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THE REACTION OF BIS(PHENYLDIMETHYLPHOSPHINE)BIS(DIPHENYLSILYL)PLATINUM(II) WITH ACETYLENES

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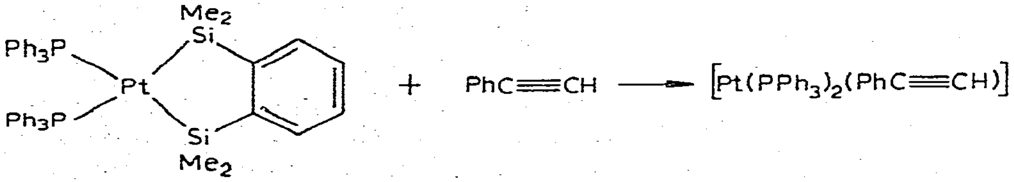
Summary

The complex *cis*-[Pt(SiPh$_2$H)$_2$L$_2$] (L = PhMe$_2$P), I, reacts with acetylene to give a product believed to be the chelate [Pt(SiPh$_2$CH=CHSiPh$_2$)L$_2$], II; phenyl-, *p*-bromophenyl-, and *p*-fluorophenyl-acetylene give analogous products. On treatment with Ph$_2$PCH$_2$CH$_2$PPh$_2$ (dppe), II gives [Pt(SiPh$_2$CH=CHSiPh$_2$)(dppe)]. The corresponding saturated compounds [Pt(SiPh$_2$CH$_2$CH$_2$SiPh$_2$)L$_2$] and [Pt(SiPh$_2$CH$_2$CH$_2$SiPh$_2$)(dppe)] and the vinylic [Pt(SiPh$_2$Me)$_2$(Ph$_2$PCH=CHPPh$_2$)] have also been made. Reactions of I with bromine and hydrogen halides are described.

Introduction

Acetylenes are known to be able to displace silicon ligands from some silyl-platinum hydrides and bis-silyl-platinum complexes [1—3]; e.g.

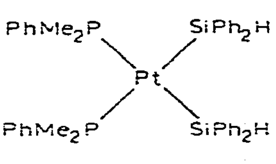
$$[PtH(SiMePh_2)(PPh_3)_2] + PhC{\equiv}CH \rightarrow [Pt(PPh_3)_2(PhC{\equiv}CH)]$$



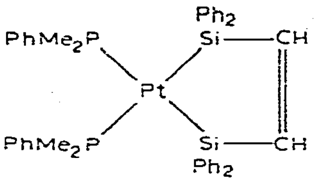
However, when we examined the interaction of acetylene and some of its derivatives with the bis(hydridosilyl)-platinum complex I we observed a coupling rather than a displacement reaction, as described below.

Results and discussion

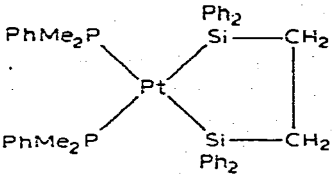
When acetylene was bubbled through a benzene solution of *cis*-$[Pt(SiPh_2H_2)_2L_2]$ (L = $PhMe_2P$), I, at 60°C for 1 h a pale yellow compound, II, was obtained. The carbon and hydrogen contents and molecular weight were consistent with



(I)



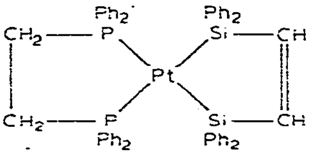
(II)



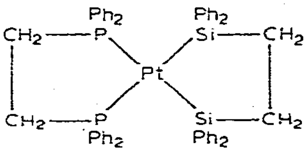
(III)

the composition $PtL_2(SiPh_2H)_2(CH{\equiv}CH)$ or $PtL_2(SiPh_2)_2(CH{\equiv}CH)$, but the IR spectra showed no bands in the region (viz. ca. 1680 cm^{-1}) associated with π-bonded alkynes or that (viz. 2200—2000 cm^{-1}) associated with either σ-bonded alkynes or Pt—H or Si—H bonds. The ^{31}P-$\{^1H\}$ NMR spectrum indicated that it was symmetrical and of *cis* configuration, with a ^1J(Pt—P) coupling constant of 1604 Hz in the range observed for *cis*-bis-phosphine-bis-silylplatinum(II) complexes [4,5].

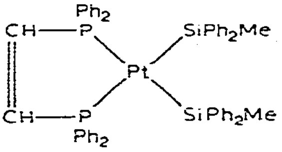
We suggest that II has the structure shown. We were able to rule out an obvious alternative III by synthesizing it unambiguously (from $[PtL_2(CO)_3]$ and $HPh_2SiCH_2CH_2SiPh_2H$ [5]) and showing it to be different from II. Thus the IR spectra of II and III, while very similar overall, show distinct differences, and the coupling constant ^1J(Pt—P) for III (1563 Hz) is quite distinct from, though close to, that for II (1604 Hz). We demonstrated that the two complexes, which have rather similar melting points, were not simply different crystal forms of the same compound by recrystallizing a 1 : 1 mixture and observing that the IR spectrum of the material obtained corresponded to a superposition of the two separate spectra.



(IV)

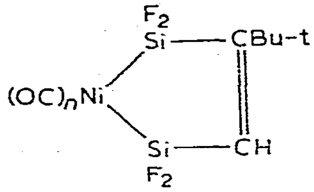


(V)



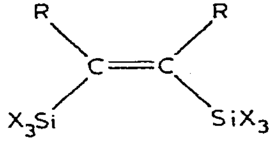
(VI)

Complexes II and III were converted by treatment with 1,2-bis(diphenylphosphino)ethane (dppe), into the corresponding chelate complexes IV and V, and the differences in physical properties between these were rather greater than those between II and III. In the ^1H NMR spectra, IV and V showed the expected complex multiplet in the region τ 2.6—3.2 ppm associated with the phenyl protons, and the characteristic broad pattern at τ 7.6—8.4 ppm associated with the PCH_2 protons. Complex V showed the expected triplet, centred at τ 8.9 ppm, associated with the Si—CH_2 protons, but no signal associated with the Si—CH=CH—Si protons could be identified in the case of IV, and we assume that it is masked by the resonances of the phenyl protons. Complex II likewise showed the expected phenyl—proton and P—Me resonances but no identifiable Si—CH=CH—Si signal. The assumption that the signal for the vinylic-proton is masked by the signal from the aryl group is justified by two items of evidence, viz. (a) complex VI was synthesized, and also found to have no identifiable —CH=CH— signals, and (b) the resonances from the vinylic protons of complexes VII and VIII are centred (at τ 3.36 and 2.73 ppm, respectively, [14]) in the range associated with the phenyl protons in our complexes.

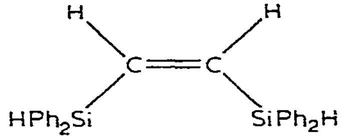


(VII, $n = 2$)
(VIII, $n = 4$)

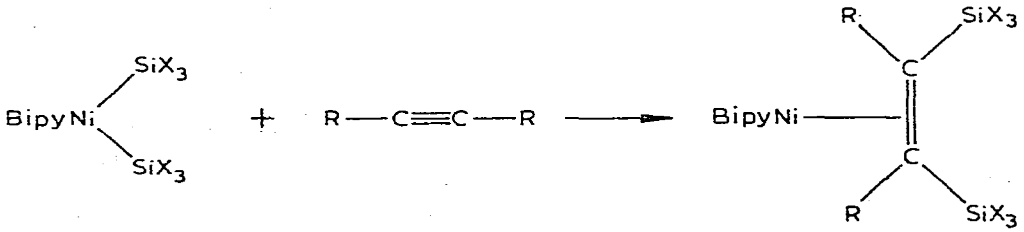
While we have been unable to demonstrate directly the presence of an olefinic linkage in the product we believe to have structure II *, this assignment of structure, which we arrived at some years ago [6], has received substantial indirect support from recent fine work by Kumada and his colleagues involving nickel complexes [7]. In that work, they found that silicon hydrides X_3SiH react with some acetylenes, RC≡CR, in the presence of diethyl(bipyridyl)Ni(II) to give, along with the expected hydrosilylation products, bis-silylated compounds of the type IX. If the bis-silyl group could be displaced from II or IV by an excess of a silicon hydride or an acetylene it should give compound X, which would, in principle, be produced in the Kumada bis-silylation from acetylene and diphenylsilane. Indeed, Kumada and his colleagues postulated that the products of type IX are produced as coordinated ligands from bis-silylnickel species in a reaction of the type



(IX)



(X)



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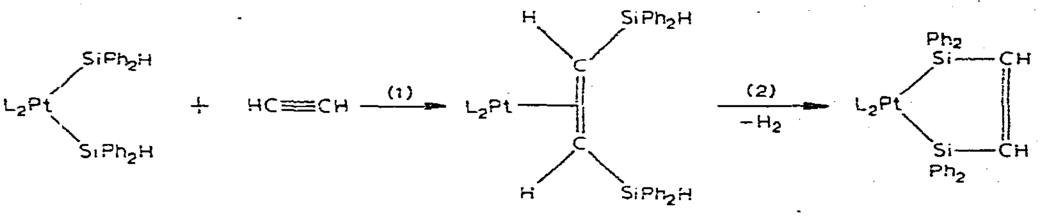
* The intense yellow colour in solution prevented identification of a C=C bond in the Raman spectrum. An attempt was made to carry out an X-ray crystallographic analysis of the structure but the crystal deteriorated rapidly under irradiation.

Clearly an exactly analogous process can be written for our reactants, and the π-bonded species produced would be very likely to rearrange to the σ-bonded complex II with loss of H_2, as in Scheme 1.

SCHEME 1

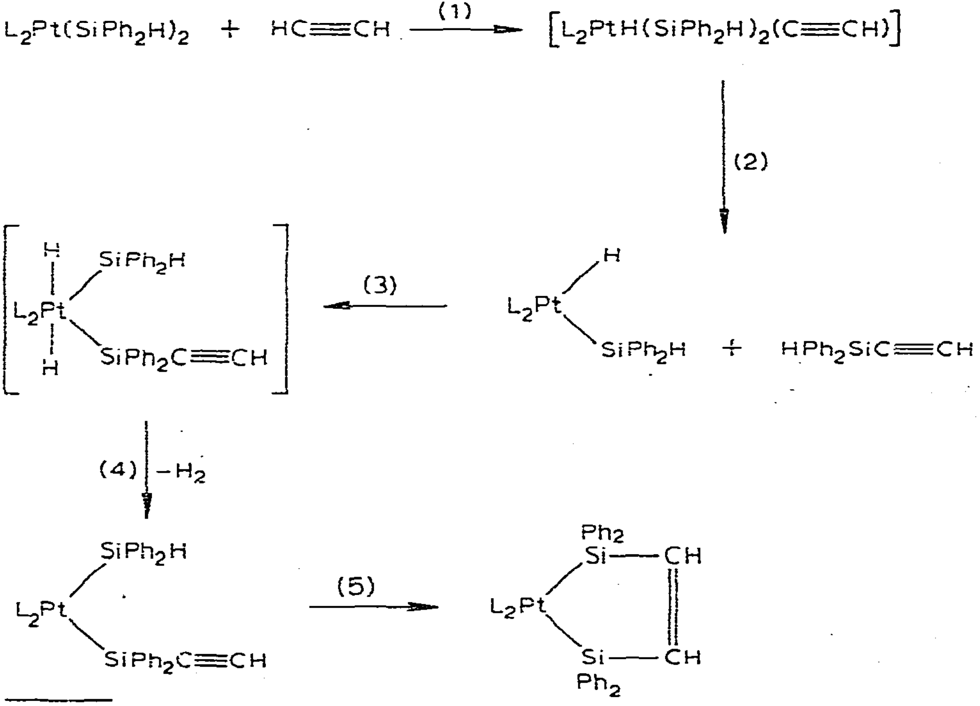


(II)

Acceptance of Scheme 1 would still leave the considerable problem of the mechanism of conversion (1), which seems unlikely to be a single-step process. We are inclined to disfavour a direct interaction of type (1), partly because the complex $[Pt(SiPh_2H)_2(dppe)]$ which might reasonably be expected to undergo such a reaction as readily as I, does not react with acetylene to give IV.

Of the many possible routes to II which can be written, we offer as one example, that shown in Scheme 2. This has the advantage that steps (1)—(4) represent well established types of reactions, but there is no precedent for the internal hydrosilylation step (5) which results in ring closure *. We note that in the pres-

SCHEME 2



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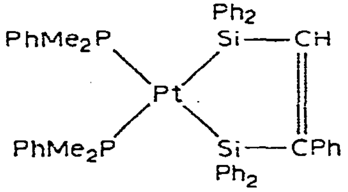
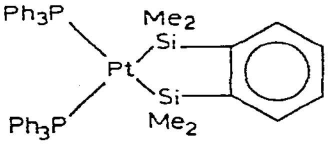
[*] Silylene intermediates, probably coordinated rather than free, could be postulated for this step by analogy with proposals by Kumada and his colleagues [8], but there is no good reason to assume that they are involved in our reactions.

ence of an excess of acetylene the [PtH(SiPh$_2$H)L$_2$] formed in steps (1)—(2) would be expected to be in equilibrium with [PtL$_2$(HC≡CH)] and Ph$_2$SiH$_2$, and the latter could hydrosilylate the HPh$_2$SiC≡CH to give HPh$_2$SiCH=CHSiPh$_2$H; the *cis*-isomer of this last species (which might in the medium be in dynamic equilibrium with the *trans*-isomer) would then react with the [PtL$_2$(HC≡CH)] with evolution of hydrogen to give II (cf. ref [3]). A mechanism which involves successive cleavages of the Pt—Si bonds of I could account for the failure of [Pt(SiPh$_2$H)$_2$(dppe)] to react with acetylene, since the cleavages might well be somewhat inhibited in the chelate complex.

It should be noted that formation of a molecule of II requires the loss of two atoms of hydrogen from the reactants. The formation of dihydrogen was, indeed, observed, though the quantity was not measured, when complex I was treated with phenylacetylene to give a product, XI, the analogue of II. It is noteworthy that XI must be resistant to cleavage by the excess of phenylacetylene (as II must be towards cleavage by acetylene), which is at first sight surprising, since the chelate complex XII, for example, is readily cleaved by phenylacetylene [2]. Possibly the presence of aryl groups on the silicon atoms in XI and II leads to a greater resistance to cleavage, and, in agreement with this, complex III was recovered unchanged after treatment with an excess of phenylacetylene in benzene.



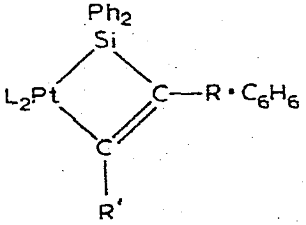
(XI)



(XII)

p-Bromo- and *p*-fluoro-phenylacetylene reacted with I to give products with properties, especially IR spectra, very similar to those of XI, and it is assumed that they are analogues of XI; the carbon and hydrogen analyses were low, but under the conditions of analysis used the parent *p*-BrC$_6$H$_4$C≡CH and *p*-FC$_6$H$_4$C≡CH gave similarly unsatisfactory analyses. The complex [Pt(SiPhMeH)$_2$L$_2$] reacted with phenylacetylene to give a product believed to be impure [Pt-(SiPhMeCH=CHSiPhMe)L$_2$] (L = PMe$_2$Ph).

Methylacetylene and diphenylacetylene react with I in benzene to give a different type of product, with carbon and hydrogen contents and ^{1}H NMR spectra reasonably consistent with the rather unlikely formulations XIII and XIV. The product from PhC≡CPh also gave a parent ion in the mass spectrum corresponding to XIV after loss of the benzene molecule [6]. Additional studies are required, however, to establish the nature of these products.



(XIII, R = H, R' = Me (or vice versa))
(XIV, R = R' = Ph)

Complex I reacted with the acetylene $ClCH_2C{\equiv}CCH_2Cl$ to give *cis*-$[PtCl_2L_2]$ in 76% yield.

Reaction of I with hydrogen halides, bromine, and methyllithium

Complex I reacted as expected [10] with a 2-molar proportion of hydrogen chloride to give *trans*-$[Pt(H)ClL_2]$. In contrast, hydrogen bromide under the same conditions gave a mixture of the 6-coordinate $[PtH_2Br_2L_2]$ and starting material (I). The presence of $[PtH_2Br_2L_2]$ was confirmed by separate preparation of this complex from treatment of *trans*-$[Pt(H)BrL_2]$ with one molar proportion of hydrogen bromide in benzene *. The chelate complex $[Pt(SiPh_2H)_2(dppe)]$ reacted differently with 2 molar proportions of hydrogen bromide to give $[PtBr_2(dppe)]$ (and presumably Ph_2SiH_2), in keeping with the known reactions of $[Pt(SiR_3)_2(dppe)]$ species with hydrogen chloride [10].

Bromine in one molar proportion reacted with I to give the cleavage product *cis*-$[PtBr_2L_2]$ in 60% yield, along with some $[PtH_2Br_2L_2]$, which was presumably formed from hydrogen bromide produced by interaction of bromine with Si—H species or by reaction of Si—Br species with traces of moisture. No substitution product of the type $[Pt(SiPh_2Br)_2L_2]$ (cf. ref. [11]) was isolated.

Experimental

General

All reactions were conducted under dry nitrogen. Molecular weights were determined by osmometry in benzene. NMR spectra were recorded on Varian HA 100 (^{1}H) and JEOL PFT 100 (^{31}P) spectrometers. The ^{31}P spectra were obtained with ^{1}H-decoupled and are referred to $P(OMe)_3$ in C_6D_6 as external standard; positive shifts are to high field of the reference.

Reaction of cis-$[Pt(SiPh_2H)_2(PMe_2Ph)_2]$ (I) with acetylene

Dry acetylene was bubbled through a solution of I (0.72 g, 0.86 mmol) in benzene (30 ml), initially for 30 min at room temperature and then for 1 h at 60°C. The initially lime-coloured solution became golden yellow. Most of the solvent was evaporated off under vacuum, and n-hexane (15 ml) was added to precipitate a pale yellow solid. This was filtered off, washed with n-hexane (3 × 5 ml), and dried under vacuum to give II (0.50 g, 68%), m.p. 176—182°C (Found: C, 58.5; H, 5.3. $C_{42}H_{44}P_2PtSi_2$ calcd.: C, 58.5; H, 5.1%). ^{1}H NMR: τ 9.42 (P—CH_3); ^2J(PCH) 4 Hz; ^3J(PtPCH) 9 Hz. ^{31}P NMR, δ 150.2 ppm, ^1J(Pt—P) 1604 Hz.

Reaction of II with dppe

A solution of 1,2-bis(diphenylphosphine)ethane (0.22 mmol) in benzene (4 ml) was added dropwise with stirring to a solution of II (0.22 mmol) in benzene (7 ml). The mixture was refluxed gently for 1 h then cooled, and most of the solvent was taken off under vacuum, n-Hexane (10 ml) was added, and the precipitated solid was filtered off, washed with n-hexane (3 × 5 ml), dried under vacuum, and recrystallized from n-hexane/benzene to give IV, m.p. 258—261°C,

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* The complex $[PtH_2Br_2L_2]$ with L = PMe_2Ph appears to be markedly more stable than the corresponding complex with Et_3P ligands [9].

in 56% yield. (Found: C, 63.2; H, 4.5. $C_{52}H_{44}P_2PtSi_2$ calcd.: C, 63.5; H, 4.7%). ^{1}H NMR: τ 8.12 (PCH_2CH_2P), ^2J(PCH) ca. 9 Hz.

Reaction of I with arylacetylenes

An excess of phenylacetylene (1 ml) was added to a solution of I (0.30 g, 0.36 mmol) in benzene (5 ml), and the mixture was refluxed for 2 h. The solution was evaporated under reduced pressure to small bulk and n-hexane (15 ml) was added. The precipitated yellow solid was filtered off, washed with n-hexane (3 × 5 ml) and dried under vacuum to give complex XI (185 mg, 55%), m.p. 200—202°C. (Found: C, 61.5; H, 5.4. $C_{48}H_{48}P_2PtSi_2$ calcd.: C, 61.45; H, 5.15%). There were no (M—H) bonds in the IR spectrum.

p-Bromoacetylene similarly gave the corresponding product (60%), m.p. 204—208°C. (Found: C, 54.5; H, 4.7%; M.W. 1020. $C_{48}H_{47}BrP_2PtSi_2$ calcd.: C, 56.7; H, 4.65%; M.W. 1017), and *p*-fluoroacetylene the corresponding product (66%), m.p. 191—195°C (Found: C, 59.2; H, 4.9; M.W. 880. $C_{48}H_{47}FP_2PtSi_2$ calcd.: C, 60.3; H, 4.95%; M.W. 956).

In a separate experiment, the gas evolved from a mixture of I and phenylacetylene was analyzed by GLC and shown to contain hydrogen.

Reaction of [Pt(SiPhMeH)$_2$L$_2$] with phenylacetylene

Interaction of phenylacetylene with [Pt(SiPhMeH)$_2$L$_2$] for 30 min under the conditions described for the reaction with I, but at 60°C for 30 min gave a product (39%) believed to be impure [Pt(PhMeSiCH=CHPhSiMePh)L$_2$], m.p. 173—175°C (Found: C, 57.3; H, 5.3; $C_{38}H_{44}P_2PtSi_2$ calcd.: C, 56.1; H, 5.45%). High temperatures and/or longer reaction times gave lower yields of the product, which is possibly decomposed by the excess of phenylacetylene. The IR spectrum showed close similarity to that of XI, but with the expected minor differences.

Reaction of [Pt(SiPh$_2$H)$_2$(dppe)] with acetylene

Interaction of acetylene with [Pt(SiPh$_2$H)$_2$(dppe)] under the conditions used for the reaction with I gave only the unchanged starting complex.

Reaction of I with $ClCH_2C{\equiv}CCH_2Cl$

An excess of $ClCH_2C{\equiv}CCH_2Cl$ (1.5 ml) was added to a solution of I (0.12 g, 0.15 mmol) in benzene (4 ml) and the mixture was heated under reflux for 1.5 h. The solvent was evaporated to small bulk and n-hexane (15 ml) was added. The white solid was filtered off, washed with n-hexane, and dried under vacuum, and shown to be *cis*-[PtCl$_2$(PMe$_2$Ph)$_2$] (60 mg, 76%), m.p. 187—189°C (lit. [12], 199—200°C) (authentic IR).

Preparation of VI

cis-1,2-Bis(diphenylphosphino)ethene (0.13 g, 0.32 mmol) was added to *cis*-[Pt(SiPh$_2$Me)$_2$L$_2$] (0.28 g, 0.32 mmol) in benzene (15 ml). The solution was kept at 70—80°C for 70 min, then the solvent was evaporated off under vacuum, and n-hexane (15 ml) was added to precipitate a cream solid. This was filtered off, washed with n-hexane (3 × 15 ml) and dried under vacuum to give VI (255 mg, 79%) m.p. 208—209°C (Found: C, 63.2; H, 5.15. $C_{52}H_{48}P_2PtSi_2$

calcd.: C, 63.3; H, 4.9%); ^1J(Pt—P) 1394 Hz. The ^{1}H NMR spectrum showed no identifiable resonance due to the P—CH=CH—P protons, and this resonance is assumed to be masked by the aromatic proton resonances. ^{1}H NMR: τ 9.55 ($SiCH_3$); τ 2.2—3.5 (ArH + PCH=CHP). ^{31}P NMR: δ 80.0 ppm, ^1J(Pt—P) 1394 Hz.

Preparation of V

A solution of III (0.085 g, 0.1 mmol) and dppe (0.04 g, 0.1 mmol) in benzene (8 ml) was boiled under reflux for 60 min. The solvent was reduced to small bulk (2 ml) under reduced pressure, and n-hexane was added to precipitate a white solid. This was filtered off, washed with n-hexane (5 × 15 ml), and dried under vacuum to give V (60 mg, 62%), m.p. 237—240°C (Found: C, 63.6; H, 4.9. $C_{52}H_{46}P_2PtSi_2$ calcd.: C, 63.6; H, 4.9%). ^{1}H NMR: τ 8.02 (PCH_2CH_2P), ^2J(PCH) ca. 9 Hz; τ 8.86 ($SiCH_2CH_2Si$), ^3J(PtSiCH) 14 Hz. ^{31}P NMR: δ 80.6 ppm, ^1J(Pt—P) 1519 Hz.

Treatment of III with phenylacetylene

A mixture of phenylacetylene (1 ml) and III (75 mg) in benzene (5 ml) was stirred at room temperature for 30 min then kept at 60°C for a further 30 min. Solvent was evaporated to small bulk, and n-hexane was added. The white solid, m.p. 173—177°C, which separated was unchanged III (41 mg, 55%), as shown by its IR spectrum.

Reactions of I with hydrogen halides and with bromine

(a) Hydrogen chloride (0.44 mmol) in benzene (10 ml) was added during 40 min with vigorous stirring to a solution of I (180 mg, 0.22 mmol) in benzene (10 ml). The mixture was stirred for an additional 40 min., most of the solvent was evaporated off, and n-hexane was added. The white solid was filtered off, washed with n-hexane, dried under vacuum and shown to be *trans*-[$PtHClL_2$] (42 mg, 39%), m.p. 101—103°C (lit. [10], 102—104°C) [authentic IR spectrum; ν(Pt—H) 2195 cm^{-1}].

(b) Bromine (0.274 mmol) in benzene (10 ml) was added during 20 min with vigorous stirring to a solution of I (0.23 g, 0.274 mmol) in benzene (15 ml). Work up as in *(a)* gave *cis*-[$PtBr_2L_2$] (52 mg, 60%), m.p. 200—203°C (lit. [11], 201—204°C (Found: C, 30.2; H, 3.5. $C_{16}H_{22}P_2PtBr_2$ calcd.: C, 30.45; H, 3.5%).

After standing overnight the mother liquor deposited a little (15 mg) white solid, m.p. 199—205°C, ν(Pt—H) 2240 cm^{-1}, thought to be [$PtH_2Br_2L_2$].

(c) Hydrogen bromide (0.42 mmol) in benzene (10 ml) was added dropwise with stirring during 30 min to a solution of I (172 mg, 0.21 mmol) in benzene (10 ml). The mixture was stirred for a further 40 min then n-hexane was added. The precipitated white solid was filtered off, washed with n-hexane, and dried under vacuum to give material of m.p. 198—202°C (45 mg, 52%, if [$PtH_2Br_2L_2$]. From the IR spectrum [ν(Pt—H) 2240, with a weak shoulder at 2210 cm^{-1}] it was adjudged to be [$PtH_2Br_2L_2$] contaminated with I (Found: C, 32.3; H, 3.8. $C_{16}H_{24}Br_2P_2Pt$ calcd.: C, 30.35; H, 3.8%).

Preparation of [$PtH_2Br_2L_2$]

Hydrogen bromide (0.13 mmol) in benzene (5 ml) was added dropwise with stirring during 15 min to a solution of *trans*-[PtBrHL$_2$] (0.13 mmol) in benzene (10 ml). Most of the solvent was evaporated off, n-hexane was added, and the cream solid which separated was filtered off, washed with n-hexane, and dried under vacuum to give [PtH$_2$Br$_2$L$_2$] (43 mg, 52%), m.p. 200—204°C; ν(Pt—H) 2245, 2210 cm^{-1}. (Found: C, 30.35; H, 3.9. $C_{16}H_{24}Br_2P_2Pt$ calcd.: C, 30.35; H, 3.8%).

Reaction of [Pt(SiPh$_2$H)$_2$(dppe)] with hydrogen bromide and with bromine

(a) Hydrogen bromide (0.52 mmol) in benzene (10 ml) was added dropwise with stirring during 70 min to a suspension of [Pt(SiPh$_2$H)$_2$(dppe)] (0.26 mmol) in benzene (15 ml) at room temperature. (A clear solution was formed during the first 15 min, and subsequently a white solid separated.) The solid was filtered off, washed with n-hexane, dried under vacuum, and shown to be [PtBr$_2$(dppe)] (160 mg, 71%), m.p. >340° C (lit. [13], >360°C) (authentic IR spectrum).

(b) The colour was immediately discharged when bromine (0.31 mmol) in benzene (5 ml) was added dropwise with stirring during 15 min to a suspension of [Pt(SiPh$_2$H)$_2$(dppe)] (300 mg, 0.31 mmol) in benzene (10 ml) at room temperature. The mixture was stirred for 60 min, and the solid was filtered off, washed with n-hexane and dried in vacuum to give [PtBr$_2$(dppe)] (110 mg, 93%), m.p. >340°C (authentic IR spectrum). After evaporation of benzene from the filtrate, addition of n-hexane gave a white solid (110 mg) m.p. 195—205°C, the IR spectrum of which indicated it to be mainly unchanged [Pt(SiPh$_2$H)$_2$(dppe)] (lit. [11], m.p. 222—225°C).

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