the compound is a 1:1 electrolyte in nitromethane, so **13** too must be formulated as a salt [PtI(CH₂CMe₃)₂(9S3)]I containing tridentate 9S3. In no case examined was there evidence for an equilibrium with an uncharged species PtX₂R₂(9S3-S,S') (II) resulting from displacement of one of the sulfur atoms by halide. In contrast, iodine oxidation of dimethylplatinum(II) complexes of tripodal N-donor ligands gives initially *neutral* dimethylplatinum(IV) species, e.g. PtI₂Me₂{(pz)₃CH-N,N'}, which isomerizes on heating to give salts, e.g. [PtIme₂{(pz)₃CH-N,N',N'}]I.³⁸

The dialkylplatinum(II) complexes **1** and **2** add methyl iodide or ethyl iodide at room temperature to give octahedral trialkylplatinum(IV) complexes [PtR₂R'(9S3)]I [R = R' = Me (**14**); R = Et, R' = Me (**15**); R = R' = Et (**16**)]. The dimethylpalladium(II) complex **8** also adds methyl iodide to give the analogous trimethylpalladium(IV) complex [PdMe₃(9S3)]I (**17**), which is converted by silver nitrate into the corresponding nitrate salt [PdMe₃(9S3)]NO₃ (**18**). The compounds are 1:1 electrolytes in nitromethane. The ^1H NMR spectra of **14**, **17**, and **18** each show a singlet due to equivalent methyl groups, accompanied in the case of **14** by ^{195}Pt satellites; as expected, $^2J_{\text{PtH}}$ (67.5 Hz) is about 0.7 of the value in **1**. The NMR parameters for **14** are very similar to those reported for [PtMe₃(9S3)]Cl·2H₂O.¹¹ The Pt-Me ^1H and ^{13}C resonances in **14** are more shielded than the corresponding Pd-Me signals in **17** and **18**, but a careful comparison of the intensities and patterns of the IR band maxima of **14** and **17** (Table IV) leaves little doubt that the cations are isostructural. The ^1H NMR spectrum of **16** contains a single quartet, with ^{195}Pt satellites, due to equivalent ethyl groups. In **15** the ethyl groups are equivalent but their CH₂ protons are

diastereotopic and appear as the AB part of an ABX₃ spectrum. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **15** shows three singlets with ^{195}Pt satellites due to the inequivalent CH₂ groups of 9S3, whereas for **14**, **17**, and **18** the 9S3 CH₂ groups are equivalent and appear as singlets. In all cases (including **15**) the 9S3 CH₂ protons appear as a well-resolved AA'BB' multiplet. The complexes undoubtedly contain endodentate 9S3 coordinated to a *fac*-trialkylmetal(IV) cation (III), as found in the X-ray structural analysis of [PtMe₃(9S3)]Cl·2H₂O.¹¹

Discussion

Qualitatively, the diorgano complexes of platinum(II) and palladium(II) containing 9S3 appear to be of similar stability to the complexes MMe₂(MeSCH₂CH₂SMe),^{35,39} the complex PdMe₂(9S3) is, however, more thermally stable than PdMe₂(EtSCH₂CH₂SEt), which decomposes even at 0 °C.³⁵ It is not clear why 9S3 should adopt an exodentate conformation in PtPh₂(9S3) (and, presumably, in all the other diorgano complexes). Since the axial interaction in PdX₂(9S3) (X = Cl, Br) is probably primarily electrostatic, the change could be attributed to a reduction in the net positive charge on the metal atom caused by the electron-donating phenyl groups, but the greater bulk of the phenyl groups could also play a role.

A remarkable feature of the organoplatinum(IV) and organopalladium(IV) complexes of 9S3 is that they show no tendency to form organometal(II) complexes M^{II}RI(9S3) by the usual reductive elimination of a pair of σ -bonded alkyl groups. This reflects the ability of 9S3, acting as an endodentate ligand, to stabilize trigonal fragments such as [MR₃]⁺ (M = Pt, Pd); as noted in the Introduction, the most stable organopalladium(IV) complexes known contain tripodal N-donor ligands. The stability of the palladium(IV) complexes **17** and **18** is notable, given that the only other well-characterized palladium(IV) complex of a thioether is [NPr₄][PdCl₅(SMe₂)], which decomposes slowly at room temperature.⁴⁰

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Supplementary Material Available: Tables giving a summary of crystallographic data, positional parameters for the hydrogen atoms, atomic anisotropic displacement parameters, torsion angles for non-hydrogen atoms, distances, angles, and torsion angles for hydrogen atoms, and selected least-squares planes (8 pages). Ordering information is given on any current masthead page.

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