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Reactions of 5,6,11,12-tetradehydrodibenzo[*a*,*e*]cyclooctene with 1,2-$C_6H_4(SiMe_2)_2Pt(PPh_3)_2$ and $Pt(CH_2{=}CH_2)(PPh_3)_2$. X-ray structure determination of resulting double silylated compounds and platinum–alkyne complexes

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Abstract

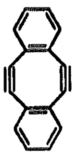
The platinum complex of 5,6,11,12-tetradehydrodibenzo[*a*,*e*]cyclooctene (**1**), $[(Ph_3P)_2Pt]_2$[**1**], was synthesized quantitatively by the reaction of **1** with $Pt(CH_2{=}CH_2)(PPh_3)_2$. The reaction of **1** with 1,2-$C_6H_4(SiMe_2)_2Pt(PPh_3)_2$ gave 5,5,10,10,15,15,20,20-octamethyl-5,10,15,20-tetrahydro-5,10,15,20-tetrasiladibenzo[*b*,*n*]tetraphenylene ($[C_6H_4(SiMe_2)_2]_2(C_{16}H_8)$) and $[(Ph_3P)_2Pt][C_6H_4(SiMe_2)_2C_{16}H_8]$ ($C_6H_4(SiMe_2)_2C_{16}H_8$ = 5,5,16,16-tetramethyl-5,16-dihydro-10,11-didehydro-5,16-disiladibenzo[*a*,*e*]naphtho[*c*]cyclooctene) as well as $[(Ph_3P)_2Pt]_2$[**1**]. The central eight-membered ring of $[C_6H_4(SiMe_2)_2]_2(C_{16}H_8)$ has a typical tub-shaped structure, while that of $[(Ph_3P)_2Pt]_2$[**1**] is much less folded. The structure of $[(Ph_3P)_2Pt][C_6H_4(SiMe_2)_2C_{16}H_8]$ lies between those of $[C_6H_4(SiMe_2)_2]_2(C_{16}H_8)$ and $[(Ph_3P)_2Pt]_2$[**1**]. Crystal data: $[(Ph_3P)_2Pt]_2$[**1**]·2toluene, $C_{88}H_{68}P_4Pt_2\cdot 2C_7H_8$, monoclinic, $P2_1/n$, $a = 16.369(2)$, $b = 30.104(6)$, $c = 17.120(3)$ Å, $\beta = 102.69(1)°$, $V = 8230(2)$ Å^3, $Z = 4$. $[C_6H_4(SiMe_2)_2]_2(C_{16}H_8)$, $C_{36}H_{40}Si_4$, monoclinic, $P2_1/c$, $a = 18.421(2)$, $b = 11.131(1)$, $c = 16.444(1)$ Å, $\beta = 94.540(4)°$, $V = 3361(4)$ Å^3, $Z = 4$. $[(Ph_3P)_2Pt][C_6H_4(SiMe_2)_2C_{16}H_8]$, $C_{62}H_{54}P_2PtSi_2$, triclinic, $P\bar{1}$, $a = 13.538(2)$, $b = 17.244(4)$, $c = 12.510(3)$ Å, $\alpha = 111.10(2)$, $\beta = 104.93(1)$, $\gamma = 80.06(2)°$, $V = 2622(1)$ Å^3, $Z = 2$. © 1997 Elsevier Science S.A.

Keywords: Crystal structures; Platinum complexes; Alkyne complexes; Organosilicon compounds

1. Introduction

5,6,11,12-Tetradehydrodibenzo[*a*,*e*]cyclooctene (**1**) [1–3] and 5,6-didehydrodibenzo[*a*,*e*]cyclooctene (**2**) [1,2,4] are planar, antiaromatic [8]annulenes, while dibenzo[*a*,*e*]-cyclooctene (**3**) is a non-planar, tub-shaped compound [5]. Dürr et al. reported that compound **4**, a cyclopropene derivative of **1**, was almost planar [6]. They attributed its planarity to the triple bond-like character of the cyclopropene double bond.

In the course of our study concerning the platinum complex-catalyzed dehydrogenative double silylation reaction of 1,2-bis(dimethylsilyl)benzene (**5**) with alkynes [7], we had interest in a platinum complex of **1** such as **6** as well as a double silylation reaction of **1**. It is well known that transition metals coordinate to alkynes and form transition metal–alkyne complexes (metalacyclopropenes) and the metal-coordinated C≡C bonds are usually between double bond and triple bond in character. Therefore, a similarity between the structures of **4** and complex **6** is expected. The double silylation reaction of **1** was expected to form the mono double silylated product **7**, a silylated derivative of **2**, as well as the bis double silylated product **8** (Eq. (1)).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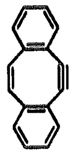
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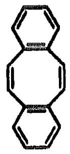
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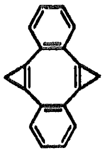
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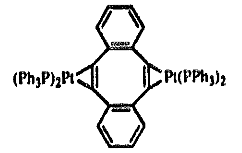

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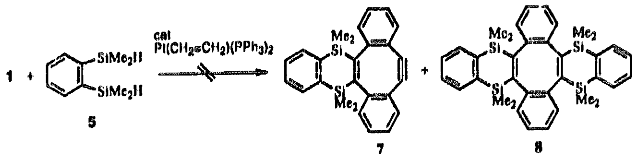

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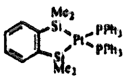
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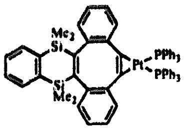
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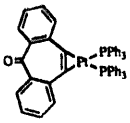
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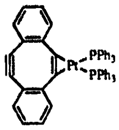
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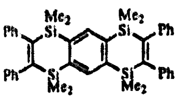
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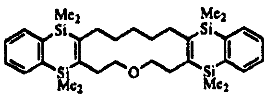
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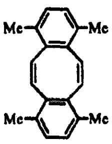
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Contrary to our expectation, the double silylation reaction of **1** did not proceed catalytically. On the other hand, a stoichiometric reaction of **1** with bis(silyl)platinum complex **9** afforded compound **7** in the form of its platinum complex **10** as well as **8** and complex **6**. Here we report the synthesis of **6**, details of the double silylation reaction of **1** and X-ray structure analysis of **6**, **8** and **10**. The effects of platinum coordination on the structures of **1** and **7** will be discussed.

2. Results and discussion

2.1. *Synthesis of complex 6*

Platinum complex **6** could be synthesized quantitatively by the reaction of **1** with 2 equiv. of $Pt(CH_2{=}CH_2)(PPh_3)_2$ or $Pt(PPh_3)_4$. The structure of **6** was unambiguously determined by ^1H, ^{13}C, ^{31}P NMR, IR, elemental analysis and X-ray structure analysis (vide infra). The ^1H NMR signal of fused benzene rings of **6** appeared at 5.8 ppm (all eight hydrogens have the same chemical shift). This high field shift would be attributed to the shielding effect of PPh_3. Similar high field shifts were reported for **11** and related complexes [8].

It is known that highly strained cyclic alkynes and dehydroarenes such as cyclohexyne, cycloheptyne and benzyne can be stabilized by complexation with transition metals [9]. Similarly, compound **6**, a platinum complex of highly strained cyclic alkyne **1**, was highly air and thermally stable, and its decomposition temperature under air was higher than

Table 1
Summary of crystallographic data for **6**, **8** and **10**

Crystal parameters			
Compound	**6**	**8**	**10**
Formula	$C_{88}H_{68}P_4Pt_2\cdot 2C_7H_8$	$C_{36}H_{40}Si_4$	$C_{62}H_{54}P_2PtSi_2$
Formula weight	1823.84	585.06	1112.32
Crystal size (mm)	0.20 × 0.15 × 0.06	0.50 × 0.26 × 0.18	0.32 × 0.18 × 0.07
a (Å)	16.369(2)	18.421(2)	13.538(2)
b (Å)	30.104(6)	11.131(1)	17.244(4)
c (Å)	17.120(3)	16.444(1)	12.510(3)
α (°)			111.10(2)
β (°)	102.69(1)	94.540(4)	104.93(1)
γ (°)			80.06(2)
V (Å^3)	8230(2)	3361(4)	2622(1)
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
Z	4	4	2
D_{calc} (g cm^{-3})	1.47	1.16	1.41
μ (cm^{-1})	35.460	18.025	28.103
Data collection			
Diffractometer	Mac Science MXC18	Enraf-Nonius CAD4	Rigaku AFC5S
Monochromator	graphite	graphite	graphite
Scan method	ω–2θ	ω	ω
λ (Å)	0.7107	1.5418	0.7107
$2\theta_{max}$ (°)	55	150	50
Absorption correction	none	empirical(ψ-scan)	none
No. reflections measured	19948	7126	9386
No. reflections $I_o > 3.0\sigma(I_o)$	5577	5285	6162
Refinement			
Refinement method	full-matrix least-squares		
R	0.070	0.044	0.053
R_w	0.117	0.055	0.060
GOF	1.75	1.60	1.18
Largest difference peak/hole (e Å^{-3})	2.95, −2.16	0.42, −0.36	2.87, −1.06
Source of atomic scattering factors		Ref. [21]	
Programs used	Crystan-GM	Enraf-Nonius MolEN/ teXsan	teXsan

200°C. Complex **6** was not very reactive in chemical reactions either. Thus, unlike $(Ph_3P)_2Pt(Ph{-}C{\equiv}C{-}Ph)$, complex **6** did not react with **5** at all, even at elevated temperatures.

2.2. *Double silylation reaction of 1*

The reaction of **1** with **5** did not proceed catalytically. However, when **1** was added to the mixture of **5** and $Pt(CH_2{=}CH_2)(PPh_3)_2$ $(\mathbf{1}/\mathbf{5}/Pt(CH_2{=}CH_2)(PPh_3)_2 = 1/2/0.2)$, small amounts (~5%) of **8** and **10** were detected by NMR. Because **5** readily reacts with $Pt(CH_2{=}CH_2)(PPh_3)_2$ to give complex **9** [10], **8** and **10** are envisioned to be formed by the reaction of **1** with **9**. Indeed, the stoichiometric reaction of **1** with **9** (**1**/**9** = 1/2) smoothly proceeded in toluene at room temperature to give **8** (59% yield based on **1**), **10** (21%) as well as **6** (12%). Complex **10** was also highly air and thermally stable; it could be separated by silica gel preparative TLC and did not decompose up to 180°C under air. The structures of **8** and **10** were unambiguously determined by ^1H, ^{13}C, ^{31}P, ^{29}Si NMR, IR, elemental analysis and X-ray structure analysis (vide infra). ^1H NMR signals of some of hydrogens of **10** also exhibited high field shifts as observed for **6** (vide supra).

A similar reaction run at the **1**/**9** ratio of 1.1/1 in $CDCl_3$ was monitored by NMR. ^{31}P NMR taken at 2 h of the reaction time indicated complete consumption of **9** and the formation of **6** and **10** as major Pt complexes along with a small amount of a third Pt complex (the ratio of **6**, **10** and the third complex based on the ^{31}P NMR integrations is 53/35/12), which displayed a signal (δ = 27.79 ppm, ^1J(Pt–P) = 3409 Hz) very similar to the ^{31}P NMR of **6** (δ = 27.18 ppm, ^1J(Pt–P) = 3415 Hz). This signal replaced that of **6** in the reaction of **9** with an excess of **1** (**1**/**9** = 5/1). Based on these results, the third platinum complex is probably the mono platinum complex **12**, although it could not be isolated.

2.3. *Crystal structures of compounds 6, 8 and 10*

Crystallographic data are summarized in Table 1. Positional parameters of **6**, **8** and **10** are given in Tables 2–4, respectively. Selected bond distances and angles are listed in Table 5. Figs. 1–3 show the molecular structures of compounds **6**, **8** and **10**, respectively.

Single crystals of **6** recrystallized from toluene contained two molecules of the solvent. Experimental errors for **6** are rather large and, therefore, precise discussion of the bond distances and angles for **6** is not possible. The geometries of Pt centers of **6** and **10** are typical of trigonal-planar Pt–alkyne complexes. Pt–C, Pt–P and C1–C2 bond distances of **10** are within the range of reported Pt–alkyne complexes [8,11–17].

Both of the disilacyclohexadiene rings of **8** are folded at the Si atoms, while that of **10** is nearly flat. The conformation of the 1,4-disilacyclohexadiene rings seems highly susceptible to the molecular structure and crystal packing. For example, the disilacyclohexadiene rings of **13** are planar [7c],

Table 2
Positional parameters for complex **6**

Atom	*x*	*y*	*z*
Pt(1)	0.77859(6)	0.14357(5)	0.19269(5)
Pt(2)	0.98187(6)	0.14171(5)	0.55208(5)
P(1)	0.8322(5)	0.1291(3)	0.0830(4)
P(2)	0.6481(5)	0.1153(3)	0.1611(5)
P(3)	1.1155(4)	0.1147(3)	0.5873(4)
P(4)	0.9337(4)	0.1263(3)	0.6657(4)
C(1)	0.871(2)	0.1745(9)	0.276(1)
C(2)	0.800(2)	0.173(1)	0.302(2)
C(3)	0.959(2)	0.173(1)	0.444(2)
C(4)	0.884(2)	0.172(1)	0.465(2)
C(5)	0.960(2)	0.191(1)	0.301(2)
C(6)	1.001(1)	0.1908(8)	0.388(1)
C(7)	1.079(2)	0.202(1)	0.403(2)
C(8)	1.120(3)	0.224(2)	0.344(2)
C(9)	1.073(2)	0.225(1)	0.265(2)
C(10)	0.999(2)	0.208(1)	0.248(2)
C(11)	0.760(2)	0.187(1)	0.369(2)
C(12)	0.804(2)	0.182(1)	0.445(2)
C(13)	0.756(2)	0.191(1)	0.505(1)
C(14)	0.676(2)	0.213(2)	0.488(2)
C(15)	0.642(2)	0.216(1)	0.405(3)
C(16)	0.678(2)	0.204(1)	0.348(2)
C(111)	0.870(2)	0.180(1)	0.043(2)
C(112)	0.824(3)	0.218(2)	0.049(3)
C(113)	0.846(3)	0.259(2)	0.017(3)
C(114)	0.915(3)	0.261(2)	−0.017(3)
C(115)	0.958(4)	0.222(2)	−0.023(3)
C(116)	0.938(3)	0.182(2)	0.009(2)
C(121)	0.926(2)	0.091(1)	0.104(2)
C(122)	0.956(2)	0.079(1)	0.182(2)
C(123)	1.020(2)	0.051(1)	0.200(2)
C(124)	1.058(4)	0.031(2)	0.142(4)
C(125)	1.028(3)	0.043(2)	0.064(3)
C(126)	0.962(2)	0.073(1)	0.046(2)
C(131)	0.770(2)	0.106(1)	−0.010(2)
C(132)	0.757(3)	0.058(2)	−0.015(3)
C(133)	0.708(4)	0.041(3)	−0.083(4)
C(134)	0.668(3)	0.066(2)	−0.141(3)
C(135)	0.678(3)	0.112(2)	−0.140(3)
C(136)	0.729(2)	0.132(1)	−0.070(2)
C(211)	0.591(2)	0.118(1)	0.242(2)
C(212)	0.507(2)	0.130(1)	0.229(2)
C(213)	0.465(3)	0.126(2)	0.298(3)
C(214)	0.508(3)	0.111(2)	0.368(3)
C(215)	0.592(2)	0.099(1)	0.381(2)
C(216)	0.634(2)	0.103(1)	0.316(2)
C(221)	0.580(2)	0.145(1)	0.078(2)
C(222)	0.562(2)	0.189(1)	0.087(2)
C(223)	0.517(3)	0.214(2)	0.025(3)
C(224)	0.491(2)	0.195(1)	−0.049(2)
C(225)	0.508(2)	0.151(2)	−0.064(3)
C(226)	0.553(2)	0.126(1)	0.003(2)
C(231)	0.636(1)	0.0561(7)	0.136(1)
C(232)	0.706(2)	0.029(1)	0.144(2)
C(233)	0.696(3)	−0.017(2)	0.137(3)
C(234)	0.615(2)	−0.035(1)	0.111(2)
C(235)	0.546(3)	−0.008(2)	0.106(3)
C(236)	0.555(2)	0.038(1)	0.115(2)
C(311)	1.123(2)	0.055(1)	0.614(2)
C(312)	1.049(2)	0.028(1)	0.593(2)
C(313)	1.062(2)	−0.019(1)	0.615(2)

(*continued*)

Table 2 (*continued*)

Atom	*x*	*y*	*z*
C(314)	1.137(4)	−0.037(2)	0.634(3)
C(315)	1.209(2)	−0.010(1)	0.654(2)
C(316)	1.201(2)	0.035(1)	0.636(2)
C(321)	1.177(2)	0.114(1)	0.511(2)
C(322)	1.263(2)	0.121(1)	0.526(2)
C(323)	1.305(2)	0.118(1)	0.467(2)
C(324)	1.269(2)	0.112(1)	0.394(2)
C(325)	1.182(2)	0.104(2)	0.375(2)
C(326)	1.136(2)	0.105(1)	0.430(2)
C(331)	1.184(2)	0.146(1)	0.671(2)
C(332)	1.221(2)	0.126(2)	0.736(2)
C(333)	1.270(2)	0.153(1)	0.799(2)
C(334)	1.282(2)	0.198(1)	0.788(3)
C(335)	1.245(2)	0.216(1)	0.717(2)
C(336)	1.197(2)	0.189(1)	0.658(2)
C(411)	0.855(2)	0.083(1)	0.651(2)
C(412)	0.822(2)	0.068(1)	0.576(2)
C(413)	0.764(3)	0.033(2)	0.561(3)
C(414)	0.740(2)	0.013(1)	0.625(2)
C(415)	0.774(2)	0.028(1)	0.700(3)
C(416)	0.831(2)	0.063(1)	0.715(2)
C(421)	0.886(2)	0.175(1)	0.698(2)
C(422)	0.818(2)	0.172(1)	0.735(2)
C(423)	0.785(2)	0.210(1)	0.762(2)
C(424)	0.820(3)	0.252(1)	0.752(3)
C(425)	0.887(2)	0.255(1)	0.714(2)
C(426)	0.920(2)	0.216(1)	0.687(2)
C(431)	1.006(2)	0.114(1)	0.763(2)
C(432)	1.043(2)	0.144(1)	0.823(2)
C(433)	1.098(2)	0.129(1)	0.891(2)
C(434)	1.117(2)	0.083(1)	0.900(2)
C(435)	1.080(2)	0.054(1)	0.841(2)
C(436)	1.025(2)	0.069(1)	0.772(2)
C(511)	0.481(7)	0.070(5)	0.653(7)
C(512)	0.445(3)	0.102(2)	0.695(3)
C(513)	0.471(5)	0.147(3)	0.688(5)
C(514)	0.533(6)	0.159(4)	0.650(6)
C(515)	0.570(4)	0.127(2)	0.614(4)
C(516)	0.544(3)	0.083(2)	0.611(3)
C(517)	0.467(7)	0.030(4)	0.662(7)
C(521)	0.778(6)	0.331(3)	0.556(6)
C(522)	0.716(5)	0.333(3)	0.601(6)
C(523)	0.705(4)	0.373(3)	0.641(4)
C(524)	0.754(6)	0.410(3)	0.635(6)
C(525)	0.815(5)	0.408(3)	0.590(5)
C(526)	0.827(4)	0.368(3)	0.550(4)
C(527)	0.789(6)	0.293(4)	0.508(7)

while those of **14** are folded at the Si atoms in the crystalline state [18].

Table 6 shows quantitative description of the fold angles [19] of eight-membered rings of **6**, **8** and **10** together with those of two other dibenzo[*a*,*e*]cyclooctenes **3** [5,20] and **15** [20]. Fold angles of **8** are larger than those of **3** and **15**. Substitution with the sterically bulky $SiMe_2$-containing moiety probably forced more folded conformation. In contrast to **4**, the central eight-membered ring of **6** is not planar. However, fold angles of **6** are almost half of those of **3**, **8** or **15**. α_c and α_g of **10**, which are almost the same as α_c of **6** and α_g of **8**, respectively, clearly show that the conformation of the

Table 3
Positional parameters for compound **8**

Atom	*x*	*y*	*z*
Si(1)	0.06830(3)	0.05013(5)	0.77845(3)
Si(2)	0.19865(3)	−0.12311(5)	0.87596(3)
Si(3)	0.30369(3)	0.30134(5)	0.71351(4)
Si(4)	0.41559(3)	0.08219(6)	0.79254(4)
C(1)	0.1511(1)	−0.0036(2)	0.7281(1)
C(2)	0.1991(1)	−0.0827(2)	0.7649(1)
C(3)	0.2856(1)	0.1369(2)	0.6918(1)
C(4)	0.3312(1)	0.0509(2)	0.7231(1)
C(5)	0.1636(1)	0.0388(2)	0.6439(1)
C(6)	0.2255(1)	0.1055(2)	0.6281(1)
C(7)	0.2342(1)	0.1400(2)	0.5476(1)
C(8)	0.1851(2)	0.1072(2)	0.4844(1)
C(9)	0.1248(1)	0.0411(2)	0.4995(1)
C(10)	0.1139(1)	0.0086(2)	0.5788(1)
C(11)	0.2563(1)	−0.1382(2)	0.7163(1)
C(12)	0.3186(1)	−0.0763(2)	0.6969(1)
C(13)	0.3685(1)	−0.1350(2)	0.6502(1)
C(14)	0.3555(2)	−0.2498(2)	0.6217(2)
C(15)	0.2940(2)	−0.3098(2)	0.6405(2)
C(16)	0.2452(1)	−0.2553(2)	0.6881(1)
C(17)	0.0481(1)	−0.0581(2)	0.8613(1)
C(18)	0.1023(1)	−0.1317(2)	0.9018(1)
C(19)	0.0825(1)	−0.2093(2)	0.9632(1)
C(20)	0.0120(2)	−0.2163(2)	0.9840(2)
C(21)	−0.0411(1)	−0.1459(3)	0.9454(2)
C(22)	−0.0230(1)	−0.0668(2)	0.8846(1)
C(23)	0.3548(1)	0.3165(2)	0.8156(1)
C(24)	0.4014(1)	0.2256(2)	0.8494(1)
C(25)	0.4403(1)	0.2466(3)	0.9254(2)
C(26)	0.4337(2)	0.3545(3)	0.9658(2)
C(27)	0.3888(2)	0.4422(3)	0.9333(2)
C(28)	0.3497(2)	0.4243(2)	0.8595(2)
C(29)	−0.0140(1)	0.0581(3)	0.7048(2)
C(30)	0.0825(2)	0.2036(2)	0.8195(2)
C(31)	0.2471(2)	−0.2675(3)	0.8989(2)
C(32)	0.2435(2)	0.0026(3)	0.9367(2)
C(33)	0.3619(1)	0.3641(2)	0.6358(2)
C(34)	0.2167(1)	0.3878(2)	0.7094(2)
C(35)	0.4956(1)	0.1014(3)	0.7306(2)
C(36)	0.4343(2)	−0.0455(3)	0.8640(2)

Table 4
Positional parameters for complex **10**

Atom	*x*	*y*	*z*
Pt(1)	0.14664(3)	0.23035(3)	0.30777(4)
P(1)	0.1782(2)	0.2611(2)	0.5070(2)
P(2)	0.3059(2)	0.2260(2)	0.2778(2)
Si(1)	−0.2828(2)	0.3522(2)	0.1076(3)
Si(2)	−0.1368(2)	0.2922(2)	−0.1045(2)
C(1)	−0.0025(8)	0.2216(5)	0.2436(8)
C(2)	0.0403(7)	0.1962(5)	0.1558(8)
C(3)	−0.1980(7)	0.2519(6)	0.0703(8)
C(4)	−0.1450(7)	0.2271(6)	−0.0141(8)
C(5)	−0.1054(8)	0.2078(6)	0.2468(8)
C(6)	−0.1943(7)	0.2074(6)	0.1581(8)
C(7)	−0.2826(8)	0.1775(7)	0.157(1)
C(8)	−0.2895(8)	0.1542(7)	0.252(1)

(*continued*)

Table 4 (*continued*)

Atom	x	y	z
C(9)	−0.2075(9)	0.1608(7)	0.344(1)
C(10)	−0.1185(8)	0.1871(7)	0.3428(8)
C(11)	0.0220(8)	0.1415(6)	0.0327(8)
C(12)	−0.0733(7)	0.1481(6)	−0.0422(8)
C(13)	−0.0962(8)	0.0840(7)	−0.149(1)
C(14)	−0.0248(9)	0.0158(6)	−0.1834(9)
C(15)	0.0702(8)	0.0123(6)	−0.1132(9)
C(16)	0.0940(8)	0.0747(6)	−0.0046(8)
C(17)	−0.2695(8)	0.4206(6)	0.0267(9)
C(18)	−0.2106(8)	0.3967(7)	−0.0601(9)
C(19)	−0.204(1)	0.4544(7)	−0.114(1)
C(20)	−0.254(1)	0.5321(8)	−0.084(1)
C(21)	−0.313(1)	0.5565(7)	−0.001(1)
C(22)	−0.3198(8)	0.5017(7)	0.055(1)
C(23)	−0.2426(9)	0.4086(7)	0.269(1)
C(24)	−0.4202(9)	0.3348(9)	0.067(1)
C(25)	−0.186(1)	0.2409(8)	−0.264(1)
C(26)	−0.000(1)	0.3097(8)	−0.079(1)
C(101)	0.3060(7)	0.2807(6)	0.5993(8)
C(102)	0.3681(9)	0.2242(7)	0.651(1)
C(103)	0.466(1)	0.2425(8)	0.720(1)
C(104)	0.5028(9)	0.3162(9)	0.740(1)
C(105)	0.4422(9)	0.3723(7)	0.688(1)
C(106)	0.3476(8)	0.3540(6)	0.619(1)
C(201)	0.1011(7)	0.3518(6)	0.5861(8)
C(202)	0.0166(8)	0.3863(6)	0.5231(8)
C(203)	−0.0432(9)	0.4540(8)	0.582(1)
C(204)	−0.018(1)	0.4883(7)	0.702(1)
C(205)	0.065(1)	0.4551(7)	0.766(1)
C(206)	0.1255(8)	0.3879(7)	0.7075(9)
C(301)	0.1490(7)	0.1730(6)	0.5408(8)
C(302)	0.1790(8)	0.0933(6)	0.4759(9)
C(303)	0.163(1)	0.0265(7)	0.503(1)
C(304)	0.115(1)	0.0369(7)	0.592(1)
C(305)	0.081(1)	0.1150(8)	0.652(1)
C(306)	0.099(1)	0.1830(7)	0.628(1)
C(401)	0.3242(8)	0.1875(6)	0.1259(9)
C(402)	0.401(1)	0.1282(8)	0.086(1)
C(403)	0.411(1)	0.103(1)	−0.029(1)
C(404)	0.344(1)	0.140(1)	−0.106(1)
C(405)	0.273(1)	0.200(1)	−0.067(1)
C(406)	0.2609(8)	0.2242(7)	0.047(1)
C(501)	0.3517(8)	0.3300(7)	0.3237(8)
C(502)	0.2860(8)	0.3993(7)	0.365(1)
C(503)	0.314(1)	0.4793(8)	0.392(1)
C(504)	0.406(1)	0.4914(8)	0.380(1)
C(505)	0.471(1)	0.422(1)	0.338(1)
C(506)	0.4449(8)	0.3417(8)	0.307(1)
C(601)	0.4053(6)	0.1619(5)	0.3431(7)
C(606)	0.3876(5)	0.0780(5)	0.3064(6)
C(605)	0.4611(6)	0.0219(4)	0.3471(7)
C(604)	0.5523(5)	0.0497(5)	0.4244(7)
C(603)	0.5701(5)	0.1336(5)	0.4611(6)
C(602)	0.4966(6)	0.1897(4)	0.4205(7)

eight-membered ring of **10** lies between those of **6** and **8**. Although the coordination of platinum to **1** and **7** folds their structures, fold angles of **6** and **10** indicate that the Pt-coordinated C≡C bonds of **6** and **10** are between double bond and triple bond in character.

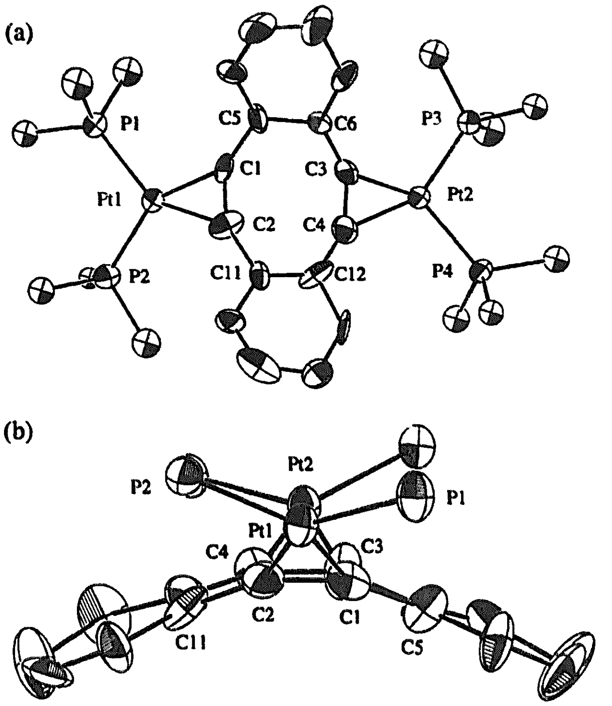


Fig. 1. Molecular structure of compound **6** with 40% probability. (a) Top view. Only the α-carbons of phenyl rings are shown for clarity. (b) Side view. Phenyl rings are omitted for clarity.

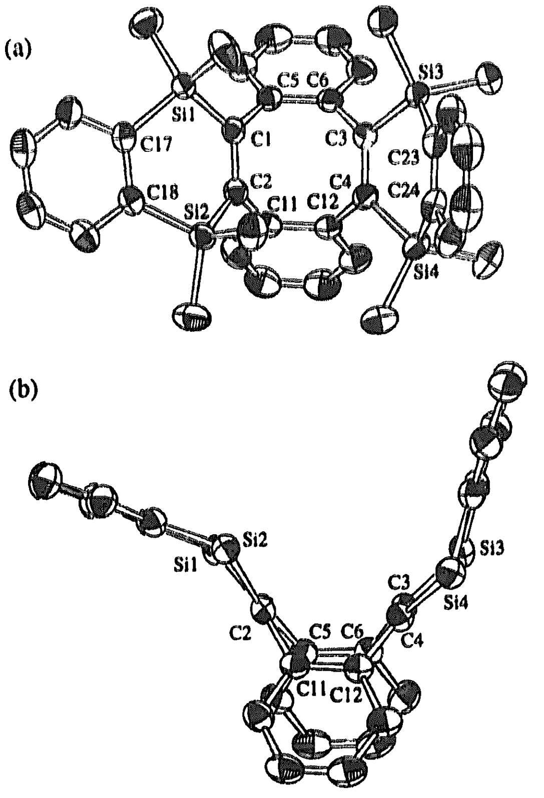


Fig. 2. Molecular structure of compound **8** with 40% probability. (a) Top view. (b) Side view. Methyl carbons are omitted for clarity.

3. Experimental

3.1. Synthesis of **6**

To a CH_2Cl_2 solution (5 ml) of **1** (20 mg) was added $Pt(CH_2{=}CH_2)(PPh_3)_2$ (150 mg) at room temperature. After stirring for 30 min, the solvent was removed under vacuum to give **6** quantitatively (163 mg); ^1H NMR analysis indicated that the crude complex was almost pure. An analytical sample was obtained by recrystallization from toluene as orange prismatic crystals containing two solvent molecules.

M.p. 250–255°C (under vacuum). IR (KBr): 1771, 1744 ($\nu C{\equiv}C$). ^1H NMR: δ 5.80 (8H, s), 7.00–7.09 (24H, m), 7.10–7.18 (12H, m), 7.32–7.42 (24H, m). ^{13}C NMR: δ 125.02 (4C), 127.43 (24C, t, P-*Ph*), 128.67 (12C, P-*Ph*), 130.59 (4C, $^3J(Pt–P) = 33$, 131.29, 132.09, 134.31 (24C, m, P-*Ph*), 136.79 (m, *ipso* P-*Ph*). ^{31}P NMR: δ 27.04 (s, $^1J(Pt–P) = 3414$). *Anal.* Calc. for $C_{88}H_{68}P_4Pt_2 \cdot 2(C_6H_5CH_3)$: C, 67.17; H, 4.64. Found: C, 67.07; H, 4.67%.

Table 5
Selected bond distances (Å) and angles (°) for **6**, **8** and **10**

	6	**8**	**10**
Bond distances			
Pt(1)–P(1)	2.284(8)		2.292(3)
Pt(1)–P(2)	2.253(8)		2.270(3)
Pt(1)–C(1)	2.06(3)		2.03(1)
Pt(1)–C(2)	2.02(4)		2.027(9)
Pt(2)–P(3)	2.285(7)		
Pt(2)–P(4)	2.301(7)		
Pt(2)–C(3)	2.04(3)		
Pt(2)–C(4)	2.14(3)		
Si(1)–C(1) or Si(1)–C(3)		1.890(2)	1.885(9)
Si(1)–C(17)		1.878(2)	1.87(1)
Si(2)–C(2) or Si(2)–C(4)		1.882(2)	1.89(1)
Si(2)–C(18)		1.860(2)	1.87(1)
Si(3)–C(3)		1.889(2)	
Si(3)–C(23)		1.866(2)	
Si(4)–C(4)		1.887(2)	
Si(4)–C(24)		1.878(2)	
C(1)–C(2)	1.34(5)	1.355(3)	1.31(2)
C(1)–C(5)	1.51(4)	1.498(3)	1.43(2)
C(2)–C(11)	1.50(5)	1.505(3)	1.46(1)
C(3)–C(4)	1.36(4)	1.348(3)	1.33(1)
C(3)–C(6)	1.41(4)	1.505(3)	1.53(2)
C(4)–C(12)	1.31(5)	1.493(3)	1.52(1)
C(5)–C(6)	1.48(4)	1.403(3)	1.41(1)
C(5)–C(10)	1.33(5)	1.394(3)	1.41(2)
C(6)–C(7)	1.29(5)	1.399(3)	1.38(2)
C(7)–C(8)	1.49(6)	1.372(3)	1.40(2)
C(8)–C(9)	1.41(6)	1.372(4)	1.37(2)
C(9)–C(10)	1.29(5)	1.383(3)	1.38(2)
C(11)–C(12)	1.36(5)	1.396(3)	1.41(1)
C(11)–C(16)	1.41(4)	1.394(3)	1.40(1)
C(12)–C(13)	1.44(5)	1.404(3)	1.38(1)
C(13)–C(14)	1.43(6)	1.376(3)	1.41(1)
C(14)–C(15)	1.41(7)	1.372(4)	1.37(1)
C(15)–C(16)	1.30(6)	1.378(3)	1.40(1)
Angles			
P(1)–Pt(1)–P(2)	104.2(3)		101.90(9)
P(1)–Pt(1)–C(1)	107.3(8)		108.9(3)
P(2)–Pt(1)–C(2)	110(1)		111.9(3)
C(1)–Pt(1)–C(2)	38(1)		37.5(4)
P(3)–Pt(2)–P(4)	101.0(3)		
P(3)–Pt(2)–C(3)	112.3(8)		
P(4)–Pt(2)–C(4)	109.2(8)		
C(3)–Pt(2)–C(4)	38(1)		
C(1)–Si(1)–C(17) or C(3)–Si(1)–C(17)		109.14(9)	111.6(5)
C(2)–Si(2)–C(18) or C(4)–Si(2)–C(18)		108.14(9)	112.0(5)
C(3)–Si(3)–C(23)		109.05(9)	
C(4)–Si(4)–C(24)		108.52(9)	
Pt(1)–C(1)–C(2)	69(2)		71.1(6)
Pt(1)–C(1)–C(5)	150(2)		152.5(8)
Si(1)–C(1)–C(2)		122.1(1)	
Si(1)–C(1)–C(5)		119.6(1)	
C(2)–C(1)–C(5)	141(3)	118.3(2)	131.4(8)
Pt(1)–C(2)–C(1)	72(2)		71.4(6)
Pt(1)–C(2)–C(11)	145(2)		145.6(7)
Si(2)–C(2)–C(1)		122.4(1)	
Si(2)–C(2)–C(11)		118.3(1)	
C(1)–C(2)–C(11)	143(3)	119.3(2)	137(1)
Pt(2)–C(3)–C(4)	75(2)		
Pt(2)–C(3)–C(6)	141(2)		
Si(3)–C(3)–C(4) or Si(1)–C(3)–C(4)		121.4(1)	124.6(9)
Si(3)–C(3)–C(6) or Si(1)–C(3)–C(6)		117.8(1)	109.0(6)
C(4)–C(3)–C(6)	143(3)	120.1(2)	126.4(8)
Pt(2)–C(4)–C(3)	67(2)		
Pt(2)–C(4)–C(12)	146(3)		
Si(4)–C(4)–C(3) or Si(2)–C(4)–C(3)		123.9(1)	124.3(8)
Si(4)–C(4)–C(12) or Si(2)–C(4)–C(12)		116.8(1)	110.2(8)
C(3)–C(4)–C(12)	147(3)	119.1(2)	125(1)
C(1)–C(5)–C(6)	119(2)	121.6(2)	124(1)
C(3)–C(6)–C(5)	120(2)	124.0(2)	120.1(9)
C(2)–C(11)–C(12)	119(3)	122.8(2)	120.6(8)
C(4)–C(12)–C(11)	124(3)	120.9(2)	120.5(7)

3.2. Reaction of **1** *with* **9**

A mixture of **1** (5.2 mg, 0.026 mmol) and **9** (47.3 mg, 0.052 mmol) in toluene (1 ml) was stirred at room temperature under nitrogen. The mixture, which was initially pale yellow–brown, became a brown suspension in 5 min. After stirred for 24 h, the mixture was separated by silica gel preparative TLC (hexane/CH_2Cl_2, 2/1) to give **8** (8.9 mg, 59% based on **1**), **10** (6.2 mg, 21%) and **6** (5 mg, 12%). Complex **6** partially decomposed under the preparative TLC conditions.

8: m.p. 226–228°C. IR (KBr): 3056, 2956, 1468, 1412, 1249, 1125, 990, 897, 864, 832, 812, 775, 739, 681, 652. ^1H NMR: δ 0.10 (12H, s), 0.47 (12H, s), 6.93 (4H, dd, $J = 3, 6$), 7.02 (4H, dd, $J = 3, 6$), 7.32 (4H, dd, $J = 3, 5$), 7.52 (4H,

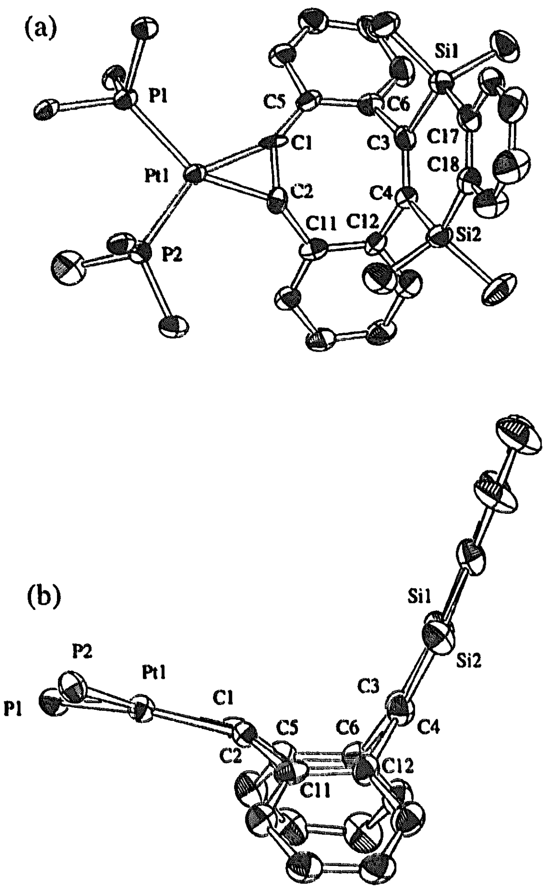


Fig. 3. Molecular structure of compound **10** with 40% probability. (a) Top view. Only the α-carbons of phenyl rings are shown for clarity. (b) Side view. Phenyl rings and methyl carbons are omitted for clarity.

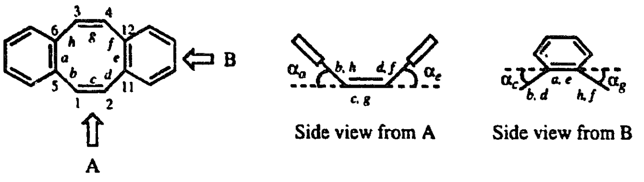
dd, $J=3, 5$). ^{13}C NMR: δ −1.12, 2.30, 125.06, 126.23, 128.06, 132.65, 142.50, 145.09, 158.63. ^{29}Si NMR: δ −20.91. *Anal.* Calc. for $C_{36}H_{40}Si_4$: C, 73.91; H, 6.85. Found: C, 73.81; H, 6.85%.

10: m.p. 215–220°C (dec., under vacuum). IR (KBr): 1715 ($\nu C\equiv C$). ^1H NMR: δ 0.04 (6H, s), 0.47 (6H, s), 6.00 (2H, d, $J=7$), 6.50 (2H, t, $J=7$), 6.88 (2H, t, $J=7$), 7.04–7.19 (20H, m), 7.32–7.39 (12H, m), 7.41 (2H, dd, $J=3, 5$), 7.63 (2H, d, $J=3, 5$). ^{13}C NMR: δ −1.96, 2.13, 124.06, 125.05, 126.56, 127.65 (t, $J=5$, P-*Ph*), 127.93, 128.75, 128.93 (s, P-*Ph*), 132.07, 132.92, 134.12 (m, P-*Ph*), 136.42 (m, *ipso* P-*Ph*), 138.13 (dd, $J=11, 84$), 145.70 (t, $J=3$), 145.99, 158.66. ^{31}P NMR: δ 24.96 (s, $^1J(Pt–P)=3409$). ^{29}Si NMR: δ −19.03. *Anal.* Calc. for $C_{62}H_{54}P_2Si_2$: C, 66.95; H, 4.89. Found: C, 66.73; H, 4.69%.

3.3. Structure determinations

A summary of the crystal parameters, data collection and refinement is listed in Table 1. Single crystals of **6** recrystallized from toluene contained two solvent molecules, the number of which was determined by ^1H NMR integration. For **6**, some carbon atoms of the solvent molecules were not found and located at calculated positions. All phenyl rings of PPh_3 were fixed as rigid groups and all other non-hydrogen atoms were refined anisotropically. Hydrogen atoms were not located for solvent molecules. All other hydrogen atoms were located at calculated positions and their positions were not refined. For **8**, all non-hydrogen atoms and hydrogen atoms were refined anisotropically and isotropically, respectively. For **10**, one phenyl ring (C601–C606 and H601–H606) was fixed as a rigid group. All other non-hydrogen atoms were refined anisotropically. All other hydrogen atoms were located at calculated positions and their positions were not refined.

Table 6
Comparison of cyclooctatetraene ring conformations of dibenzo[*a,e*]-cyclooctenes [a]



	α_a	α_e	α_c	α_g
6 [b]	22	20	32	30
8	53.3	55.8	52.7	51.7
10	40.4	40.8	35.3	55.2
3	43.1		46.3	
15	47.0		50.7	

[a] The fold angle α is defined as in Ref. [19]. In the illustrated example, α_a is the dihedral angle between the plane containing bonds b, a and h, and the plane containing bonds c and g.

[b] E.s.d.s for α_a, α_e, α_c and α_g are approximately 3.

4. Supplementary material

Further details of the crystal structure determinations are available from the authors on request.

Acknowledgements

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