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SOME PLATINUM COMPLEXES CONTAINING CHELATING BIS(SILYL) LIGANDS

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SUMMARY

The dihydrides *o*-$(HMe_2Si)_2C_6H_4$ and *o*-$(HMe_2Si)C_6H_4CH_2SiMe_2H$ react with $[PtL_2(C_2H_4)]$ ($L = PPh_3$) at room temperature to give the 5- and 6-membered cyclic bis(silyl) complexes $[Pt(SiMe_2C_6H_4SiMe_2\text{-}o)L_2]$ (I), and $[Pt\{SiMe_2C_6H_4(CH_2SiMe_2)\text{-}o\}L_2]$ (II), respectively. The disiloxane $(HPh_2Si)_2O$ reacts with $[PtL_2(C_2H_4)]$ to give a 4-membered cyclic species $[Pt(SiPh_2OSiPh_2)L_2]$ at 45°; $(HMe_2Si)_2O$ gives the hydrido(silyl) complex *cis*-$[PtH(SiMe_2OSiMe_2H)L_2]$ at 45°, but the latter cyclises at 75° to give $[Pt(SiMe_2OSiMe_2)L_2]$. The dihydrides *o*-$(HMe_2SiCH_2)_2C_6H_4$ and $HMe_2Si(CH_2)_4SiMe_2H$, which could, in principle, give complexes with 7-membered rings, in fact give only *cis*-$[PtH\{SiMe_2CH_2C_6H_4(CH_2SiMe_2H)\text{-}o\}L_2]$ and *cis*-$[PtH\{SiMe_2(CH_2)_4SiMe_2H\}L_2]$ on reaction with $[PtL_2(C_2H_4)]$.

Complexes (I) and (II) react with 1,2-bis(diphenylphosphino)ethane (Diphos) to give the doubly-chelated species $[Pt(SiMe_2C_6H_4SiMe_2\text{-}o)(\text{Diphos})]$ and $[Pt\{SiMe_2C_6H_4(CH_2SiMe_2)\text{-}o\}(\text{Diphos})]$ respectively. Both silicon atoms in complexes (I) and (II) are displaced from platinum by bromine, methyl iodide, or phenylacetylene.

The complexes *cis*-$[PtH(SiPh_2CH_2CH{=}CH_2)L_2]$ and *cis*-$[PtH(SiMe_2C{\equiv}CSiMe_2H)L_2]$ react with methyldiphenylsilane to give *cis*-$[PtH(SiPh_2Me)L_2]$.

INTRODUCTION

Many complexes containing Pt–Si bonds are now known[1-5] but no previous studies have been directed towards the preparation of complexes in which two silicon atoms are joined to a platinum atom in a cyclic structure*. We were interested in the possibility that the ring structure might confer some additional stability on the Si–Pt bonds and thus prepared a few compounds of this type and examined some of their reactions. Some reactions which did not yield cyclic systems are also described.

RESULTS AND DISCUSSION

In the preparations and attempted preparations of the cyclic systems we made

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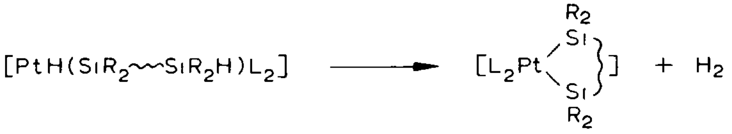
* The complex $[Pt(Ph_2SiOSiPh_2)(PMe_2Ph)_2]$ was possibly obtained previously[6], and the complex $[Pt_2(SiCl_2OSiCl_2)L_2]$ has been definitely identified recently[7].

use of the reaction between silicon hydrides and $[PtL_2(C_2H_4)]$ ($L = PPh_3$)[3]. The reaction of an $HSiR_2 \sim SiR_2H$ species with the platinum ethylene complex probably always gives a hydrido(silyl)platinum complex, according to eqn. (1)[3], but this can be followed by rapid hydrogen loss to close the ring according to eqn. (2) (*cf.* ref. 5).

$$[PtL_2(C_2H_4)] + HSiR_2 \sim\sim SiR_2H \rightarrow [PtH(SiR_2 \sim\sim SiR_2H)L_2 + C_2H_4 \quad (1)$$



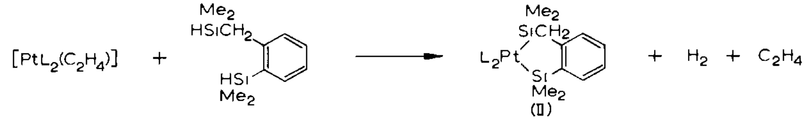
(2)

In some cases, as we shall see, the $[PtH(SiR_2 \sim\sim SiR_2H)L_2]$ complex can be isolated but gives the cyclic system, by the reaction of eqn. (2), on heating, while in other cases the reaction cannot be made to proceed beyond the first step.

The two reactions which led directly to the cyclic systems from $[PtL_2(C_2H_4)]$ at room temperature are shown in eqns. (3) and (4). In these, 5- or 6-membered rings are produced*.

(I)

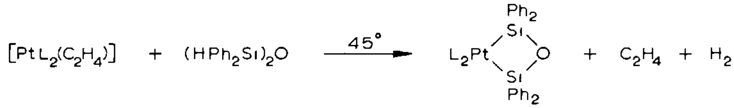
(3)



(II)

(4)

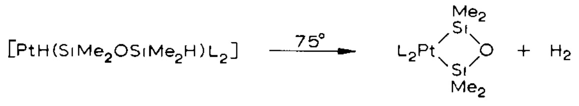
The siloxane $(HPh_2Si)_2O$ similarly gives the 4-membered cyclic system when the reaction is conducted at 45°, according to eqn. (5).



(5)

The corresponding methylsiloxane $(HMe_2Si)_2O$ gives only the hydrido(silyl) complex at 45°, according to eqn. (6), but when the reaction mixture is heated to 75°, ring closure occurs, as represented in eqn. (7).

$$[PtL_2(C_2H_4)] + (HMe_2Si)_2O \xrightarrow{45^\circ} cis\text{-}[PtH(SiMe_2OSiMe_2H)L_2] + C_2H_4 (6)$$



(7)

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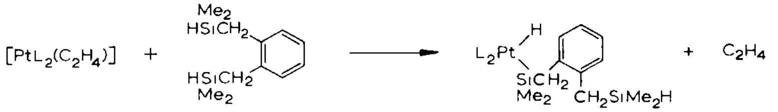
* In these, as in all the other reactions described, the gaseous products were not examined, and their nature is assumed

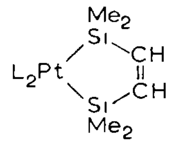
Attempts to prepare 7-membered ring systems gave only hydrido(silyl) species, as shown in eqns. (8) and (9). Heating of the hydrido(silyl) species in these cases led only to decomposition.



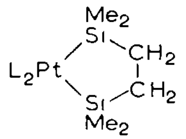
(8)

$$[PtL_2(C_2H_4)] + HSiMe_2(CH_2)_4SiMe_2H \rightarrow$$
$$\rightarrow cis\text{-}[PtH\{SiPh_2(CH_2)_nCH{=}CH_2\}L_2] + C_2H_4 \quad (9)$$

As expected, the linear dihydride $HMe_2SiC{\equiv}CSiMe_2H$ also gave the hydrido(silyl) species *cis*-$[PtH(SiMe_2C{\equiv}CSiMe_2H)L_2]$. An attempt to hydrogenate the triple bond and so possibly produce the cyclic complex (IIIa) or (IIIb) was unsuccessful.



(IIIa)

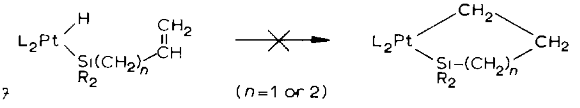


(IIIb)

We also prepared hydrido complexes having allyl or butenyl groups on the silicon atom attached to the platinum, as represented in eqns. (10) and (11), in the hope that the hydrogen atom might migrate from platinum to carbon in the process represented in eqn. (12). However, only decomposition was observed when benzene solutions of the hydrido(silyl) complexes were refluxed.

$$[PtL_2(C_2H_4)] + HMe_2SiCH_2CH{=}CH_2 \rightarrow$$
$$\rightarrow cis\text{-}[PtH(SiMe_2CH_2CH{=}CH_2)L_2] + C_2H_4 \quad (10)$$

$$[PtL_2(C_2H_4)] + HPh_2Si(CH_2)_nCH{=}CH_2 \rightarrow$$
$$\rightarrow cis\text{-}[PtH\{SiPh_2(CH_2)_nCH{=}CH_2\}L_2] + C_2H_4 \quad (11)$$



(12)

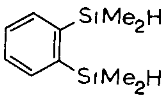
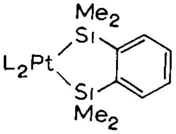
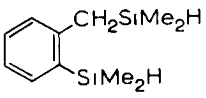
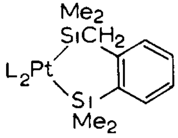
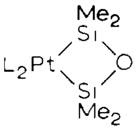
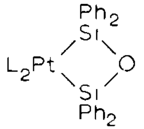
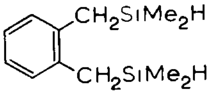
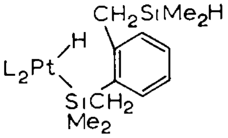
Reaction conditions, yields, m.p.'s, analyses, and other data for the complexes prepared from $[PtL_2(C_2H_4)]$ are shown in Table 1. The dry, solid complexes were stable in air except for *cis*-$[PtH\{SiMe_2CH_2C_6H_4(CH_2SiMe_2H)\text{-}o\}L_2]$. The cyclic bis(silyl) complexes are stable in benzene for at least 24 h, but the hydrido(silyl) complexes are unstable in benzene (*cf.* ref. 3).

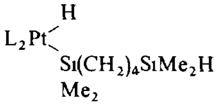
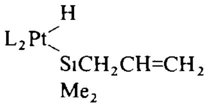
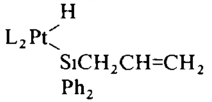
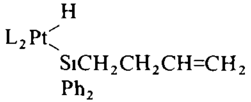
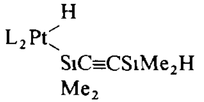
The chelate complex (I) was found to react readily with 2 molar proportions of bromine, methyl iodide, or phenylacetylene to give the products $[PtBr_2L_2]$, $[PtI(Me)L_2](+[PtI_2L_2])$, and $[PtL_2(PhC{\equiv}CH)]$ respectively. When only one molar proportion of each of these reagents was used, the same products appeared to be formed, mixed with unchanged (I). [In so far as they were examined, the reactions

(*Continued on p* 112)

TABLE 1

REACTION CONDITIONS AND DETAILS OF PRODUCTS FROM THE INTERACTION OF SILICON HYDRIDES AND [$PtL_2(C_2H_4)$]

Silane	*Product*[a]	*Conditions*		*Yield* (%)	*M p*[b] (°C)	*Analysis found (calcd.)* %		*Mol Wt found (calcd)*	*IR*		*Colour*
		temp ,	*time (h)*			*C*	*H*			*ν(Pt–H)*	
		20°,	½	95	146–149	60.6 (60.6)	5.1 (5.1)	916 (912)			White
		20°,	½	95	142–146	60.8 (60.95)	5.45 (5.2)	880 (926)			Yellow
$(HMe_2Si)_2O$	$L_2PtH(SiMe_2OSiMe_2H)$	45°,	¾	75	100–104	56.2 (56.2)	5.4 (5.2)	682[c] (854)	2135	2050	Pale brown
$(HMe_2Si)_2O$		75°,	2	92	172–174	57.3 (56.4)	5.4 (4.95)	820 (852)			Pale brown
$(HPh_2Si)_2O$		45°,	4	37	166–170	65.5 (65.5)	4.9 (4.6)	1075 (1100)			White
		20°,	1½	28[d]	75–78	60.8 (61.2)	5.7 (5.6)	(942)	2115	2085	Yellow

$HMe_2Si(CH_2)_4SiMe_2H$	 $\mathrm{L_2Pt}\genfrac{}{}{0pt}{}{\diagup H}{\diagdown \underset{Me_2}{Si}(CH_2)_4SiMe_2H}$	20°,	2	71	110–112	59.0 (59.1)	5.4 (5.9)	605[c] (893)		2105[e]	White
$HMe_2SiCH_2CH{=}CH_2$	 $\mathrm{L_2Pt}\genfrac{}{}{0pt}{}{\diagup H}{\diagdown \underset{Me_2}{Si}CH_2CH{=}CH_2}$	20°,	2	46	98–100	59.5 (60.0)	5.4 (5.2)	(819)		2070[f]	Cream
$HPh_2SiCH_2CH{=}CH_2$	 $\mathrm{L_2Pt}\genfrac{}{}{0pt}{}{\diagup H}{\diagdown \underset{Ph_2}{Si}CH_2CH{=}CH_2}$	20°,	¼	80	121–124	64.8 (64.9)	5.1 (4.9)	619[c] (944)		2070[g]	Cream
$HPh_2SiCH_2CH_2CH{=}CH_2$	 $\mathrm{L_2Pt}\genfrac{}{}{0pt}{}{\diagup H}{\diagdown \underset{Ph_2}{Si}CH_2CH_2CH{=}CH_2}$	45°,	1	50	104–106	65.7 (65.2)	5.2 (5.05)	582[c] (958)		2095[h]	Cream
$HMe_2SiC{\equiv}CSiMe_2H$	 $\mathrm{L_2Pt}\genfrac{}{}{0pt}{}{\diagup H}{\diagdown \underset{Me_2}{Si}C{\equiv}CSiMe_2H}$	45°,	1	92	114–116	58.4 (58.5)	5.4 (5.15)	613[c] (862)	2140	2070[i]	White

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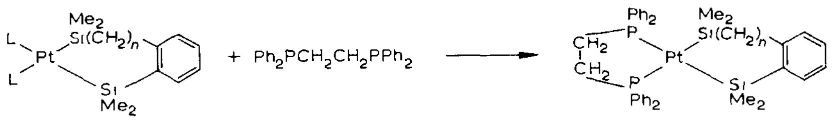
[a] The hydrido complexes are all thought to have *cis*-configurations [b] While there was no evidence of gross decomposition, melting was accompanied by darkening in colour, and it is unlikely that the original complexes are reformed on cooling [c] The low mol wt. is attributable to dissociation [d] Low yield attributable to high solubility of product in n-hexane [e] Only one band observed, presumably overlap of ν(Si–H) and ν(Pt–H) [f] ν(C=C), 1625 cm^{-1} [g] ν(C=C), 1635 cm^{-1} [h] ν(C=C), 1620 cm^{-1} [i] ν(C≡C), 2100 cm^{-1}

proceeded in similar fashion with complex (II), but both 1/1 and 1/2 ratios of complex to reagent were not examined in all cases with (II).] It would seem that once the first Pt–Si is cleaved to open the ring, the second such bond is cleaved markedly more readily. This is consistent with the existence of some stabilization of the Pt–Si bonds in the cyclic structure, but does not provide clear evidence for it, since other explanations are possible.

Treatment of complexes (I) and (II) with 1,2-bis(diphenylphosphino)ethane (Diphos) produced the novel doubly-chelated complexes (IV) and (V), as represented in eqn (13).



(13)

(IV, $n=0$), (V, $n=1$)

It is reasonable to assume that all the hydrido(silyl) complexes have *cis*-configurations, and the ν(Pt–H) values, which lie in the range 2050–2095 cm^{-1}, are consistent with this[3,4]. All the hydrido(silyl) species for which molecular weight measurements (in benzene) were carried out gave very low values. This can be attributed to dissociation (to give the $\equiv$SiH species) (*cf.* refs. 3 and 4), and possibly further decomposition.

Attempts to add diphenylsilane to the multiple bonds of the complexes $[PtH\{SiR_2(CH_2)_nCH{=}CH_2\}L_2]$ ($R = Me$ or Ph, $n=1$; $R = Ph$, $n=2$) and $[PtH(SiMe_2C{\equiv}CSiMe_2H)L_2]$, in the hope of cyclizing the products, were unsuccessful, probably because the diphenylsilane preferentially displaced the alkenyl- and alkynylsilicon ligands from platinum. This kind of displacement (see refs. 3–5) was observed when one of the allylsilicon complexes or the alkynylsilicon complex was treated with methyldiphenylsilane, as represented in eqns. (14) and (15).

$$cis\text{-}[PtH(SiPh_2CH_2CH{=}CH_2)L_2] + Ph_2MeSiH \rightarrow cis\text{-}[PtH(SiPh_2Me)L_2] \quad (14)$$

$$cis\text{-}[PtH(SiMe_2C{\equiv}CSiMe_2H)L_2] + Ph_2MeSiH \rightarrow cis\text{-}[PtH(SiPh_2Me)L_2] \quad (15)$$

Triethylsilane was found not to react with $[PtH(SiPh_2CH_2CH{=}CH_2)L_2]$.

Treatment of $[PtH(SiPh_2CH_2CH{=}CH_2)L_2]$ with 1 molar proportion of bromine in benzene gave only $[PtBr_2L_2]$, cleavage of the Pt–Si bond apparently occurring in preference to the addition across the double bond*.

EXPERIMENTAL

General

All reactions involving platinum complexes were carried out under dry nitrogen. Solvents were dried and freed from air before use.

The $[Pt(PPh_3)_2(C_2H_4)]$ was prepared as previously described[8].

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* Triethylamine was added after the bromine had reacted, in the hope of producing cyclic products by elimination of hydrogen bromide from Pt–H and C–Br bonds, but there is nor reason to believe that it influenced the nature of the product

TABLE 2

DETAILS OF PREPARATIONS VIA GRIGNARD REAGENTS AND PHYSICAL CONSTANTS OF SILICON HYDRIDES

Starting material	*Solvent*	*Product*	*Yield* (%)	*B p* (°C/mmHg)	*ν(Si–H)* (cm^{-1})	*ν(C=C)* (cm^{-1})	*Ref*
o-BrC_6H_4I	THF	*o*-$(HMe_2Si)_2C_6H_4$	78	70/2 5	2125		15, 16
o-$BrC_6H_4CH_2Br$	Et_2O (0°)	*o*-$BrC_6H_4CH_2SiMe_2H$	68	78/1	2115		17
o-$BrC_6H_4CH_2SiMe_2H$	Et_2O	*o*-$HMe_2SiC_6H_4CH_2SiMe_2H$	62	62/1	2115		17
o-$(BrCH_2)_2C_6H_4$	THF	*o*-$(HMe_2SiCH_2)_2C_6H_4$	86	88/3	2110		18
$Br(CH_2)_4Br$	THF	$HMe_2Si(CH_2)_4SiMe_2H$	54	178/750	2100		16
$BrCH_2CH=CH_2$	Et_2O	$HMe_2SiCH_2CH=CH_2$	22	69/750	2115	1630	19
$BrCH_2CH=CH_2$	Et_2O	$HPh_2SiCH_2CH=CH_2$	35	128/3	2120	1630	20
$Br(CH_2)_2CH=CH_2$	Et_2O	$HPh_2Si(CH_2)_2CH=CH_2$	55	140/2	2115	1630	19
HC=CH	THF/Et_2O	$HMe_2SiC{\equiv}CSiMe_2H$	14[a]	118/750	2140		21

[a] A better yield was obtained by using $LiC{\equiv}CLi$ (see text)

IR spectra were recorded on a Perkin–Elmer 457 grating spectrometer. Solids were examined as Nujol mulls, and liquids (*i.e.*, most silicon hydrides) as liquid smears.

Molecular weights were measured in benzene with a Mechrolab vapour phase osmometer.

Silicon hydrides

Chlorodimethylsilane was purchased from the Pierce Chemical Company. Chlorodiphenylsilane was prepared from phosphorus pentachloride and diphenylsilane[9].

Other silicon hydrides were obtained by treating the appropriate Grignard reagent with chlorodimethyl- or chlorodiphenyl-silane. Details of solvents, yields, b.p.'s and ν(Si–H) frequencies are shown in Table 2. A low yield of the dihydride $HMe_2SiC{\equiv}CSiMe_2H$ was obtained in this way, and use of the dilithioacetylene[10], obtained from acetylene and n-butyllithium was more satisfactory, giving a 51% yield.

The disiloxane $(HMe_2Si)_2O$, b.p. 71°/731 mm, and $(HPh_2Si)_2O$, m.p. 45–48°, were obtained by treatment of chlorodimethyl- and chlorodiphenyl-silane, respectively, with water, followed by fractional distillation in the first case and recrystallization the second.

Preparation of silyl–platinum complexes

(*i*). $[PtL_2(C_2H_4)]$ (453 mg, 0.61 mmole) was placed in a Schlenk tube, which was then evacuated and flushed with nitrogen several times. An excess of *o*-bis(dimethylsilyl)benzene, sufficient to cover the solid, was added. A vigorous reaction ensued, with gas evolution. During a few minutes all the solid dissolved to produce an oily yellow solution. On standing a solid separated; precipitation was completed by addition of n-hexane (5 ml). The solid was filtered off under nitrogen, washed with n-hexane (3 × 5 ml) and dried under vacuum, to give complex (I) (480 mg, 95%) with the properties shown in Table 1. There was no ν(M–H) band in the IR spectrum.

(*ii*). Preparations of the other complexes listed in Table 1 were conducted in similar fashion, except that in some cases solid was present throughout and so the mixture was stirred vigorously. In some other cases, in which reaction appeared sluggish, gentle warming to ca. 45° was used. Sometimes no solid separated until n-hexane was added. Details are given in Table 1.

Reactions of complexes (I) and (II) with 1,2-bis(diphenylphosphino)ethane

(*i*). 1,2-Bis(diphenylphosphino)ethane (0.088 g, 0.22 mmole) in benzene (4 ml) was added dropwise with stirring to a solution of (II) (0.208 g, 0.22 mmole) in benzene (7 ml). The mixture was refluxed gently for 10 min, then cooled, and most solvent evaporated off under vacuum. n-Hexane (10 ml) was added and the solid filtered off, washed well with n-hexane (3 x 5 ml), and dried under vacuum. The product (110 mg, 63%), m.p. 245–248°, was recrystallized from benzene/n-hexane to give (V) (80 mg, 46%), m.p. 246–248°. (Found: C, 55.5; H, 5.2; mol. wt., 836; $C_{37}H_{36}P_2PtSi_2$calcd.; C, 55.55; H, 5.2%; mol. wt., 800.) The IR spectrum was clearly different from that of the starting material, and showed no ν(M–H) bands.

(*ii*). A similar procedure from (I) gave (IV) (64%), m.p. 263–266°. (Found: C, 55.3; H, 5.3. $C_{36}H_{34}P_2PtSi_2$ calcd.; C, 55.0; H, 5.1%.)

Other reactions of complex (I)

(*i*). Bromine (0.18 mmole) in benzene (1 ml) was added dropwise to a vigorously stirred solution of (I), (85 mg, 0.093 mmole) in benzene (5 ml). The mixture became cloudy. n-Hexane (5 ml) was added and the mixture set aside for one hour. The solid was filtered off, washed with n-hexane (3 x 5 ml), dried under vacuum, and shown to be [$PtBr_2L_2$] (77 mg, 94%), m.p. 315–320° (lit.[11] m.p. 308° dec.) by comparison of its IR spectrum with that of an authentic sample.

(*ii*) (*a*). Methyl iodide (28.4 mg, 0.20 mmole) in benzene was added dropwise to a vigorously stirred solution of (I) (91 mg, 0.10 mmole) in benzene (2 ml). The mixture was kept at 84° (bath temperature) for 30 min, then cooled. Most of the solvent was evaporated off under vacuum, and n-hexane was added. The solid was filtered, washed with n-hexane, dried under vacuum, and shown to be mainly [PtI(Me)L_2] (63 mg, 73%), m.p. 260–268° (lit.[12] m.p. 270–274°), by the virtual identity of its IR spectrum with that of an authentic sample. The somewhat low m.p. and carbon content (Found: C, 49.1; H, 3.8. $C_{37}H_{33}IPt$ calcd.: C, 51.6; H, 3.9%) are attributable to the presence of some [PtI_2L_2], some of which was isolated from the corresponding reaction of (II) (see below).

(*ii*) (*b*). A similar procedure but using only 0.091 mmole of methyl iodide, gave a solid mixture (53 mg) which had an indistinct m.p., but which all became molten by 120°, with decomposition. The IR spectrum indicated that it was substantially a mixture of [PtI(Me)L_2] and (I). GLC examination of the benzene solution revealed the presence of small amounts of a large number of products.

(*iii*) (*a*). Phenylacetylene (15.3 mg, 0.15 mmole) in benzene (1 ml) was added dropwise with stirring to a solution of (I) (68 mg, 0.075 mmole) in benzene (4 ml). The solution turned orange during the addition. Most of the benzene was evaporated under vacuum and n-hexane was added. The solid which separated was filtered, washed with n-hexane, dried under vacuum and shown to be [$PtL_2(PhC{\equiv}CH)$] (30 mg, 50%), m.p. 138–140° (lit.[13] m.p. 141–148°), by the identity of its IR spectrum with that of an authentic sample; $\nu(C{\equiv}C)$, 1684 cm^{-1}. The relatively low yield is attributable to the marked solubility of the complex in n-hexane.

(*iii*) (*b*). A similar procedure, but starting from (I) (91 mg, 0.10 mmole) and phenylacetylene (10.2 mg, 0.10 mmole), gave a yellow solid (38 mg), m.p. 97–105°. The IR spectrum indicated that it was substantially a mixture of (I) and [PtL_2-($PhC{\equiv}CH$)].

Other reactions of complex (II)

(*i*). Bromine (0.055 mmole) in benzene (1 ml) was added dropwise with stirring to a solution of (II) (100 mg, 0.11 mmole) in benzene (5 ml). After the addition, the cloudy solution was stirred for 10 min, n-hexane (5 ml) then added, and the mixture was set aside for 15 min. The white solid was filtered off, washed well with n-hexane, dried under vacuum and shown to be (somewhat impure) [$PtBr_2L_2$] (20 mg, 21 %), m.p. 315°, after softening at 300° [lit.[11] m.p. 308° (dec.)] by the essential identity of its IR spectrum with that of an authentic sample.

The filtrate was evaporated to small bulk, and n-hexane (10 ml) was added to precipitate more solid. This was filtered, washed with n-hexane, and dried to give a yellow powder (62 mg), m.p. 112–120°. The product had an IR spectrum very similar to that of the starting material (II) (m.p. 142–146°), and it was considered to be a mixture of (II) with some [$PtBr_2L_2$].

(*ii*). Methyl iodide (21 mg, 0.15 mmole) in benzene (3 ml) was added to a solution of (II) (68 mg, 0.073 mmole) in benzene (5 ml) and the mixture was gently refluxed for 30 min, during which the colour of the solution changed from yellow to red. The mixture was cooled and the solvent evaporated to small bulk. The addition of n-hexane (10 ml) precipitated an orange-brown solid. This was filtered, washed with n-hexane and dried under vacuum. The material darkened on heating, contracted at ≈200–210° and was molten at 220–230°. Its IR spectrum was identical with that of the pale yellow solid, m.p. 240–245° (dec. and much darkening before melting), which was obtained by a similar procedure from [$PtL_2(C_2H_4)$] and an excess of methyl iodide. Both materials were thought to be impure [$PtI(Me)L_2$].

The filtrate on cooling and standing several days gave a bright orange solid (10 mg, 14 %), m.p. ca. 306°, thought to be [PtI_2L_2] (lit.[14] m.p. 306°).

(*iii*). Phenylacetylene (0.36 mmole) was added to a solution of (II) (113 mg, 0.12 mmole) in benzene (5 ml). The resulting bright red solution was stirred for a further 10 min. The benzene was evaporated to small bulk, n-hexane was added, and the mixture was kept overnight in the refrigerator. The solid which separated was filtered off, washed with a little cold n-hexane, dried under vacuum, and shown to be [$PtL_2(PhC{\equiv}CH)$] (75 mg, 75 %), m.p. 140–141° (lit.[13] 141–148°) by the identity of its IR spectrum [$\nu(C{\equiv}C)$, 1684 cm^{-1}] with that of an authentic sample.

Interaction of [$PtH(SiPh_2CH_2CH{=}CH_2)L_2$] and [$PtH(SiMe_2C{\equiv}CSiMe_2H)L_2$] with methyldiphenylsilane

(*i*). Methyldiphenylsilane (5 ml) was added to *cis*-[$PtH(SiPh_2CH_2CH{=}CH_2)$-L_2] (100 mg, 0.106 mmole) and the mixture was heated at 50° for 5 min, during which the solid dissolved to give a pale yellow solution. The mixture was cooled and n-hexane (15 ml) was added, to give an off-white solid. This was filtered off, washed with n-hexane (3 × 5 ml) and dried under vacuum, to give *cis*-[$PtH(SiPh_2Me)L_2$] (70 mg, 72 %), m.p. 126–129° (lit.[3] 122–126°) (Found. C, 64.2; H, 5.0. $C_{49}H_{44}P_2PtSi$ calcd.:

C, 64.1; H, 4.8%) The IR spectrum was identical with that of an authentic sample; ν(Pt–H), 2100 cm^{-1}.

(*ii*). Similarly, *cis*-[PtH($SiMe_2C{\equiv}CSiMe_2H$)L_2] (70 mg, 0.08 mmole) gave *cis*-[PtH($SiPh_2Me$)L_2] (62 mg, 84%), m.p. 126–129° (lit.[3] 123–126°) (Found: C, 63.6; H, 5.0. $C_{49}H_{44}P_2PtSi$ calcd.: C, 64.1; H, 4.8%). The IR spectrum was identical with an authentic sample; ν(Pt–H) 2100 cm^{-1}.

Interaction of [*PtH*($SiMe_2C{\equiv}CSiMe_2H$)L_2] *and* [*PtH*($SiPh_2CH_2CH{=}CH_2$)L_2] *with one molar proportion of diphenylsilane*

(*i*). Diphenylsilane (17.5 mg, 0.095 mmole) in benzene (1 ml) was added dropwise to a stirred solution of *cis*-[PtH($SiMe_2C{\equiv}CSiMe_2H$)L_2] (82 mg, 0.095 mmole) in benzene (5 ml). The yellow solution was warmed to ca. 50° for 2 min, then cooled, and the solvent was evaporated to small bulk under vacuum. n-Hexane (10 ml) was added to precipitate a pale yellow solid, which was filtered off, washed with n-hexane, and dried under vacuum. The solid (61 mg) darkened rapidly at 138–140° and finally became molten at 185° with decomposition. The IR spectrum [ν(Pt–H, Si–H), broad complex band at 2100–2000 cm^{-1}] was very similar to that of *cis*-[PtH($SiPh_2H$)L_2], but the latter has a much lower m.p.[3], *viz.* 108–110°, and the elemental analysis did not agree with this formula. (Found: C, 61.9; H, 4.8. $C_{48}H_{42}P_2PtSi$ calcd.: C, 63.8; H, 4.7%.)

(*ii*). Similarly, *cis*-[PtH($SiPh_2CH_2CH{=}CH_2$)L_2], (142 mg, 0.15 mmole) in benzene (3 ml) reacted with diphenylsilane (27.5 mg, 0.15 mmole) in benzene (1 ml) to give a yellow solid (81 mg). The solid darkened rapidly at 139–140° and was all molten by 180°. The IR spectrum was very similar to that of *cis*-[PtH($SiPh_2H$)L_2], but the m.p. and analysis (Found: C, 63.1; H, 5.9. $C_{48}H_{42}P_2PtSi$ calcd.: C, 63.8; H, 4.7%) showed that it was not, in fact, the latter complex.

Interaction of [*PtH*($SiPh_2CH_2CH{=}CH_2$)L_2] *and bromine*

Bromine (15.5 mg, 0.10 mmole) in benzene (2 ml) was added dropwise with stirring to a yellow solution of *cis*-[PtH($SiPh_2CH_2CH{=}CH_2$)L_2] (94.4 mg, 0.10 mmole) in benzene (2 ml). The colour of the bromine was rapidly discharged and the mixture became cloudy as a white solid separated. More benzene (2 ml) was added, but the precipitate did not dissolve. Triethylamine (0.25 ml) was added, and the mixture stirred for 20 min, after which n-hexane (4 ml) was added, and the solid which separated was filtered off, washed with n-hexane, and dried under vacuum to give [$PtBr_2L_2$] (40 mg, 44%), m.p. 315–320°, (lit.[11], m.p. 308° dec.), the IR spectrum of which was identical with that of an authentic sample. Additional solid, m.p. 305–315°, separated when the mother liquor was kept overnight in the refrigerator.

Action of heat on cis-[*PtH*{$SiR_2(CH_2)_nCH{=}CH_2$}L_2] ($n=1$, $R=Me$ *and* Ph; $n=2$, $R=Ph$), [*PtH*{$SiMe_2(CH_2)_4SiMe_2H$}L_2] *and cis*-[*PtH*{$SiMe_2CH_2C_6H_4(CH_2SiMe_2H)$-*o*}$L_2$]

When solutions of the above complexes were refluxed in benzene for 60 minutes, a deep red colour developed. The products were very soluble in benzene and in n-hexane, and only small amounts were isolated. None of them could be identified.

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