Reactions of Triorganosilanes with Tris-μ-(t-butyl isocyanide)-tris(t-butyl isocyanide)-*triangulo*-triplatinum: Crystal Structure of the Complex $[\{Pt(CH{:}NBu^t)(SiMePh_2)(CNBu^t)\}_2]$ †

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The triplatinum compound $[Pt_3(CNBu^t)_6]$ reacts with triorganosilanes SiR_3H [SiR_3 = $SiMe_3$, $SiEt_3$, $SiMe_2Ph$, $SiMePh_2$, $SiPh_3$, or $Si(OEt)_3$] to give diplatinum complexes $[\{Pt(CH{:}NBu^t)(SiR_3)(CNBu^t)\}_2]$, arising from insertion of an isocyanide ligand into a Pt–H bond, formed in an initial oxidative-addition step. The reaction with $SiPh_3H$ also afforded the bis(silyl)platinum complex $[Pt(SiPh_3)_2(CNBu^t)_2]$. The structure of the diplatinum compounds has been established by a single-crystal *X*-ray diffraction study of $[\{Pt(CH{:}NBu^t)(SiMePh_2)(CNBu^t)\}_2]$ which showed that the two platinum atoms, each in a square-planar environment, are bridged by $HC{:}NBu^t$ ligands to give a six-membered ring of boat conformation. The terminal ligands are such that the silyl groups are *trans* to the N atoms of the central ring. The Pt–N bond is exceptionally long (2.17_3 Å) and the *trans*-annular Pt ⋯ Pt distance of 3.05_6 Å suggests little metal–metal interaction. Crystals of the title compound are monoclinic, space group $P2_1/c$, with $Z = 4$ in a unit cell of dimensions $a = 11.649(4)$, $b = 18.778(15)$, $c = 21.825(15)$ Å, and $\beta = 97.31(3)°$. The structure has been solved by heavy-atom methods from 7 096 intensity data [$I \geqslant 2.0\sigma(I)$] measured on a four-circle diffractometer at −50 °C, and refined to *R* 0.057. The compound $[Pt_3(CNBu^t)_6]$ reacts with $GeMe_3H$ to give an analogous diplatinum complex $[\{Pt(CH{:}NBu^t)(GeMe_3)(CNBu^t)\}_2]$.

As part of studies on zerovalent platinum complexes the triplatinum compound $[Pt_3(CNBu^t)_6]$ [1] was prepared from bis(cyclo-octa-1,5-diene)platinum,[2] and we have shown that the former readily undergoes oxidative-addition reactions with unsaturated fluorocarbons,[3] diphenylcyclopropenone,[4] and acetylenes,[5,6] and forms adducts $[Pt(CNBu^t)_2(RCH{:}CHR)]$ with olefins having electron-withdrawing substituents.[7] In this paper we report on the reactivity of $[Pt_3(CNBu^t)_6]$ towards triorganosilanes. This study was prompted by the discovery of novel di-μ-hydrido-diplatinum complexes $[\{Pt(\mu\text{-}H)(SiR_3)(PR'_3)\}_2]$ formed by oxidative addition of SiR_3H to $[Pt(C_2H_4)_2(PR'_3)]$.[8]

RESULTS AND DISCUSSION

In general, reactions between silanes SiR_3H or $SiCl_3H$ and the platinum(0) species $[Pt(PPh_3)_4]$ or $[Pt(dppe)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) afford bis(silyl)platinum compounds and release hydrogen rather than form hydridoplatinum complexes.[9] However, Eaborn *et al.*[10] have shown that the ethylene complex $[Pt(C_2H_4)(PPh_3)_2]$ reacts with silanes SiR_3H to give products $[PtH(SiR_3)(PPh_3)_2]$ expected from a simple oxidative-elimination reaction. Since the reactivity patterns of both $[Pt(C_2H_4)(PPh_3)_2]$ and $[Pt_3(CNBu^t)_6]$ correspond to these compounds acting as formal sources of 14-electron $[PtL_2]$ (L = PPh_3 or $CNBu^t$) moieties, it was anticipated that the isocyanide complex would yield hydrides $[PtH(SiR_3)(CNBu^t)_2]$ analogous to the phosphine complexes $[PtH(SiR_3)(PPh_3)_2]$. However, Clark and co-workers [11] have found that the salts $[\{PtH(CNC_6H_4Me\text{-}4)(PR_3)_2\}Cl]$ undergo insertion of isocyanide into the Pt–H bonds to give formimidoyl complexes $[PtCl(CH{:}NC_6H_4Me\text{-}4)(PR_3)_2]$. Hence the nature of the final products of reactions between SiR_3H and $[Pt_3(CNBu^t)_6]$ was of interest.

In diethyl ether, the silanes SiR_3H [SiR_3 = $SiMe_3$, $SiEt_3$, $SiMe_2Ph$, $SiMePh_2$, $SiPh_3$, or $Si(OEt)_3$] react with $[Pt_3(CNBu^t)_6]$ at room temperature to give white or pale yellow crystalline complexes (1)—(6). Qualitatively, the rate of reaction, as judged by the rate of consumption of the triplatinum compound, is in the order $SiMe_3H < SiEt_3H < Si(OEt)_3H < SiMe_2PhH < SiMePh_2H \simeq SiPh_3H$. The i.r. spectra of the products (Table 1) each

TABLE 1

Infrared spectra (cm^{-1}) of the diplatinum complexes $[\{Pt(CH{:}NBu^t)(MR_3)(CNBu^t)\}_2]$ (M = Si or Ge) *

Compound		$\nu_{max.}$
(1)	MR_3 = $SiMe_3$	2 166vs, 2 080w, 1 553w(br), 1 544m, 1 372m, 1 362m, 1 234s, 1 212s, 1 200s, 883w, 830s(br), 778w, 742m, 666m, 623m, 522w, 504w, 456w
(2)	= $SiEt_3$	2 170vs, 2 074w, 1 558w, 1 535m, 1 416w, 1 372m, 1 363m, 1 234m, 1 214s, 1 202s, 1 008s, 965w, 948w, 883w, 779w, 723s, 712s, 687s, 654w, 593m, 522w, 504w, 456w, 435w
(3)	= $SiMe_2Ph$	3 050mw, 2 185vs, 2 082w, 1 566mw, 1 541m, 1 432m, 1 391m, 1 378m, 1 370m, 1 316w, 1 269w, 1 239s, 1 207s, 1 100m, 1 068vw, 894w, 840sm, 808s, 787w, 768vw, 751wm, 737s, 712m, 692w, 670w, 657m, 528m, 512w, 480w, 461w, 430w
(4)	= $SiMePh_2$	3 070m, 2 192vs, 2 075w, 1 560mw, 1 540m, 1 430s, 1 387m, 1 373m, 1 364m, 1 325w, 1 306vs, 1 260w, 1 237ms, 1 206s(br), 1 100s, 1 063w, 1 018w, 997w, 920w, 882mw, 792vs, 782vs, 751s, 743s, 710vs, 687w, 667ms, 523wm, 506vs, 472s, 456w, 437ms, 418ms
(5)	= $SiPh_3$	3 072m, 3 050m, 2 182vs, 2 074w, 1 952w, 1 880w, 1 820w, 1 764w, 1 582w, 1 563w, 1 550(sh), 1 538m, 1 430s, 1 396m, 1 374m, 1 360m, 1 312w(br), 1 259w, 1 236m, 1 205s, 1 101s, 1 029w, 1 000w, 891wm, 788w, 748s, 710vs, 680m, 526vs, 504s, 493s, 452w, 430m
(6)	= $Si(OEt)_3$	2 180vs, 2 078w, 1 564w, 1 540wm, 1 387m, 1 363m, 1 238m, 1 207s, 1 172m, 1 107vs, 1 078vs, 942s, 889w, 762ms, 707ms, 515m, 460w
(8)	= $GeMe_3$	2 142vs, 2 070mw, 1 558w, 1 533w, 1 374s, 1 234ms, 1 224ms, 1 210s(br), 805s, 737mw, 571s, 552ms, 525s, 453m

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† Bis-μ-(*N*-t-butylformimidoyl-*CN*)-bis[(methyldiphenylsilyl)-(t-butyl isocyanide)platinum].

TABLE 2

Hydrogen-1 and ^{13}C n.m.r. data [a]

	Complex	^{1}H (τ)	^{13}C (δ/p.p.m.)
(1) [b]	$[\{Pt(CH{:}NBu^t)(SiMe_3)(CNBu^t)\}_2]$	$-$0.52 [s, CH, *J*(PtH) 133, 69], 8.53 and 8.86 (s, Bu^t), 9.88 [s, Me_3Si, *J*(PtH) 34]	199.6 [PtCH, *J*(PtC) 946, 11], 62.2 [*C*Me_3, *J*(PtC) 17], 55.8 (*C*Me_3), 29.7 (Me), 4.8 [MeSi, *J*(PtC) 85]
(2)	$[\{Pt(CH{:}NBu^t)(SiEt_3)(CNBu^t)\}_2]$	$-$0.90 [s, CH, *J*(PtH) 139, 80], 8.58 (m, *Me*CH_2Si), 8.71 (s, Bu^t), 8.89 (s, Bu^t), *ca.* 8.9 (m, CH_2Si)	199.3 (PtCH), 62.6 (*C*Me_3), 55.8 (*C*Me_3), 29.9 and 29.7 (Me), 10.2 [*Me*CH_2Si, *J*(PtC) 31], 8.2 [CH_2Si, *J*(PtC) 73]
(3)	$[\{Pt(CH{:}NBu^t)(SiMe_2Ph)(CNBu^t)\}_2]$	$-$0.75 [s, CH, *J*(PtH) 130, 84], 1.85 and 2.64 (m, Ph), 8.80 and 9.13 (s, Bu^t), 9.16 [s, MeSi, *J*(PtH) 32], 9.28 [s, MeSi, *J*(PtH) 32]	199.1 (PtCH), 148.6 [Ph(C^1)Si], 135.1 [Ph(C^2)Si, *J*(PtC) 23], 127.1 [Ph(C^3,C^4)Si], 62.5 (*C*Me_3), 55.8 (*C*Me_3), 29.8 (Me), 29.4 (Me), 3.6 (MeSi), 3.1 [MeSi, *J*(PtC) 79]
(4) [b,c]	$[\{Pt(CH{:}NBu^t)(SiMePh_2)(CNBu^t)\}_2]$	$-$0.02 [s, CH, *J*(PtH) 127, 88], 2.32 and 2.78 (m, Ph), 8.88 and 9.01 (s, Bu^t), 9.28 [s, MeSi, *J*(PtH) 34]	197.9 [PtCH, *J*(PtC) 914], 146.3 and 145.2 [Ph(C^1)Si], 135.7 and 135.4 [Ph(C^2)Si], 127 [Ph(C^3,C^4)Si], 62.7 (*C*Me_3), 56.4 (*C*Me_3), 1.3 [MeSi, *J*(PtC) 79]
(5)	$[\{Pt(CH{:}NBu^t)(SiPh_3)(CNBu^t)\}_2]$	$-$0.06 [s, CH, *J*(PtH) 130, 89], 2.03 and 2.86 (m, Ph), 9.01 and 9.31 (s, Bu^t)	198.2 [PtCH, *J*(PtC) 908], 143.8 [Ph(C^1)Si, *J*(PtC) 57], 137.4 [Ph(C^2)Si, *J*(PtC) 24], 127.1 [Ph(C^3,C^4)], 63.4 (*C*Me_3), 56 (*C*Me_3), 29.5 and 29.2 (Me)
(6)	$[\{Pt(CH{:}NBu^t)[Si(OEt)_3](CNBu^t)\}_2]$	$-$0.89 [s, CH, *J*(PtH) 137, 80], 5.74 [q, CH_2, *J*(HH) 7], 8.49 [t, C$H_3$$CH_2$-Si, *J*(HH) 7], 8.81 (s, Bu^t)	196.3 (PtCH), 61.4 (*C*Me_3), 55.7 [CH_2, *J*(PtC) 22], 28.5 and 28.1 (Me), 17.8 ($MeCH_2$)
(7) [d]	$[Pt(SiPh_3)_2(CNBu^t)_2]$	2.42 and 2.85 (m, Ph), 9.36 (s, Bu^t)	145.8 [Ph(C^1)Si, *J*(PtC) 29], 136.9 [Ph(C^2)Si, *J*(PtC) 12], 127.4 [Ph(C^3,C^4)], 58.4 [*C*Me_3, *J*(PtC) 14], 29.1 (Me)
(8)	$[\{Pt(CH{:}NBu^t)(GeMe_3)(CNBu^t)\}_2]$	$-$1.03 [s, CH, *J*(PtH) 114, 100], 8.96 and 9.06 (s, Bu^t), 9.23 [s, *J*(PtH) 26]	

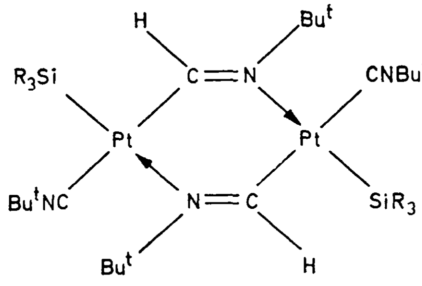
[a] Measured in [$^2H_6$]benzene unless otherwise indicated; ^{13}C chemical shifts relative to $SiMe_4$ (0.0 p.p.m.), coupling constants (*J*) in Hz. [b] Hydrogen-1 spectrum in [$^2H_6$]acetone. [c] Carbon-13 spectrum in [$^2H_6$]acetone. [d] Hydrogen-1 spectrum in [$^2H_1$]chloroform and ^{13}C spectrum in CH_2Cl_2.

showed a very strong band near 2 180 cm^{-1} characteristic of a terminally bonded $CNBu^t$ ligand; the absence of two such absorptions indicated that *cis*-$[Pt(CNBu^t)_2]$ groups are not present in these molecules. The spectra also showed a band of medium intensity near 1 540 cm^{-1} in the region expected for the absorption of a C:N group.

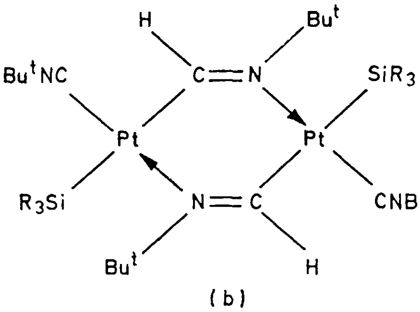
The ^{1}H n.m.r. spectra of all the complexes (Table 2) displayed a singlet resonance between τ 0 and -1, as previously observed[11] for compounds containing the Pt·C*H*:NR imidoyl ligand. However, this resonance showed coupling to two platinum nuclei establishing that compounds (1)—(6) were diplatinum species. Thus, for the product (4) from $SiMePh_2H$ the resonance at τ -0.02 shows two sets of ^{1}H–^{195}Pt couplings (127 and 88 Hz), together with satellite resonances due to molecules with two ^{195}Pt nuclei [$|J(PtH) + J(Pt'H)| = 215$ Hz]. Moreover, the ^{13}C n.m.r. spectra (Table 2) showed a resonance at about 200 p.p.m. with *J*(PtC) *ca.* 900 Hz, a value characteristic of a carbon atom σ-bonded to platinum.[12] This signal in the spectrum of (1) showed coupling (*ca.* 10 Hz) with a second platinum nucleus. The dimeric nature of the complexes was further confirmed by molecular weights measured in solution.

The spectroscopic properties can be accommodated by six-membered ring structures (1a)—(6a) or (1b)—(6b). The relative simplicity of the ^{1}H n.m.r. spectra, *e.g.* only two resonances for the Bu^t groups and one PtC*H* signal for each compound, corresponded to the formation of one isomer.

In order to fully understand the geometry of these ring systems and to define which isomer was actually produced, a single-crystal *X*-ray diffraction study was undertaken with compound (4) for which suitable crystals were available. Such an investigation was an obvious prerequisite for any consideration of mechanism.



(a)



(b)

SiR_3
(1) $SiMe_3$
(2) $SiEt_3$
(3) $SiMe_2Ph$
(4) $SiMePh_2$
(5) $SiPh_3$
(6) $Si(OEt)_3$

TABLE 3

Atomic-positional parameters (fractional co-ordinates) for complex (4a) with estimated standard deviations in parentheses

Atom	x	y	z
Central diplatina-ring system			
Pt(1)	0.490 88(4)	0.168 08(2)	0.099 23(2)
C(1)	0.605 3(11)	0.161 0(6)	0.038 5(5)
H(1)	0.590	0.140	−0.006
N(2)	0.704 7(8)	0.190 6(5)	0.052 8(4)
Pt(2)	0.720 63(4)	0.242 00(2)	0.142 59(2)
C(2)	0.708 4(12)	0.140 5(6)	0.176 5(6)
H(2)	0.800	0.120	0.200
N(1)	0.616 8(8)	0.105 9(5)	0.159 1(4)
t-Butyl ligands on central ring			
C(11)	0.600 5(11)	0.029 7(6)	0.176 4(6)
C(12)	0.507 8(13)	0.028 4(7)	0.219 7(7)
H(121)	0.420	0.040	0.200
H(122)	0.507	−0.017	0.240
H(123)	0.528	0.063	0.253
C(13)	0.564 4(15)	−0.009 3(7)	0.115 7(8)
H(131)	0.640	0.000	0.100
H(132)	0.550	−0.060	0.119
H(133)	0.501	0.011	0.090
C(14)	0.712 1(12)	−0.004 5(6)	0.208 2(7)
H(141)	0.760	0.000	0.180
H(142)	0.744	0.020	0.246
H(143)	0.705	−0.054	0.219
C(21)	0.801 7(11)	0.181 9(7)	0.013 6(6)
C(22)	0.895 0(13)	0.143 2(10)	0.053 9(7)
H(221)	0.920	0.160	0.100
H(222)	0.871	0.095	0.056
H(223)	0.963	0.144	0.034
C(23)	0.844 6(14)	0.257 6(8)	0.001 2(8)
H(231)	0.880	0.280	0.040
H(232)	0.898	0.258	−0.028
H(233)	0.779	0.287	−0.015
C(24)	0.768 0(13)	0.145 9(9)	−0.047 6(6)
H(241)	0.860	0.360	0.440
H(242)	0.722	0.166	−0.084
H(243)	0.795	0.100	−0.061
Terminal silyl ligands			
Si(1)	0.370 2(3)	0.228 7(2)	0.024 5(2)
C(51)	0.441 1(16)	0.272 3(9)	−0.040 3(7)
H(511)	0.515(16)	0.193(10)	0.486(8)
H(512)	0.449(12)	0.259(7)	0.441(6)
H(513)	0.376(14)	0.294(9)	−0.061(7)
C(61)	0.255 3(11)	0.165 2(6)	−0.013 1(6)
C(62)	0.192 3(15)	0.176 3(8)	−0.070 4(7)
H(62)	0.216(16)	0.291(10)	0.413(8)
C(63)	0.110 5(17)	0.127 8(10)	−0.096 9(8)
H(63)	0.090(11)	0.358(7)	0.378(5)
C(64)	0.085 5(13)	0.068 4(8)	−0.066 5(7)
H(64)	0.002(19)	0.467(12)	0.419(9)
C(65)	0.145 9(13)	0.056 0(7)	−0.008 7(7)
H(65)	0.129(14)	0.016(9)	0.012(7)
C(66)	0.228 0(12)	0.102 9(8)	0.018 3(7)
H(66)	0.278(18)	0.108(11)	0.044(9)
C(71)	0.290 1(11)	0.304 7(6)	0.057 2(5)
C(72)	0.172 5(13)	0.317 8(7)	0.043 3(7)
H(72)	0.120(14)	0.299(9)	0.010(7)
C(73)	0.119 0(14)	0.374 5(8)	0.067 7(8)
H(73)	0.042(15)	0.386(9)	0.051(8)
C(74)	0.183 5(16)	0.421 5(7)	0.108 6(8)
H(74)	0.132(20)	0.458(12)	0.130(9)
C(75)	0.301 4(16)	0.410 8(7)	0.124 2(7)
H(75)	0.344(8)	0.440(5)	0.155(4)
C(76)	0.350 7(14)	0.354 1(7)	0.097 9(7)
H(76)	0.414(10)	0.346(6)	0.099(5)
Si(2)	0.725 3(3)	0.285 4(2)	0.242 2(1)
C(81)	0.575 1(12)	0.307 5(7)	0.261 7(7)
H(811)	0.570	0.320	0.315
H(812)	0.550	0.346	0.237
H(813)	0.531	0.266	0.250
C(91)	0.787 9(11)	0.219 4(6)	0.304 3(5)
C(92)	0.719 3(18)	0.166 0(8)	0.325 6(7)
H(92)	0.653(11)	0.172(7)	0.316(6)
Terminal silyl ligands (*Continued*)			
C(93)	0.764 2(17)	0.114 3(7)	0.368 2(7)
H(93)	0.673(15)	0.081(9)	0.395(7)
C(94)	0.880 5(17)	0.114 0(8)	0.388 9(7)
H(94)	0.940(29)	0.079(18)	0.457(14)
C(95)	0.951 2(16)	0.165 3(9)	0.368 4(6)
H(95)	0.030(14)	0.164(8)	0.386(7)
C(96)	0.902 5(15)	0.216 7(7)	0.326 4(6)
H(96)	0.956(9)	0.247(5)	0.317(4)
C(101)	0.815 3(10)	0.368 9(5)	0.258 5(5)
C(102)	0.783 8(12)	0.422 4(6)	0.298 1(5)
H(102)	0.707(14)	0.426(8)	0.326(7)
C(103)	0.852 5(14)	0.483 7(7)	0.309 5(6)
H(103)	0.834(11)	0.523(7)	0.341(6)
C(104)	0.951 5(13)	0.492 0(8)	0.282 2(7)
H(104)	0.002(16)	0.020(10)	0.215(8)
C(105)	0.987 3(13)	0.439 8(7)	0.243 5(6)
H(105)	0.057(13)	0.451(8)	0.204(6)
C(106)	0.917 5(11)	0.377 2(6)	0.231 9(6)
H(106)	0.934(10)	0.347(6)	0.188(5)
Terminal t-butyl ligands			
C(31)	0.377 6(11)	0.182 6(6)	0.158 1(5)
N(3)	0.311 4(9)	0.195 9(5)	0.190 1(5)
C(32)	0.221 8(11)	0.210 1(7)	0.228 6(5)
C(33)	0.235 5(14)	0.159 7(8)	0.284 3(6)
H(331)	0.320	0.160	0.300
H(332)	0.195	0.175	0.317
H(333)	0.215	0.113	0.273
C(34)	0.236 3(13)	0.287 2(7)	0.251 6(7)
H(341)	0.237	0.323	0.208
H(342)	0.174	0.300	0.274
H(343)	0.307	0.291	0.279
C(35)	0.106 7(11)	0.198 9(7)	0.189 0(6)
H(351)	0.100	0.240	0.160
H(352)	0.105	0.156	0.167
H(353)	0.043	0.201	0.213
C(41)	0.720 5(12)	0.340 5(6)	0.111 8(5)
N(4)	0.715 9(11)	0.398 5(5)	0.097 4(4)
C(42)	0.707 0(11)	0.473 2(6)	0.080 1(6)
C(43)	0.620 1(17)	0.507 5(8)	0.117 4(8)
H(431)	0.640	0.500	0.160
H(432)	0.617	0.559	0.111
H(433)	0.544	0.489	0.105
C(44)	0.661 9(18)	0.477 2(9)	0.013 0(7)
H(441)	0.720	0.460	0.000
H(442)	0.594	0.447	0.002
H(443)	0.642	0.523	−0.003
C(45)	0.824 0(16)	0.509 3(7)	0.095 0(9)
H(451)	0.840	0.500	0.140
H(452)	0.883	0.488	0.073
H(453)	0.825	0.560	0.086

The results of the *X*-ray diffraction study are embodied in Figure 1, which also shows the atom-numbering system. Figure 2 shows the packing of molecules within the monoclinic unit cell, Table 3 the atomic fractional co-ordinates, Table 4 bond lengths and interbond angles, and Table 5 planarities of significant portions of the molecule. Compound (4) does indeed contain a central diplatina-ring structure, the six-membered ring being of ' boat ' conformation with two $\mathrm{HC{:}NBu^t}$ bridges between the two Pt atoms. Each Pt atom is itself the centre of a square-planar fragment, the two terminal groups ($\mathrm{SiMePh_2}$ and $\mathrm{CNBu^t}$) being arranged with the silyl group *trans* to the ring N atom in both cases. The isomer is therefore (4a) and not (4b). Within the ring, the Pt–N bond length (mean 2.173 Å) is exceptionally long, presumably because of the high *trans* influence of the silyl ligand.[13] As far as we are aware, only one longer Pt–N bond has been recorded, in [PtCl(py)-

$(C_8H_{12}OMe)]$ (py = pyridine), which has the N atom of the pyridine ring *trans* to a σ-bonded carbon atom.[14]

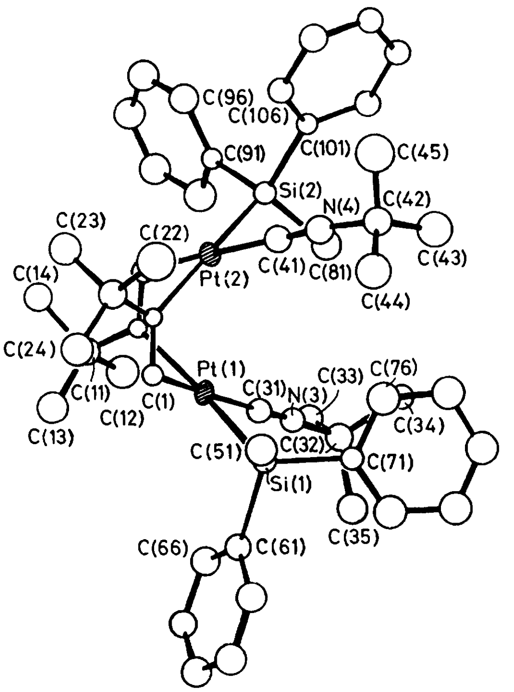


FIGURE 1 The molecular structure of $[\{Pt(CH{:}NBu^t)(SiMePh_2)(CNBu^t)\}_2]$ (4a), showing the crystallographic numbering system

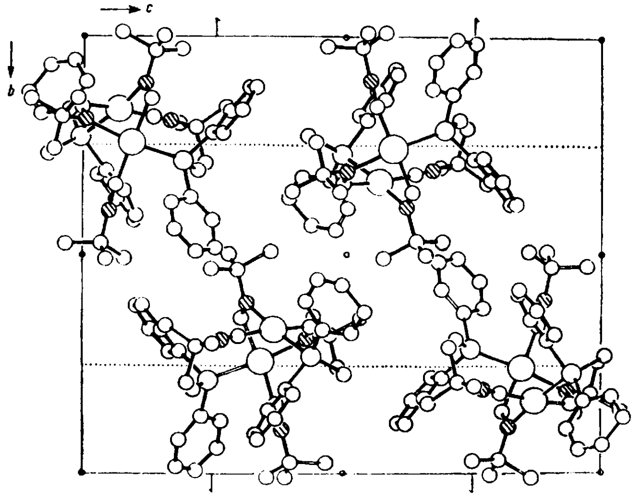


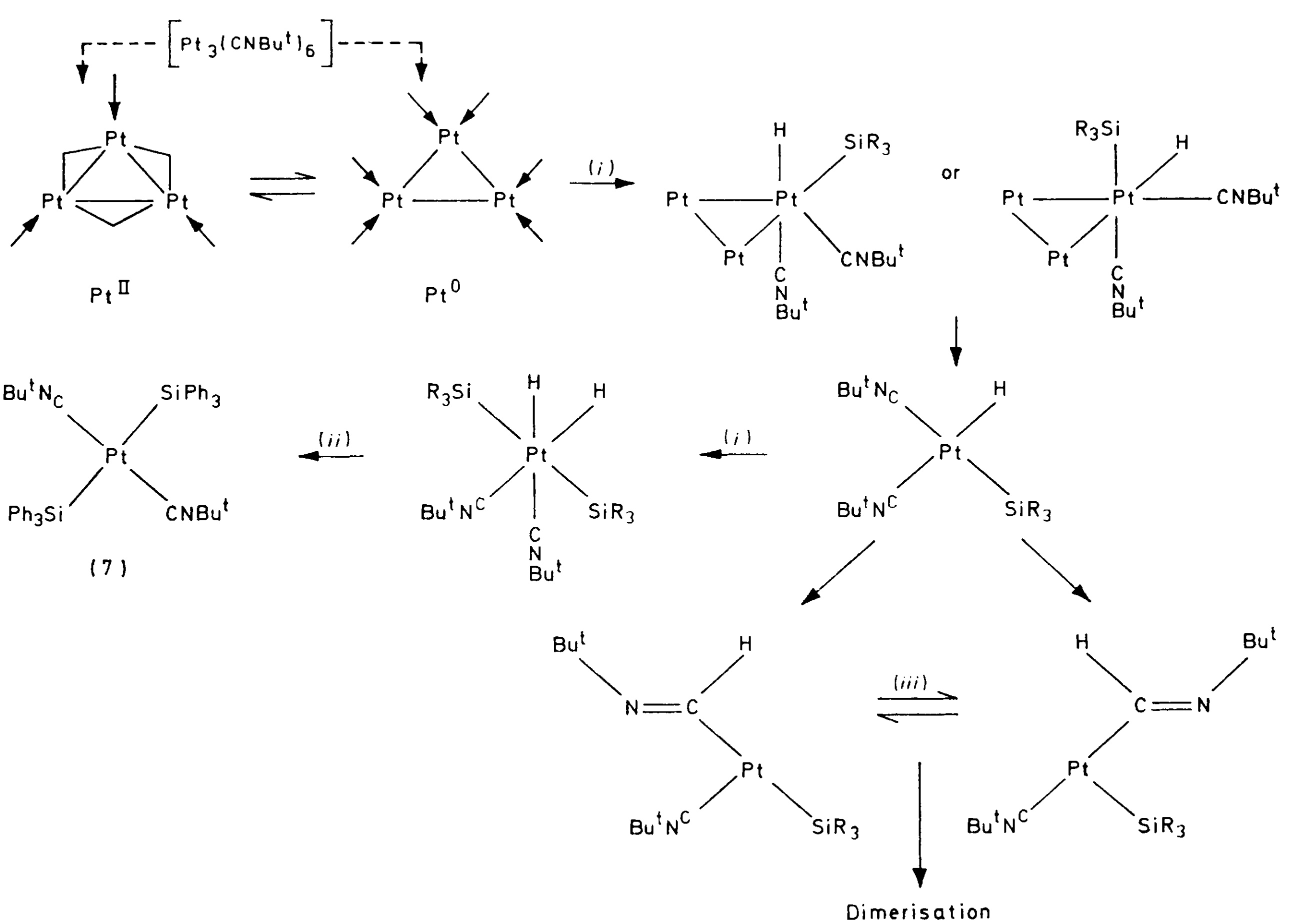
FIGURE 2 Contents of the monoclinic cell projected on to the *bc* plane (*i.e.* looking down *a** towards the origin). The molecule nearest to the origin comprises the atoms of the crystallographic asymmetric unit listed in Table 3

The ring C=N bond length of 1.277 Å (mean) is reasonably characteristic of what might be expected for a double bond. Likewise the Pt–C bond length of 2.028 Å (mean) is indicative of a single σ bond. The central ring system shows symmetrical folds across C(1) · · · N(1) and C(2) · · · N(2), of dihedral angle *ca.* 124° (Table 5), but the co-ordination sites around each Pt atom remain substantially planar. The *trans*-

TABLE 4

Interatomic distances (Å) and bond angles (°) for complex (4a)

(*a*) Distances			
Central diplatina-ring system			
Pt(1)–C(1)	1.999(13)	Pt(2)–C(2)	2.056(12)
Pt(1)–N(1)	2.175(9)	Pt(2)–N(2)	2.172(9)
C(1)–N(2)	1.287(15)	C(2)–N(1)	1.267(16)
C(1)–H(1)	1.05(9)	C(2)–H(2)	1.19(13)
N(1)–C(11)	1.498(14)	N(2)–C(21)	1.509(17)
t-Butyl ligands on central ring			
C(11)–C(12)	1.525(21)	C(21)–C(22)	1.497(19)
C(11)–C(13)	1.524(20)	C(21)–C(23)	1.542(21)
C(11)–C(14)	1.534(18)	C(21)–C(24)	1.504(19)
Terminal silyl ligands			
Pt(1)–Si(1)	2.312(4)	Pt(2)–Si(2)	2.316(4)
Si(1)–C(51)	1.911(18)	Si(2)–C(81)	1.899(15)
Si(1)–C(61)	1.900(12)	Si(2)–C(91)	1.909(11)
Si(1)–C(71)	1.893(13)	Si(2)–C(101)	1.894(11)
C(61)–C(62)	1.383(19)	C(91)–C(92)	1.398(22)
C(62)–C(63)	1.390(24)	C(92)–C(93)	1.398(21)
C(63)–C(64)	1.349(24)	C(93)–C(94)	1.373(27)
C(64)–C(65)	1.383(20)	C(94)–C(95)	1.378(25)
C(65)–C(66)	1.377(20)	C(95)–C(96)	1.401(20)
C(66)–C(61)	1.412(19)	C(96)–C(91)	1.362(20)
C(71)–C(72)	1.387(19)	C(101)–C(102)	1.404(16)
C(72)–C(73)	1.374(22)	C(102)–C(103)	1.406(18)
C(73)–C(74)	1.404(23)	C(103)–C(104)	1.373(23)
C(74)–C(75)	1.386(25)	C(104)–C(105)	1.393(21)
C(75)–C(76)	1.369(21)	C(105)–C(106)	1.434(18)
C(76)–C(71)	1.410(18)	C(106)–C(101)	1.398(18)
Terminal t-butyl ligands			
Pt(1)–C(31)	1.975(13)	Pt(2)–C(41)	1.968(12)
C(31)–N(3)	1.131(17)	C(41)–N(4)	1.133(16)
N(3)–C(32)	1.446(17)	N(4)–C(42)	1.451(15)
C(32)–C(33)	1.532(18)	C(42)–C(43)	1.521(23)
C(32)–C(34)	1.535(18)	C(42)–C(44)	1.495(21)
C(32)–C(35)	1.515(17)	C(42)–C(45)	1.521(21)
(*b*) Angles			
Central diplatina-ring system			
N(1)–Pt(1)–C(1)	84.6(4)	N(2)–Pt(2)–C(2)	84.9(4)
Pt(1)–C(1)–N(2)	117.8(8)	Pt(2)–C(2)–N(1)	117.5(9)
Pt(1)–N(1)–C(2)	112.5(8)	Pt(2)–N(2)–C(1)	112.3(8)
N(1)–Pt(1)–C(31)	98.0(4)	N(2)–Pt(2)–C(41)	96.5(4)
C(1)–Pt(1)–Si(1)	87.8(3)	C(2)–Pt(2)–Si(2)	89.0(4)
C(31)–Pt(1)–Si(1)	89.6(4)	C(41)–Pt(2)–Si(2)	89.4(3)
t-Butyl ligands on central ring			
C(2)–N(1)–C(11)	122.9(10)	C(1)–N(2)–C(21)	122.2(10)
Pt(1)–N(1)–C(11)	124.5(7)	Pt(2)–N(2)–C(21)	125.1(7)
N(1)–C(11)–C(12)	107.1(9)	N(2)–C(21)–C(22)	105.0(10)
N(1)–C(11)–C(13)	105.7(10)	N(2)–C(21)–C(23)	106.4(11)
N(1)–C(11)–C(14)	112.8(10)	N(2)–C(21)–C(24)	114.9(11)
C(12)–C(11)–C(13)	113.1(11)	C(22)–C(21)–C(23)	108.9(11)
C(12)–C(11)–C(14)	109.8(11)	C(22)–C(21)–C(24)	113.0(12)
C(13)–C(11)–C(14)	108.5(11)	C(23)–C(21)–C(24)	108.3(12)
Terminal silyl ligands			
Pt(1)–Si(1)–C(51)	116.8(6)	Pt(2)–Si(2)–C(81)	112.0(5)
Pt(1)–Si(1)–C(61)	109.1(4)	Pt(2)–Si(2)–C(91)	113.5(4)
Pt(1)–Si(1)–C(71)	113.0(4)	Pt(2)–Si(2)–C(101)	114.5(4)
C(51)–Si(1)–C(61)	107.2(6)	C(81)–Si(2)–C(91)	105.2(6)
C(61)–Si(1)–C(71)	106.4(5)	C(91)–Si(2)–C(101)	104.5(5)
C(51)–Si(1)–C(71)	103.7(7)	C(81)–Si(2)–C(101)	106.2(6)
Si(1)–C(61)–C(62)	124.1(10)	Si(2)–C(91)–C(92)	121.3(10)
Si(1)–C(61)–C(66)	120.0(9)	Si(2)–C(91)–C(96)	123.0(10)
Si(1)–C(71)–C(72)	124.9(9)	Si(2)–C(101)–C(102)	121.8(9)
Si(1)–C(71)–C(76)	120.1(10)	Si(2)–C(101)–C(106)	118.6(10)
Terminal t-butyl ligands			
Pt(1)–C(31)–N(3)	174.9(11)	Pt(2)–C(41)–N(4)	175.0(12)
C(31)–N(3)–C(32)	176.5(12)	C(41)–N(4)–C(42)	178.1(14)
N(3)–C(32)–C(33)	109.8(10)	N(4)–C(42)–C(43)	107.6(11)
N(3)–C(32)–C(34)	107.8(11)	N(4)–C(42)–C(44)	108.0(11)
N(3)–C(32)–C(35)	107.1(10)	N(4)–C(42)–C(45)	110.0(11)
C(33)–C(32)–C(34)	109.1(10)	C(43)–C(42)–C(44)	109.1(13)
C(33)–C(32)–C(35)	111.2(11)	C(43)–C(42)–C(45)	109.6(12)
C(34)–C(32)–C(35)	111.7(11)	C(44)–C(42)–C(45)	112.4(14)



SCHEME (*i*) $SiHR_3$; (*ii*) $-H_2$; (*iii*) *via* a Y-shaped intermediate (ref. 16)

annular Pt · · · Pt distance of 3.056(2) Å suggests little metal–metal interaction in this class of complex.

The geometry of the terminal ligands calls for no special comment. The difference between the Pt–C bond lengths in the terminal Bu^t groups, relative to those in the central ring, can be accounted for by the difference in the hybridisation states of the C atoms (sp^2 in the ring, sp in the Bu^t ligand) to which the Pt atoms are bonded. There is no lengthening of the C–N bond.

TABLE 5

Some least-squares planes and interplanar angles for complex (4a): distances (Å) of relevant atoms from these planes are given in square brackets

Plane (1): Pt(1), Si(1), C(1), N(1), C(31)

$4.704x + 16.029y + 6.001z = 5.604$

[Pt(1) −0.005, Si(1) −0.048, C(1) 0.055, N(1) −0.050, C(31) 0.048]

Plane (2): Pt(2), Si(2), C(2), N(2), C(41)

$11.584x - 0.961y - 0.771z = 7.951$

[Pt(2) 0.055, Si(2) −0.010, C(2) −0.016, N(2) −0.011, C(41) −0.018]

Plane (3): C(1), N(1), C(2), N(2)

$-6.229x + 15.157y + 6.898z = -1.102$

[C(1) 0.037, N(1) −0.037, C(2) 0.037, N(2) −0.036]

Angles (°) between least-squares planes: (1)–(2) 67.2; (2)–(3) 123.4; (1)–(3) 123.7

There is, however, a significant shortening of the Pt–Si bond (2.314 Å, mean) relative to the sum of the covalent radii of Pt and Si,[15] which would suggest a covalent bond length of *ca.* 2.53 Å. Some degree of multiple-bond character may thus be implied. Furthermore, the C–Si–C angles are all significantly less than the ideal tetrahedral value.

Although in many of the reactions of $[Pt_3(CNBu^t)_6]$ mononuclear compounds are formed, this does not require that fragmentation of the cluster occurs before reaction occurs. In fact a detailed examination of this Pt_3 cluster provided no evidence for such a dissociative process.[1] It is possible that on the approach of a silane molecule to one of the platinum centres of the Pt_3 cluster the bonding mode of the bridging isocyanides is transformed to the terminal mode with a formal decrease ($Pt^{II} \longrightarrow Pt^0$) in the oxidation state of the platinum thus allowing consecutive *cis*-oxidative addition of the silane to the platinum centres (Scheme). The availability of low-lying 3*d* orbitals on the silicon atom would facilitate nucleophilic attack by the platinum(0) centre thus initiating the formal insertion into the Si–H bond. Fragmentation of the resulting platinum(II) cluster might occur readily and this is probably the penultimate step before formal *cis* insertion of a co-ordinated isocyanide into the platinum–hydrogen bond. The driving force for this step is not obvious, and it is particularly interesting that such a reaction occurs easily with isocyanide, whereas the generation of a formyl ligand by an analogous process with co-ordinated carbon monoxide, while of considerable interest in relationship to the Fischer–Tropsch process, is proving somewhat elusive.

In the case of the isocyanide system this insertion generates *via* a least-motion process a three-co-ordinate platinum(II) species with a T-shaped structure. Calculations[16] with the isoelectronic gold(III) potential-energy surface indicate that T-shaped structures are of lower energy than Y-shaped configurations. Depending on whether the hydrogen migrates onto the isocyanide or the isocyanide inserts into the Pt–H bond, a T-shaped molecule would be formed with the imidoyl ligand either *trans* or *cis* to the SiR_3 group. Since it is not possible to ascertain the stereochemical stability of such a T-shaped platinum(II) intermediate, it is not possible to deduce the precise mechanism of the imidoyl-generating reaction from the established stereochemistry of compound (4). Moreover, there is also the possibility that (4a) is formed in a subsequent thermodynamically controlled rearrangement.

TABLE 6

Analytical [a] and physical data for the complexes

	Compound	M.p. (θ_c/°C) (decomp.)	Colour	Yield (%)	Analysis (%)			M [b]
					C	H	N	
(1)	$[\{Pt(CH{:}NBu^t)(SiMe_3)(CNBu^t)\}_2]$	135—136	Pale yellow	52	36.9 (35.9)	6.7 (6.5)	6.4 (6.4)	
(2)	$[\{Pt(CH{:}NBu^t)(SiEt_3)(CNBu^t)\}_2]$	123—124	Cream	50	42.3 (40.2)	7.9 (7.2)	5.1 (5.8)	954 (955)
(3)	$[\{Pt(CH{:}NBu^t)(SiMe_2Ph)(CNBu^t)\}_2]$	126—132	Pale yellow	95	43.6 (43.4)	6.4 (5.9)	5.4 (5.6)	1 005 (995)
(4)	$[\{Pt(CH{:}NBu^t)(SiMePh_2)(CNBu^t)\}_2]$	159—161	Pale yellow	60	49.4 (49.8)	5.8 (5.8)	5.0 (4.8)	1 080 (1 119)
(5)	$[\{Pt(CH{:}NBu^t)(SiPh_3)(CNBu^t)\}_2]$	188—189	Cream	27	54.2 (54.1)	5.5 (5.6)	4.4 (4.5)	
(6)	$[\{Pt(CH{:}NBu^t)[Si(OEt)_3](CNBu^t)\}_2]$	152	White	50	37.5 (36.6)	6.9 (6.5)	4.5 (5.3)	
(7)	$[Pt(SiPh_3)_2(CNBu^t)_2]$	207—208	Yellow	45	61.8 (62.8)	5.6 (5.5)	3.2 (3.2)	
(8)	$[\{Pt(CH{:}NBu^t)(GeMe_3)(CNBu^t)\}_2]$	180	Yellow	75	33.3 (32.5)	6.4 (5.9)	4.9 (5.8)	

[a] Calculated values are given in parentheses. [b] Vapour-pressure osmometer.

During the reactions which gave complexes (1a)—(4a) or (6a) there was evidence for formation of a second product yellow in colour but produced in such small quantity that characterisation was not possible. It was of interest, therefore, that reaction of $[Pt_3(CNBu^t)_6]$ with $SiPh_3H$ gave, in addition to (5a) (27%), the yellow complex *trans*-$[Pt(SiPh_3)_2(CNBu^t)_2]$ (7) (45%), characterised by analysis, ^1H and ^{13}C n.m.r. spectra, and the appearance in the i.r. of a single $\nu(N{\equiv}C)$ band at 2 176s cm^{-1}. Formation of (7) in the reaction parallels the results mentioned earlier,[9] concerning the isolation of bis(silyl)platinum complexes from reactions of silanes SiR_3H and (tertiary phosphine)platinum(0) complexes. Evidently, with $SiPh_3H$, an initially formed hydride complex $[PtH(SiPh_3)(CNBu^t)_2]$ reacts with a second molecule of triphenylsilane, possibly *via* an oxidative-addition reductive-elimination (H_2) pathway, to give (7) more rapidly than isocyanide insertion occurs to give (5) (Scheme). Release of hydrogen was observed.

The reaction between $[Pt_3(CNBu^t)_6]$ and trimethylgermane was also investigated, and found to give the complex $[\{Pt(CH{:}NBu^t)(GeMe_3)(CNBu^t)\}_2]$ (8), the germanium analogue of (1). Compound (8) decomposes over a period of days even when stored under nitrogen below room temperature.

EXPERIMENTAL

N.m.r. studies were made with JEOL PFT and PS 100 spectrometers. Infrared spectra were recorded on a Perkin-Elmer 457 grating spectrometer. Experiments were carried out under a dry oxygen-free nitrogen atmosphere using Schlenk-tube techniques, and with solvents which were dried and distilled under nitrogen prior to use. Light petroleum refers to that fraction of b.p. 40—60 °C. The triorganosilanes were prepared by reduction of chlorotriorganosilanes with lithium tetrahydroaluminate. Analytical data are given in Table 6.

Preparation of the Diplatinum Complexes $[\{Pt(CH{:}NBu^t)(SiR_3)(CNBu^t)\}_2]$.—The following representative syntheses are given for the complexes listed in the Tables.

(*a*) The complex $[Pt_3(CNBu^t)_6]$ (0.36 g, 0.33 mmol) was suspended in diethyl ether (15 cm^3) in a Schlenk tube and dimethylphenylsilane (0.5 cm^3, *ca.* 3.7 mmol) was added with a syringe. After 0.5 h at room temperature, the solvent was removed *in vacuo*. The oily residue was treated with diethyl ether (15 cm^3) and filtered through an alumina column (Brockman activity II, 1 × 1 cm^3). Solvent was pumped off, and the residue was dissolved in light petroleum and cooled to −78 °C giving complex (3), $[\{Pt(CH{:}NBu^t)(SiMe_2Ph)(CNBu^t)\}_2]$, as pale yellow slightly air-sensitive *crystals* (0.46 g, 95%), washed with hexane and dried *in vacuo*.

(*b*) The complex $[Pt_3(CNBu^t)_6]$ (0.33 g, 0.30 mmol) was suspended in diethyl ether (10 cm^3) and treated with triphenylsilane (0.52 g, 2 mmol) at room temperature. Gas evolution (H_2) was observed on mixing, and a yellow crystalline solid precipitated. After 15 min the solvent was removed *in vacuo*, and the residue was suspended in light petroleum (2 cm^3) for 3 h, then filtered off and washed with light petroleum to give a mixture (*ca.* 0.5 g) of complexes (5) and (7). These compounds were readily separated because of the insolubility of (7) in diethyl ether. Extraction of the mixture with diethyl ether (10 cm^3) gave yellow *crystals* (0.35 g, 45%) of $[Pt(SiPh_3)_2(CNBu^t)_2]$ (7). Infrared spectrum: $\nu_{max.}$ at 3 078s, 3 058s, 2 176vs (NC), 2 068w, 1 944w, 1 874w, 1 812w, 1 583w, 1 560w, 1 431s, 1 325w, 1 300w, 1 257w, 1 239w, 1 202w(br), 1 110s, 1 031w, 1 002w, 912w, 854w, 751s, 743s, 708vs, 680m, 539mw, 504vs, 485s, 450s, 427s, and 416s cm^{-1}. The extract was concentrated to 1 cm^3 and light petroleum (10 cm^3) was added, affording cream *crystals* (0.15 g, 27%) of $[\{Pt(CH{:}NBu^t)(SiPh_3)(CNBu^t)\}_2]$ (5).

(*c*) The complex $[Pt_3(CNBu^t)_6]$ (0.33 g, 0.30 mmol) in diethyl ether (10 cm^3) was placed in a tube fitted with a Westef high-pressure stopcock. Trimethylsilane (2.0 mmol) was distilled into the tube, and the mixture was shaken for 3 h at room temperature affording a yellow solution. Solvent was removed *in vacuo* and the residue dissolved in light petroleum (1 cm^3) giving cream *crystals* (0.20 g, 52%) of $[\{Pt(CH{:}NBu^t)(SiMe_3)(CNBu^t)\}_2]$ (1), washed with the minimum volume of cold light petroleum and dried *in vacuo*.

Reaction of $[Pt_3(CNBu^t)_6]$ *with Trimethylgermane*.—A sealed tube fitted with a Westef stopcock was charged with $[Pt_3(CNBu^t)_6]$ (0.36 g, 0.33 mmol), trimethylgermane (1.5 mmol), and diethyl ether (10 cm^3). The suspension was warmed to room temperature and reaction was complete in 1 h giving a yellow solution. Solvent was removed *in vacuo* and the resulting oil was dissolved in light petroleum. On standing (2 h), yellow *crystals* (75%) of $[\{Pt(CH{:}NBu^t)(GeMe_3)(CNBu^t)\}_2]$ (8) formed.

Crystal-structure Determination of $[\{Pt(CH{:}NBu^t)(SiMePh_2)(CNBu^t)\}_2]$.—The complex crystallises as colourless prisms from diethyl ether. Diffracted intensities were collected from a crystal of dimensions 0.10 × 0.10 × 0.22 mm on a Syntex $P2_1$ four-circle diffractometer according to methods described earlier.[17] Of the total 9 805 reflections for $2.9 < 2\theta < 60.0°$, 7 096 satisfied the criterion $I \geqslant 2.0\sigma(I)$, and only these were used in the solution and refinement of the structure. The intensities were corrected for Lorentz, polarisation, and *X*-ray absorption effects.

Crystal Data.—$C_{46}H_{64}N_2Pt_2Si_2$, $M = 1\,119.2$, Monoclinic, $a = 11.649(4)$, $b = 18.778(15)$, $c = 21.825(15)$ Å, $\beta = 97.31(3)°$, $D_m = 1.50$, $Z = 4$, $D_c = 1.57$ g cm^{-3}, $U = 4\,735$ Å^3, $F(000) = 2\,208$, space group $P2_1/c$, Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 62.7$ cm^{-1}. The structure was solved by heavy-atom methods, and refined by blocked-matrix least squares. Some of the hydrogen atoms were located on the electron-density difference maps and these were allowed to refine with isotropic thermal parameters. The remaining hydrogen atoms were incorporated at calculated positions and were not refined. All other atoms were ascribed anisotropic thermal parameters (Appendix). Atomic scattering factors were those of ref. 18 for Pt, Si, C, and N; those for Pt and Si were corrected for anomalous dispersion [19] (Pt, $\Delta f'$ −2.35, $\Delta f''$ 8.39; Si, $\Delta f'$ 0.07, $\Delta f''$ 0.07). Scattering factors for hydrogen were from ref. 20. Weights were applied according to the scheme $1/w = \sigma(F_o) + \alpha|F_o|$, where $\alpha = 0.085$ and $\sigma(F_o)$ is the estimated standard deviation in $|F_{obs.}|$ based on counting statistics. This gave a satisfactory weight analysis. Refinement converged at R 0.057, R' 0.067, and a final electron-density difference synthesis showed no peaks >0.9 or <-0.5 e Å^{-3}, except in the neighbourhood of the Pt atoms where values of *ca.* ± 3 e Å^{-3} occurred. All the computational work was carried out at the University of London Computing Centre with the '*X*-Ray' system of programs.[21] Observed and calculated structure factors, and all thermal parameters, are listed in Supplementary Publication No. SUP 22506 (32 pp.).*

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

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