

Syntheses, spectroscopic characteristics and thermolytic rearrangements of bis-[(trimethylgermyl)methyl]platinum(II) and bis-[(trimethylstannyl)methyl]platinum(II) complexes

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Abstract

The preparations and spectroscopic characteristics are reported of a series of (trimethylgermyl)methyl- and (trimethylstannyl)methylplatinum(II) complexes with diene and *P*-donor ancillary ligands, *cis*-Pt(CH₂GeMe₃)₂L₂ (L = PPh₃ or PPh₂Me; L₂ = dppe or cod) and *cis*-Pt(CH₂SnMe₃)₂L₂ (L = PPh₃; L₂ = cod). Thermolysis of toluene solutions of *cis*-Pt(CH₂GeMe₃)₂(PPh₃)₂ leads to *cis*-Pt(Me)(CH₂GeMe₂CH₂GeMe₃)(PPh₃)₂ via β -alkyl migration, after (non-rate-limiting) phosphine dissociation. Estimated activation parameters ($\Delta H_{298\text{ K}}^\ddagger = 126 \pm 3 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = +17 \pm 7 \text{ J mol}^{-1} \text{ K}^{-1}$ and hence $\Delta G_{298\text{ K}}^\ddagger = 121 \pm 5 \text{ kJ mol}^{-1}$) suggest that this system is more migration labile than its silicon analogue, primarily as a result of a lower activation enthalpy. While *cis*-Pt(CH₂GeMe₃)₂(PPh₂Me)₂ reacts similarly but less readily, Pt(CH₂GeMe₃)₂(dppe)₂ is inert at operable temperatures. Thermolysis of Pt(CH₂GeMe₃)₂(cod) generates 1,1,3,3-tetramethyldi-1,3-germacyclobutane as the major organogermanium product, while from *cis*-Pt(CH₂SnMe₃)₂(PPh₃)₂, 1,1,3,3-tetramethyldi-1,3-stannacyclobutane predominates. Mechanistic implications are discussed.

Keywords: Germanium; Platinum; Tin; Thermolysis; Kinetics; Mechanism

1. Introduction

Recently, we reported on the unusual reactivity of a series of silylmethylplatinum(II) derivatives, *cis*-Pt(CH₂SiMe₂R)₂(PR'₃)₂. These undergo thermolytic β -carbon migrations, generating, in most cases, *cis*-Pt(R)(CH₂SiCH₂SiMe₂R)(PR'₃)₂ via (η^2 -silene)metal intermediates [1]. It was of obvious interest to evaluate corresponding patterns of reactivity for germylmethylplatinum and stannylmethylplatinum analogues. Here we report the synthesis and spectroscopic characteristics of the complexes *cis*-Pt(CH₂GeMe₃)₂L₂ (L = PPh₃ or PPh₂Me; L₂ = Ph₂PCH₂CH₂PPh₂ (dppe) or cod) and *cis*-Pt(CH₂SnMe₃)₂L₂ (L = PPh₃; L₂ = cod) as well as their thermolytic behaviour. β -Heteroalkylmetal species of these types [2] remain relatively rare and no such

organoplatinum derivatives have appeared previously [3].

2. Results and discussion

2.1. Synthesis

The haloalkanes Ge(CH₂Cl)Me₃ and Sn(CH₂Cl)Me₃ — precursors to organomagnesium reagents — were prepared using modifications of published procedures [4,5]. The synthesis of Pt(CH₂GeMe₃)₂(cod), a colourless crystalline solid, may be achieved with at least 70% yield by the reaction of Mg(CH₂GeMe₃)Cl with PtCl₂(cod). Similarly, treatment of PtCl₂(cod) with Mg(CH₂SnMe₃)Cl gave good yields of Pt(CH₂SnMe₃)₂(cod) as a waxy colourless solid. Subsequent replacement of the diene with phosphine ligands produced *cis*-Pt(CH₂GeMe₃)₂L₂ (E = Ge; L = PPh₃ or PPh₂Me; L₂ = dppe) (E = Sn; L = PPh₃), with essen-

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tially quantitative yields. These ligand metatheses were generally complete within 21 days at 70°C.

All the complexes, $\text{cis-Pt}(\text{CH}_2\text{EMe}_3)_2\text{L}_2$, are air-inert colourless crystalline solids. In solution, however, the phosphine complexes are air sensitive. The tin compounds also react particularly readily with chlorocarbon solvents, to form (on NMR evidence) several organotin fragments and $\text{cis-PtCl}_2\text{L}_2$. The mechanism of this transformation has not been explored further. All new complexes have been characterised by elemental analysis and IR spectroscopy (see Section 3) as well as ^1H NMR, ^{13}C NMR and ^{31}P NMR (vide infra) where applicable.

2.2. Spectroscopic characteristics

2.2.1. ^1H NMR

The ^1H NMR characteristics of the germylmethylplatinum and stannylmethylplatinum complexes are detailed in Table 1. Common features of all these spectra are the singlet near 0 ppm generated by the methyl substituents, $\text{E}(\text{CH}_3)_3$, and the 1:4:1 pattern around 1 ppm, arising from the methylene hydrogen atoms and their spin–spin coupling to (33.8% abundant) ^{195}Pt . $^2J_{\text{Pt-H}}$ values lie within the range 70–85 Hz for

both the tin and the germanium compounds. Both sets of coupling constants are noticeably smaller than in silicon-containing [6] or carbon-containing [7] analogues, with the $^2J_{\text{Pt-H}}$ values for the stanna-neopentyl complexes emerging as the smallest in the group.

A further notable aspect of the ^1H NMR spectra is the emergence of $^2J_{\text{Sn-H}}$, due to spin–spin coupling to ^{117}Sn (7.6% abundant) and ^{119}Sn (8.6% abundant). Low intensity satellites appear symmetrically about both the methylene and the methyl hydrogen resonances. The $^2J_{\text{Sn-H}}$ values of about 50 Hz are not affected significantly by platinum coordination and are comparable with those for related compounds [8].

2.2.2. ^{13}C NMR

The $^{13}\text{C}\{^1\text{H}\}$ NMR characteristics of the germanium- and tin-substituted neopentylplatinum complexes appear in Table 2. Recurrent aspects of all these spectra are the 1:4:1 platinum satellite patterns for the methylene and methyl carbon atoms, with the methylene carbons showing additional coupling to both the *cis*- and the *trans*-phosphorus nuclei. The chemical shifts for these carbons in the stannylmethyl ligand are noticeably upfield of the analogous germylmethyl resonances.

The magnitudes of $^1J_{\text{Pt-C}}$ for the phosphine com-

Table 1
 ^1H NMR characteristics of germylmethyl and stannylmethylplatinum(II) complexes ^a

Complex	δ (^1H) (neopentyl) (ppm)		δ (^1H) (ancillary ligand) (ppm)
	CH_2	CH_3	
$\text{Pt}(\text{CH}_2\text{GeMe}_3)_2(\text{cod})$	1.01 ($J_{\text{Pt-H}} = 84$ Hz)	0.05	2.30–2.17 (m, CH_2), 4.62 (“t”, $J_{\text{Pt-H}} = 45$ Hz CH_2)
<i>cis</i> - $\text{Pt}(\text{CH}_2\text{GeMe}_3)_2(\text{PPh}_3)_2$	0.84 ($J_{\text{Pt-H}} = 79$ Hz)	0.09	7.39 (m, $\text{H}_{2,9}$), 7.18 (m, $\text{H}_{3,5}$), 7.70 (m, H_4)
<i>cis</i> - $\text{Pt}(\text{CH}_2\text{GeMe}_3)_2(\text{PPh}_2\text{Me})_2$	0.71 ($J_{\text{Pt-H}} = 77$ Hz)	0.01	7.40 (m, $\text{H}_{2,6}$), 7.25 (m, $\text{H}_{3,5}$), 7.21 (m, H_4), 1.61 (m, $J_{\text{Pt-H}} = 20$ Hz, Me, $J_{\text{P-H}} = 7$ Hz)
$\text{Pt}(\text{CH}_2\text{GeMe}_3)_2(\text{dppe})$	0.92 ($J_{\text{Pt-H}} = 75$ Hz)	–0.18	7.66–7.58 (m, $\text{H}_{2,6}$), 7.43–7.37 (m, $\text{H}_{3,4,5}$), 2.16 (m, $J_{\text{Pt-H}} = 12$ Hz, P– CH_2 , $J_{\text{P-H}} = 17$ Hz)
$\text{Pt}(\text{CH}_2\text{SnMe}_3)_2(\text{cod})$	1.06 ($J_{\text{Pt-H}} = 73$ Hz, $J_{\text{Sn-H}} = 13$ Hz)	0.04 ($J_{\text{Sn-H}} = 47$ Hz)	2.31–2.22 (m, CH_2), 4.58 (“t”, $J_{\text{Pt-H}} = 43$ Hz, CH)
<i>cis</i> - $\text{Pt}(\text{CH}_2\text{SnMe}_3)_2(\text{PPh}_3)_2$	0.78 ($J_{\text{Pt-H}} = 67$ Hz)	0.06	7.83–7.78 (m, H_4), 7.58–7.41 (m, $\text{H}_{2,6}$), 7.26–7.13 (m, $\text{H}_{3,5}$)
<i>cis</i> - $\text{Pt}(\text{CH}_2\text{GeMe}_2\text{CH}_2\text{GeMe}_3)(\text{Me})(\text{PPh}_3)_2$	1.13 ($J_{\text{Pt-H}} = 68$ Hz, Pt– CH_2 , $J_{\text{P-H}} = 12,7$ Hz), 0.49 (– CH_2 –)	0.88 ($J_{\text{Pt-H}} = 65$ Hz, Pt– CH_3 , $J_{\text{P-H}} = 10,8$ Hz), 0.47 (GeMe ₂), 0.46 (GeMe ₃)	8.23–8.09 (m, H_4), 7.95–7.22 (m, $\text{H}_{2,6}$), 7.63–7.48 (m, $\text{H}_{3,5}$)
<i>cis</i> - $\text{Pt}(\text{CH}_2\text{GeMe}_2\text{CH}_2\text{GeMe}_3)(\text{Me})(\text{PPh}_2\text{Me})_2$	0.74 ($J_{\text{Pt-H}} = 70$ Hz, Pt– Cl_2 , $J_{\text{P-H}} = 10,7$ Hz), –0.17 (– CH_2 –)	0.42 ($J_{\text{Pt-H}} = 68$ Hz, Pt– CH_3 , $J_{\text{P-H}} = 11,7$ Hz), 0.46 (GeMe ₂), 0.61 (GeMe ₃)	7.48–7.38 (m, H_4), 7.36–7.28 (m, $\text{H}_{2,6}$), 7.21–7.18 (m, $\text{H}_{3,5}$), 1.56 ($J_{\text{Pt-H}} = 24$ Hz, Me, $J_{\text{P-H}} = 8$ Hz), 1.70 ($J_{\text{Pt-H}} = 30$ Hz, Me, $J_{\text{P-H}} = 10$ Hz)

^a Obtained in chloroform-*d*₁.

Table 2
¹³C NMR characteristics of germylmethyl and stannylmethylplatinum(II) complexes ^a

Complex	δ (¹³ C) (neopentyl) (ppm)		δ (¹³ C) (ancillary ligand) (ppm)
	CH ₂	CH ₃	
Pt(CH ₂ GeMe ₃) ₂ (cod)	15.45 ($J_{\text{Pt-C}} = 773$ Hz)	3.29 ($J_{\text{Pt-C}} = 32$ Hz)	30.30 (CH ₂), 97.96 ("t"), $J_{\text{Pt-C}} = 71$ Hz, CH),
<i>cis</i> -Pt(CH ₂ GeMe ₃) ₂ (PPh ₃) ₂ ^b	12.51 ($J_{\text{Pt-C}} = 639$ Hz, $J_{\text{P-C}} = 91,6$ Hz)	4.09 ($J_{\text{Pt-C}} = 29$ Hz)	136.11–133.86 (C _{2,4,6}), 131.47–132.73 (C _{1,3,5})
<i>cis</i> -Pt(CH ₂ GeMe ₃) ₂ (PPh ₂ Me) ₂	10.12 ($J_{\text{Pt-C}} = 647$ Hz)	3.86 ($J_{\text{Pt-C}} = 29$ Hz)	136.66 ($J_{\text{Pt-C}} = 20$ Hz, C ₁ , $J_{\text{P-C}} = 44$ Hz), 129.84 (C ₄), 133.56–132.82 (C _{2,6}), 128.47–128.24 (C _{3,5}), 14.86 ($J_{\text{Pt-C}} = 24$ Hz, Me, $J_{\text{P-C}} = 32$ Hz)
Pt(CH ₂ GeMe ₃) ₂ (dppe)	4.17 ($J_{\text{Pt-C}} = 566$ Hz, $J_{\text{P-C}} = 96,6$ Hz)	3.01 ($J_{\text{Pt-C}} = 28$ Hz)	133.51 ($J_{\text{Pt-C}} = 18$ Hz), C _{2,6} , ($J_{\text{P-C}} = 11$ Hz), 132.78 ($J_{\text{Pt-H}} = 27$ Hz, C ₁ , $J_{\text{P-C}} = 40$ Hz), 130.20 (C ₄), 128.39 ($J_{\text{Pt-C}} = 5$ Hz, C _{3,5}), 28.50 ($J_{\text{Pt-C}} = 32$ Hz, CH ₂ , $J_{\text{P-C}} = 33$ Hz)
Pt(CH ₂ SnMe ₃) ₂ (cod)	16.37 ($J_{\text{Pt-C}} = 73$ Hz, $J_{\text{P-C}} = 13$ Hz)	−7.89 ($J_{\text{Pt-C}} = 26$ Hz)	30.08 (CH ₂), 98.86 ("t"), $J_{\text{Pt-C}} = 65$ Hz, CH)
<i>cis</i> -Pt(CH ₂ SnMe ₃) ₂ (PPh ₃) ₂	9.73 ($J_{\text{Pt-C}} = 533$ Hz, $J_{\text{P-C}} = 99,6$ Hz)	1.84	136.05 (C _{2,6}), 128.84 (C _{3,5}), 133.10 (C ₁), 130.62 (C ₂)
<i>cis</i> -Pt(CH ₂ GeMe ₂ CH ₂ GeMe ₃)(Me)(PPh ₃) ₂	15.9 ($J_{\text{Pt-C}} = 662$ Hz, Pt–CH ₂ , $J_{\text{P-C}} = 95$ Hz), 7.31 (–CH ₂ –)	5.65 ($J_{\text{Pt-C}} = 612$ Hz, Pt–CH ₃ , $J_{\text{P-C}} = 95$ Hz), 4.23 ($J_{\text{Pt-C}} = 30$ Hz, GeMe ₂), 0.90 (GeMe ₃)	139.70 (C _{2,6}), 127.46 (C _{3,5}), 132.05 (C ₁), 129.07 (C ₄)

^a Obtained in chloroform-*d*₁.

^b Obtained in benzene-*d*₆.

plexes are intermediate between those of β -silicon [6] and β -carbon [7] analogues (Table 3). The increment in $^1J_{\text{Pt-C}}$ from *cis*-Pt(CH₂SiMe₂R)₂L₂ to *cis*-Pt(CH₂CMe₂R)₂L₂ has been proposed to indicate an increase

in carbon 2s character in the Pt–C bond (on the generally accepted assumption that the Fermi contact contribution predominates in determining magnitudes of $^1J_{\text{Pt-C}}$). This might have an electronic origin (Bent's [9])

Table 3
³¹P NMR characteristics of germylmethyl and stannylmethylplatinum(II) complexes ^a

Complex	δ ^a (ppm)	$J_{\text{Pt-P}}$ (Hz)	$J_{\text{P-P}}$ (Hz)
<i>cis</i> -Pt(CH ₂ GeMe ₃) ₂ (PPh ₃) ₂	25.47	1968	—
<i>cis</i> -Pt(CH ₂ GeMe ₃) ₂ (PPh ₂ Me) ₂	3.49	1958	—
Pt(CH ₂ GeMe ₃) ₂ (dppe)	44.10	1903	—
<i>cis</i> -Pt(CH ₂ SnMe ₃) ₂ (PPh ₃) ₂	27.85	1883	—
<i>cis</i> -Pt(CH ₂ GeMe ₂ CH ₂ GeMe ₃)(Me)(PPh ₃) ₂	29.11 ^b	1940	11
	25.84 ^c	1902	
<i>cis</i> -Pt(CH ₂ GeMe ₂ CH ₂ GeMe ₃)(Me)(PPh ₂ Me) ₂	5.59 ^c	1865	8
	5.28 ^b	1914	

^a Observed in chloroform-*d*₁.

^b *trans* to methyl.

^c *trans* to germylmethyl.

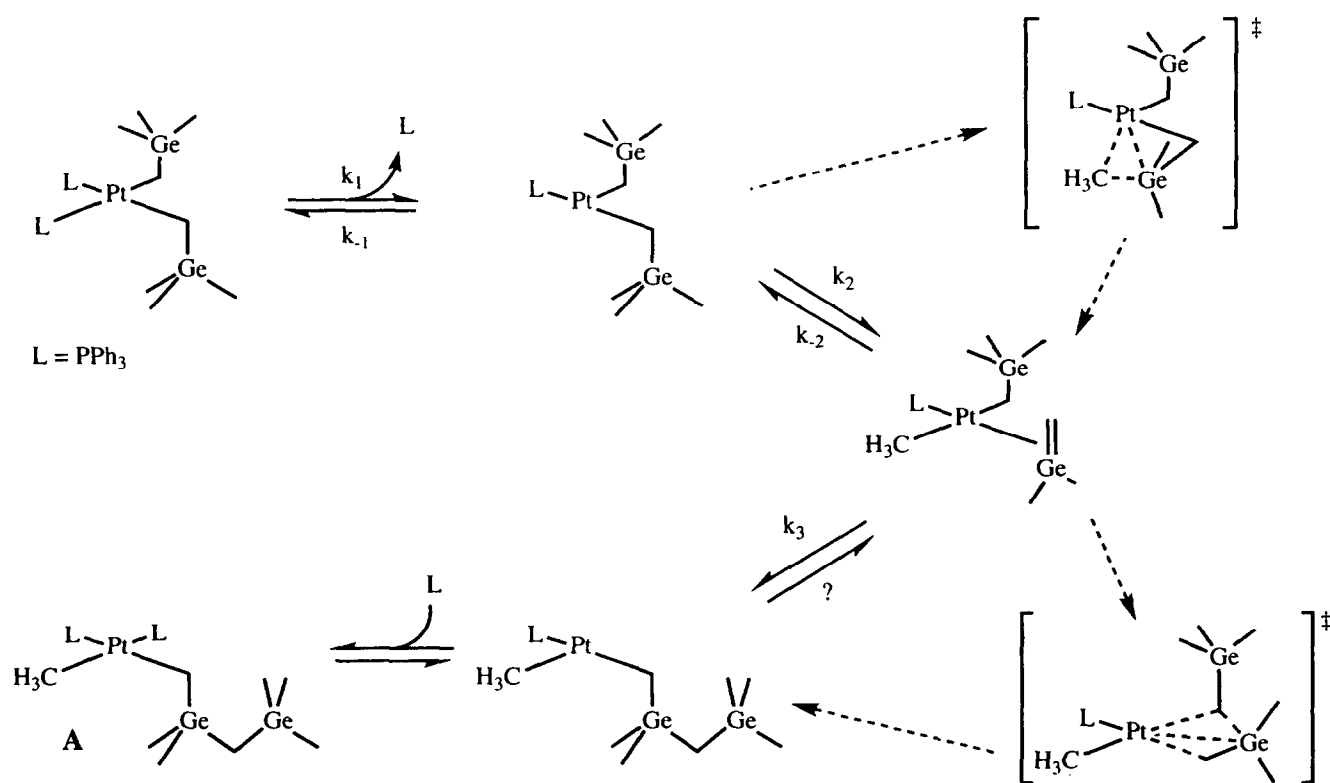
theory of isovalent hybridization) or may reflect steric distortion around the ligating carbon as EMe_2R varies [6–10]. The present results reveal that the trend in $^1J_{\text{Pt-C}}$ is continued for Ge and Sn in the series of complexes $\text{cis-Pt}(\text{CH}_2\text{EMe}_3)_2\text{L}_2$ and does reflect, broadly, the Pauling electronegativity of E. Although this accords with Bent's theory across a wider range of Group 14 β -substituted analogues than discussed previously [6,10,11], we have been unable to assess structural contributions by way of comparative crystallographic studies. We have established independently, however, that the generally higher value of $^1J_{\text{Pt-C}}$ for $\text{Pt}(\text{CH}_2\text{-CMe}_2\text{R})$ does indeed reflect a greater Pt–C bond strength. Calorimetric measurements on $\text{trans-Pt}(\text{Cl})(\text{CH}_2\text{EMe}_3)(\text{PMe}_3)_2$ reveal that $D(\text{Pt-CH}_2\text{CMe}_3)$ exceeds $D(\text{Pt-CH}_2\text{SiMe}_3)$ by $14 \pm 6 \text{ kJ mol}^{-1}$ [12].

2.2.3. ^{31}P NMR

$^{31}\text{P}\{^1\text{H}\}$ NMR data for these complexes are listed in Table 3. Spin–spin coupling of ^{31}P with ^{195}Pt results in

the expected 1:4:1 satellite patterns observed for all these complexes. Coupling constants $^1J_{\text{Pt-P}}$ are in the range 1880–1950 Hz, typical of *cis*-bis(phosphine)dialkylplatinum(II) complexes [13].

The estimation of relative *trans*-influence based on $^1J_{\text{Pt-P}}$ values [14] also usually assumes predominance of the Fermi contact term in transmission of spin–spin coupling. Hence, $^1J_{\text{Pt-P}}$ depends on the s character of the orbitals directed towards platinum by phosphorus and — by inference — the ligand opposite (see Section 2.1.2) and their relative interactions with the platinum 6s orbital. On these essentially electronic arguments, the low value of $^1J_{\text{Pt-P}}$ for the stannylmethyl ligand would indicate a notably higher *trans* influence for this group. As noted above, however, such variations might also derive from structural modifications — around platinum, in this case — as the steric requirement of EMe_3 changes. We have been unable to address this possibility by crystallographic comparisons of $\text{cis-Pt}(\text{CH}_2\text{-EMe}_3)_2\text{L}_2$.



Scheme 1.

2.2.4. IR spectroscopy

IR data are listed in Section 3. As with related platinum derivatives of the neopentyl family, the spectra — although characteristic — are of little diagnostic value owing to their complexity. Neither Pt–C nor Pt–P stretching modes could be assigned unequivocally. There is, however, correspondence with data for related complexes [6,10].

2.3. Thermolytic rearrangements

2.3.1. Rearrangement of *cis*-Pt(CH₂GeMe₃)₂(PPh₃)₂

The ³¹P{¹H} NMR spectrum of the single product from thermolysis of *cis*-Pt(CH₂GeMe₃)₂(PPh₃)₂ in toluene solution clearly indicates two non-equivalent ³¹P nuclei, both coupled to ¹⁹⁵Pt and both *trans* to alkyl substituents (Table 3). The ¹H NMR spectrum (Table 1) also shows some distinctive features, notably two distinct resonances for Ge(CH₃)_n hydrogen atoms, with integral ratios 2:3. The ¹³C{¹H} NMR spectrum (Table 2), similarly, reveals resonances due to two distinct Ge(CH₃)_n environments. One has ³J_{Pt–C} = 20 Hz, while the second displays no detectable coupling to ¹⁹⁵Pt. An additional aliphatic carbon resonance, which shows ³J_{Pt–C} coupling, is also observed. Further distinctive features are the Pt(CH_n) resonances at 15.90 and 5.65 ppm, both with ¹J_{Pt–C} coupling. All these were assigned unequivocally by an ADEPT experiment. The phase modulation in this technique produces normal absorption for CH₃ (and CH) carbon nuclei but inverted signals for CH₂ groupings. From these measurements it emerged that the lower field resonance corresponds to the fragment Pt–CH₂–Ge, while the higher field signal originates from a Pt–CH₃ group. The Ge(CH₃)_n assignments were confirmed and the aliphatic carbon displaying ³J_{Pt–C} coupling was shown to be a Ge–CH₂–Ge grouping.

A product structure **A** consistent with all observations, is depicted in Scheme 1. Analysis confirms an elemental composition identical with that of the parent species. Clearly, *cis*-Pt(CH₂GeMe₃)₂(PPh₃)₂ undergoes

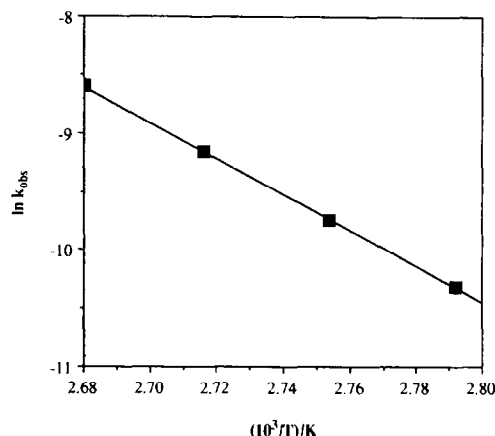


Fig. 1. Arrhenius correlation for rearrangement of *cis*-Pt(CH₂GeMe₃)₂(PPh₃)₂.

a thermolytic rearrangement analogous to that of *cis*-Pt(CH₂SiMe₃)₂(PPh₃)₂, affording *cis*-Pt(Me)(CH₂–GeMe₂CH₂GeMe₃)(PPh₃)₂.

Kinetic monitoring of the rearrangement by ³¹P NMR indicated smooth, quantitative formation of *cis*-Pt(Me)(CH₂GeMe₂CH₂GeMe₃)(PPh₃)₂ from Pt(CH₂GeMe₃)₂(PPh₃)₂. The reaction was first order in platinum substrate, independent of initial concentration (in the range 1.0 × 10^{−4}–8.0 × 10^{−3} mol dm^{−3}), for at least two half-lives. Rate constants are collected in Table 4. The rearrangement of *cis*-Pt(CH₂GeMe₃)₂(PPh₃)₂ was studied over the temperature range 85–100°C and the first order rate constants *k*_{obs} show linear Arrhenius correlation: log_e *k*_{obs} = (32.55 ± 0.9) − (15.4 ± 0.3)/*T* (Fig. 1). Hence, *A* = 1.36 × 10¹⁴ and *E*_a = 128 ± 3 kJ mol^{−1}, from which activation parameters may be estimated [15] as Δ*H*_{298 K}[‡] = 126 ± 3 kJ mol^{−1}, Δ*S*[‡] = +17 ± 7 J mol^{−1} K^{−1} and, hence, Δ*G*_{298 K}[‡] = 121 ± 5 kJ mol^{−1}.

Addition of triphenylphosphine to solutions of *cis*-Pt(CH₂GeMe₃)₂(PPh₃)₂ severely inhibits the reaction, which — as we have argued elsewhere — is consistent with dissociation of PPh₃ as a prerequisite for rearrangement. This is supported by the emergence of a linear correlation between 1/*k*_{obs} and [PPh₃], which is predicted [1] — assuming steady state concentrations of intermediates — for the pathway (and derived rate law) illustrated in Scheme 1. The rate constant *k*₁ for Pt–P scission, may be estimated — from the intercept of a plot of 1/*k*_{obs} vs. [PPh₃] — as (7.9 ± 0.09) × 10^{−5} s^{−1} (Fig. 2). This is significantly greater than those observed for overall rearrangement — and is similar in magnitude to that estimated [1] for phosphine dissociation from *cis*-Pt(CH₂SiMe₃)₂(PPh₃)₂ — reinforcing the contention that ligand loss is not rate limiting.

The broad comparability of activation parameters for this rearrangement and those of *cis*-Pt(CH₂SiMe₂R)₂L₂

Table 4
Rate constants for thermolytic rearrangement of *cis*-Pt(CH₂GeMe₃)₂(PPh₃)₂

Added [PPh ₃] (mol dm ^{−3})	<i>T</i> (K)	10 ⁵ <i>k</i> _{obs} (s ^{−1})
0.0	358	3.32 ± 0.11
0.0	363	5.84 ± 0.08
0.0	368	10.53 ± 0.10
0.0	373	18.50 ± 0.12
0.025	403	5.52 ± 0.08
0.10	403	2.81 ± 0.08
0.15	403	2.09 ± 0.09
0.20	403	1.72 ± 0.10

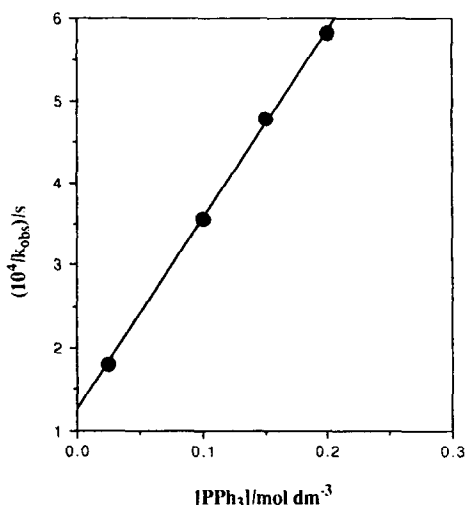


Fig. 2. Inverse rate constant correlation with phosphine concentration for rearrangement of *cis*-Pt(CH₂GeMe₃)₂(PPh₃)₂.

($\Delta H_{298\text{ K}}^\ddagger = 143\text{--}170\text{ kJ mol}^{-1}$; $\Delta S^\ddagger = +34\text{--}142\text{ J mol}^{-1}\text{ K}^{-1}$; $\Delta G_{298\text{ K}}^\ddagger = 125\text{--}140\text{ kJ mol}^{-1}$; R = Me, Ph, 4-C₆H₄F or 4-C₆H₄^tBu; L = PEt₃, PPhMe₂, PPh₂Me, PPh₃ or P(4-C₆H₄Me)₃), coupled with the fact that all show analogous inhibition in the presence of added phosphine [1], suggests parallel reaction mechanisms for *cis*-Pt(CH₂GeMe₃)₂(PPh₃)₂ and *cis*-Pt(CH₂-SiMe₂R)₂L₂, as outlined in Scheme 1. Initial phosphine dissociation is followed by transfer of a methyl group from germanium to platinum, generating an (η^2 -germene)platinum intermediate. We note that isolable germenes remain relatively rare [16] and, while a number of isolable (η^2 -silene)metal derivatives have emerged (although none as yet feature platinum) [17], we are aware of no reports, to date, of similar (η^2 -germene)metal species. Regiospecific migration of the remaining trimethylgermylmethyl group to the Ge terminus and phosphine recoordination generates the product. The deuteration studies which allowed the additional proposal of agostic interactions between platinum and neighbouring C—H bonds during reactions of *cis*-Pt(CH₂SiMe₂R)₂L₂ [1] have not been undertaken in this case.

In fact, direct comparison of germylmethyl and silylmethyl analogues under the same conditions, indicates that *cis*-Pt(CH₂GeMe₃)₂(PPh₃)₂ is somewhat more labile than *cis*-Pt(CH₂SiMe₃)₂(PPh₃)₂ ($\Delta H_{298\text{ K}}^\ddagger = 161 \pm 3\text{ kJ mol}^{-1}$; $\Delta S^\ddagger = +94 \pm 9\text{ J mol}^{-1}\text{ K}^{-1}$ and $\Delta G_{298\text{ K}}^\ddagger = 133 \pm 6\text{ kJ mol}^{-1}$) [1]. This is primarily an enthalpy-derived difference — $\Delta S^\ddagger$ for the germylmethyl complex is less favourable for *cis*-Pt(CH₂-GeMe₃)₂(PPh₃)₂ — and, presumably, reflects a more facile alkyl migration for germanium than for silicon.

2.3.2. Rearrangement of *cis*-Pt(CH₂GeMe₃)₂(PPh₂Me)₂ and *cis*-Pt(CH₂GeMe₃)₂(dppe)₂

Both complexes are qualitatively more inert than the corresponding triphenylphosphine complex. While *cis*-Pt(CH₂GeMe₃)₂(PPh₂Me)₂ requires temperatures in excess of 130°C to effect β -methyl transfer, Pt(CH₂GeMe₃)₂(dppe) resists rearrangement up to 180°C. NMR measurements indicate that a single platinum-containing product is formed quantitatively from Pt(CH₂GeMe₃)₂(PPh₂Me)₂ and that it is analogous to that produced by the triphenylphosphine complex (Tables 1 and 3). These observations parallel the trends in reactivity of *cis*-Pt(CH₂SiMe₃)₂L₂, which — as we have argued previously — reflect differences in the contribution to activation entropy from the Pt–P dislocation step, as the phosphine varies [1].

2.3.3. Rearrangement of *cis*-Pt(CH₂GeMe₃)₂(cod)

The thermolysis of *cis*-Pt(CH₂GeMe₃)₂(cod) at 90°C in toluene generates metallic platinum and various products which were characterized by gas chromatography (GC)–mass spectroscopy (MS). The major fragments identified were 1,1,3,3-tetramethyldi-1,3-germacyclobutane (60 mol.%) and 1,2-bis(trimethylgermyl)ethane (15 mol.%) as well as cyclooctadiene (85 mol.%). The presence of cycloocta-1,5-diene as reaction product was also confirmed by ¹H NMR. The kinetics of rearrangement showed poor reproducibility and were not quantified in detail.

Observation of 1,1,3,3-tetramethyldi-1,3-germacyclobutane as the preponderant organogermanium product is interesting. The silicon analogue is well known to arise from head-to-tail dimerisation of dimethylsilene [18] and Et₂Ge=CH₂ has been reported to dimerize in like fashion [19]. Plausibly, dimethylgermene intermediates do arise via β -methyl transfer. In that event, however, the subsequent pattern of reactivity differs from corresponding phosphine complexes, arguably owing to an inherently greater dissociation lability of alkene–platinum derivatives. Whether germene oligomerization might be the result of a metal-centred process or is a natural consequence of release of Me₂Ge=CH₂ cannot be concluded from these results (although there was no evidence of products from reaction of free dimethylgermene with, for example, cyclooctadiene). Similarly, it has not been established that 1,2-bis-(trimethylgermyl)ethane is the product of intramolecular reductive C–C elimination from platinum(II). This is an intriguing possibility, however, since such reactivity is still relatively rare for divalent platinum [3].

2.3.4. Rearrangement of *cis*-Pt(CH₂SnMe₃)₂(PPh₃)₂

Thermolysis of *cis*-Pt(CH₂SnMe₃)₂(PPh₃)₂ in toluene was not a clean rearrangement. The reaction(s) generated Pt(PPh₃)₃ as the only soluble phosphine–

platinum species as well as several organic and organotin species among which 1,1,3,3-tetramethyl-1,3-distannacyclobutane was identified (by GC–MS) as the major organotin product (about 50 mol.%). There was no spectroscopic evidence for the formation of *cis*-Pt(Me)(CH₂SnMe₂CH₂SnMe₃)(PPh₃)₂ at any stage during reaction. We conclude that, while β -methyl transfer would seem a likely step in the rearrangement leading to distannacyclobutane, *cis*-Pt(Me)(CH₂SnMe₂CH₂SnMe₃)(PPh₃)₂, if formed, is itself labile under the prevailing conditions.

3. Experimental details

3.1. General comments

Elemental analyses were by Imperial College Micro-analytical Laboratories. NMR spectra were recorded on Brüker AM500 (¹H, 500.17 MHz; ¹³C, 125.78 MHz; ³¹P, 202.48 MHz), Brüker WM250 (¹H, 250.15 MHz; ¹³C, 62.9 MHz; ³¹P, 101.30 MHz), JEOL GSX270 (¹H, 270.17 MHz; ¹³C, 67.90 MHz) and JEOL FX90Q (¹H, 89.55 MHz; ³¹P, 36.21 MHz) spectrometers. GC–MS analyses, performed at Kings College as part of the ULIRS, were obtained on a Kratos MS25 mass spectrometer linked to a Sigma 3 gas-liquid chromatograph. IR data were collected on a Perkin–Elmer 683 instrument as 4% KBr dispersions.

Triphenylphosphine and 1,2-bis(diphenylphosphino)ethane were obtained from Aldrich Chemical Co. and were recrystallized from propan-2-ol prior to use. Diphenylmethylphosphine was used as supplied by Strem Chemicals. PtCl₂(cod) [20] and Sn(CH₂Cl)Me₃ [4] were prepared according to published procedures. Toluene-*d*₈ and benzene-*d*₆, supplied by MSD Isotopes, were distilled from sodium–benzophenone anion and stored under argon prior to use.

3.2. Synthesis

3.2.1. Preparation of Ge(CH₂Cl)Me₃

In a modification of a published procedure [3], a solution of GeCl₄ (7.00 g, 30 mmol, 3.70 cm³) in diethyl ether (70 cm³) was cooled to –60°C and 0.05 g of copper powder (which had been washed with dilute hydrochloric acid and dried overnight at 100°C in vacuo) was added. One equivalent of a cold solution of anhydrous diazomethane in diethyl ether was then introduced dropwise, with vigorous stirring, via a polytetrafluoroethylene cannula. The solution was maintained at –60°C for a further 2 h and then allowed to warm slowly to ambient temperature.

Removal of the ether afforded a pale-yellow liquid (4.0 g) which emerged (¹H NMR) as a 4:1 mixture of Ge(CH₂Cl)Cl₃ and Ge(CH₂Cl)₂Cl₂. This mixture of

products was added cautiously to a threefold excess of MgMeBr (250 cm³ of a 1.10 M solution in diethyl ether (275 mmol)) — CARE is required, since a vigorous reaction occurs during addition — and was then heated at reflux for 10 h. The resulting mixture was quenched with saturated aqueous ammonium chloride (30 cm³), filtered and the ethereal layer separated from the aqueous phase, which was washed with diethyl ether (3 × 20 cm³). The organic extracts were combined and dried over anhydrous magnesium sulphate. Removal of ether afforded a mixture of Ge(CH₂Cl)₂Me₃ and Ge(CH₂Cl)₂Me₂, which were separated by distillation.

Ge(CH₂Cl)₂Me₃: Yield, 1.96 g; 12.0 mmol, (40%); boiling point (b.p.), 110–115°C. ¹H NMR: δ 2.91 (s, CH₂), 0.24 (s, CH₃) ppm.

Ge(CH₂Cl)₂Me₂: Yield, 0.46 g, 2.3 mmol, (8%); b.p., 130–135°C. ¹H NMR: δ 3.05 (s, CH₂), 0.37 (s, CH₃) ppm.

3.2.2. Preparation of bis-[(trimethylgermyl)methyl]-(cycloocta-1,5-diene)platinum(II)

To a stirred suspension of PtCl₂(cod) (1.14 g, 3.00 mmol) in diethyl ether (30 cm³), at 78°C, was added, over a period of 30 min, a solution of Mg(CH₂GeMe₃)Cl (20 cm³ of a 0.35 M solution in diethyl ether (7.0 mmol)). The mixture was then stirred for 7 h whilst warming to ambient temperature and then for a further 3 days. The resulting golden-brown solution was quenched with a saturated aqueous ammonium chloride solution (20 cm³) and filtered; the ethereal layer was separated from the aqueous phase, which was then washed with diethyl ether (3 × 20 cm³). The organic extracts were combined, dried over anhydrous magnesium sulphate and decolourized with charcoal. Removal of the ether afforded the product as a colourless microcrystalline solid (yield, 1.22 g, 2.16 mmol (72%)).

Anal. Found: C, 34.1; H, 5.9. Calc.: C, 34.0; H, 5.7%. IR: ν 3048w, 2991s, 2918s, 2894s, 2838sh, 2433w, 1971w, 1811w, 1643w, br, 1580w, 1516m, 1474m, 1431m, 1404m, 1385sh, 1339m, 1261s, 1225vs, 1181m, 1160m, 1086s, br, 1018s, br, 993m, 979m, 959m, 863m, 816vs, br, 763s, br, 646s, br, 587s, br, 565s, 535m, 453m, 390m, br cm^{–1}.

3.2.3. Bis-[(trimethylstannyl)methyl]-(cycloocta-1,5-diene)platinum(II)

This was prepared by similar method. The product was a light-sensitive pale-brown, low melting point solid (yield, 0.8 g, 1.29 mmol (75%)).

Anal. Found: C, 28.9; H, 5.1. Calc.: C, 29.6; H, 5.2%. IR: ν 2898s, 2941s, 2912s, 2869s, 2335w, 1669w, br, 1516m, 1475m, 1435m, 1339m, 1311w, 1261m, 1187m, 1180m, 1160w, 1097w, br, 1036w, br, 967w, 934w, 862w, 820m, 763vs, br, 604s, br, 520s, br, 454w cm^{–1}.

3.2.4. Preparation of *cis*-bis-[(trimethylgermyl)methyl]-bis-(triphenylphosphine)platinum(II)

Pt(CH₂GeMe₃)₂(cod) (0.20 g, 0.35 mmol) and PPh₃ (0.184 g, 0.70 mmol) were dissolved in toluene (20 cm³) and heated at 70°C in a grease-free (Teflon-stoppered) vessel for 3 weeks. Concentration in vacuo and cooling afforded the product as a colourless crystalline solid (yield, 0.29 g, 0.30 mmol (86%)).

Anal. Found: C, 51.6; H, 5.0. Calc.: C, 51.6; H, 5.1%. IR: ν 3055m, 2963m, 2890m, 1587w, 1484m, 1432s, 1262s, br, 1220m, 1098vs, br, 1027s, br, 906vs, br, 751m, 740m, 706m, 658m, 640m, 580m, 560m, 539s, 524s, 396m, br cm⁻¹.

3.2.5. *Cis*-bis-(trimethylstannylmethyl)-bis-(triphenylphosphine)platinum(II)

This was prepared by an analogous procedure. The product was a colourless crystalline solid (yield, 0.42 g, 0.39 mmol (90%)).

Anal. Found: C, 50.0; H, 2.7. Calc.: C, 50.2; H, 2.8%. IR: ν 3054w, 2960w, 2898w, 1958w, 1895w, 1812w, 1585w, 1572w, 1479m, 1434s, 1309w, 1261w, 1182w, br, 1095s, 1027m, 811m, br, 742m, br, 693s, br, 585m, br, 582m, br cm⁻¹.

3.2.6. *Cis*-bis-(trimethylgermylmethyl)-bis-(diphenylmethylphosphine)platinum(II)

This was also prepared by an analogous procedure. The product was a colourless microcrystalline solid (yield, 0.95 g, 1.11 mmol (95%)).

Anal. Found: C, 47.5; H, 5.6. Calc.: C, 47.5; H, 5.6%. IR: ν 3075m, 2959m, 2930m, 2894s, 1954w, 1900w, 1808w, 1587w, 1572w, 1482m, 1435s, 1420m, 1376w, 1327w, 1308w, 1215m, 1192w, 1161w, 1096s, 1028w, 1000m, 971m, 884s, 809s, br, 749s, 737s, 695s, br, 646s, 582s, br, 560w, 512vs, 484m, 432m, 418m, 361w cm⁻¹.

3.2.7. Bis-(trimethylgermylmethyl)[1,2-bis-(dimethylphosphino)ethane]platinum(II)

This was also prepared by an analogous procedure. The product was a colourless crystalline solid (yield, 0.76 g, 0.89 mmol (95%)).

Anal. Found: C, 47.7; H, 5.3. Calc.: C, 47.6; H, 5.4%. IR: ν 3068m, 2958m, 2895s, 2861s, 1966w, 1900w, 1824w, 1588m, 1483m, 1436s, 1410m, 1309m, 1275m, 1232m, 1185m, 1107m, 1077w, 1027m, 999w, 961m, 878w, 828vs, br, 743s, 693s, br, 652m, 581s, 533s, 482m, 467m, 438m, 399w, 355w cm⁻¹.

3.3. Thermolytic data

3.3.1. Thermolyses of *cis*-Pt(CH₂GeMe₃)₂L₂

Measurements were performed in medium-walled NMR sample tubes of 5 mm diameter equipped with coaxial Teflon valves (J. Young Scientific Ltd., Acton).

Samples were prepared by freeze-thaw degassing freshly prepared toluene-*d*₈ or benzene-*d*₆ solutions (1.0 × 10⁻⁴–8.0 × 10⁻³ mol dm⁻³) through five deoxygenating cycles and then sealed under argon. When thermolyses were conducted in the presence of triphenylphosphine, solutions of known concentrations of PPh₃ were prepared and then transferred to reaction tubes containing the appropriate amount of platinum substrate.

The tube was maintained at the required temperature (±0.1°C) with a variable-temperature probe heater in either the JEOL FX90Q or the Brüker WM250 spectrometers or by immersion in a Haake W13 thermoregulated silicone oil bath (±0.2°C). Progress of rearrangements was monitored quantitatively by ¹H or ³¹P NMR spectroscopy. Data were analysed using linear regression or exponential curve fitting routines supplied with the kinetics workstation of the Applied Photophysics SF-17 stopped flow spectrometer. Errors quoted are ±3 standard deviations. Product solutions from several thermolyses of *cis*-Pt(CH₂GeMe₃)₂(PPh₃)₂ were combined, concentrated and cooled to afford colourless crystals of *cis*-Pt(Me)(CH₂GeMe₂CH₂GeMe₃)(PPh₃)₂. Anal. Found: C, 51.4, H, 5.0. Calc.: C, 51.6; H, 5.1%. Pt(CH₂GeMe₃)₂(dppe) was heated in toluene-*d*₈ at 180°C for several weeks but no reaction was observed.

3.3.2. Thermolysis of bis-(trimethylgermylmethyl)-(cycloocta-1,5-diene)platinum(II)

A 5 mm medium-walled NMR tube containing Pt(CH₂GeMe₃)₂(cod) (5.0 × 10⁻⁴ mol dm⁻³) in benzene-*d*₆ was heated at 90°C. As thermolysis progressed platinum metal was deposited in increasing amounts. After 7 h, the parent compound had disappeared and the only species identifiable by ¹H NMR was cycloocta-1,5-diene. The volatile products were removed in vacuo and characterized by GC–MS as follows: 25 m BP1 column, 0.22 mm diameter, 1 μm coating; helium carrier gas, flow rate, 2 cm³ min⁻¹; 1 μl injected, 25:1 split ratio; injector temperature, 220°C; initial temperature, 120°C; final temperature, 275°C; ramp rate, 4°C min⁻¹.

3.3.3. Thermolysis of *cis*-bis-(trimethylstannylmethyl)-bis-(triphenylphosphine)platinum(II)

A 5 mm medium-walled NMR tube containing *cis*-Pt(CH₂SnMe₃)₂(PPh₃)₂ (0.10 g, 0.10 mmol) in toluene-*d*₈ (2 cm³) was heated at 90°C. As thermolysis progressed, the solution turned dark brown. After 14 days, signals due to the parent complex had disappeared and a new resonance with platinum satellites, at δ = 29.44 ppm in the ³¹P NMR spectrum had appeared (¹J_{Pt–P} = 4360 Hz), ascribed to Pt(PPh₃)₃ [21]. The ¹H NMR spectrum of this product indicated the presence of phenyl groups as the only hydrogen-bearing species (δ = 6.75–7.95 ppm). The volatile products were re-

moved in vacuo and characterized by GC–MS. GC–MS conditions were as follows: 25 m BP1 column, 0.22 mm diameter, 1 mm coating; helium carrier gas at 10 lbf in⁻², flow rate, 2 cm³ min⁻¹; 1 µl injected using a 25:1 split ratio; injector temperature, 220°C; initial temperature, 120°C; ramp rate, 4°C min⁻¹; final temperature, 275°C.

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