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ORGANOBORATION OF *cis*-DIETHYNYLPLATINUM(II) COMPLEXES WITH $R_2P(CH_2)_2PR_2$ LIGANDS: PLATINACYCLOPENTADIENES AND THEIR BEHAVIOUR IN SOLUTION

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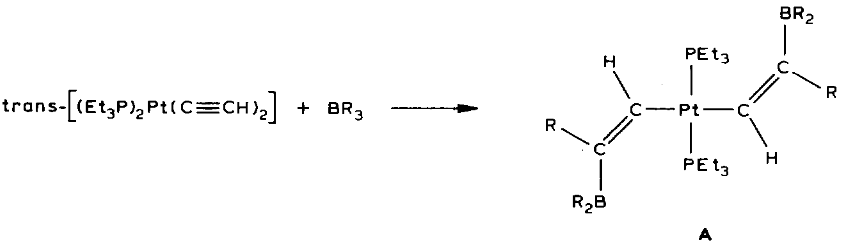
Summary

Organoboration of dppePt(C≡CH)$_2$ (**1a**) and depePt(C≡CH)$_2$ (**1b**) with BR$^1_3$ (**2**) (R^1 = Me (**a**), Et$_2$ (**b**), or Pr^i (**c**)) gives the platinacyclopentadienes, **3a–c** and **4c**, respectively, in high yield. The stability of **3** in solution increases with the size of R^1. In addition to slow decomposition of **3a** (R^1 = Me) in solution rearrangement into a platinum-borol complex was observed. **4a** (R^1 = Me) decomposes at room temperature, but **4b** (R^1 = Et$_2$) reacts readily with an excess of triethylborane to give a new type of platinum-borol complex with an exocyclic BEt$_2$ group and Pt coordination to only one half of the borol π-system. Variable-temperature ^{31}P NMR shows that rotation of the Pt fragment about the axis linking it to the borol ring is rapid on the NMR time scale. The new compounds have been characterized by ^{1}H, ^{11}B, ^{13}C, ^{31}P and ^{195}Pt NMR spectroscopy.

The reaction between organoboranes and other organometallic compounds has been of interest for organic and organometallic syntheses in the last three decades [1–3]. Our interest has focused on the organoboration of metal acetylides, with emphasis on alkynylstannanes [4]. More recently we started to study the reaction of trialkylboranes with transition metal acetylides. In the case of platinum we have reported in a preliminary communication that organoboration takes place [5] (eq. 1).



(1)

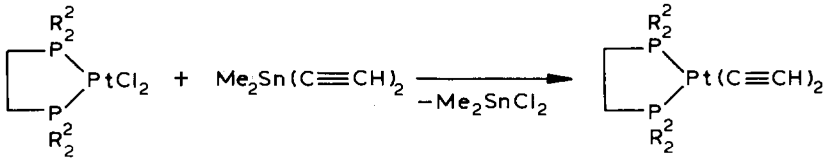
A

0022-328X/86/$03.50

The products **A** are formed with high stereospecificity, and the stereochemistry is the same as for the organoboration of most alkynylstannanes. Since in the case of diethynylstannanes it was possible to obtain stannoles via organoboration [6], the success of the organoboration of the *cis*-platinum(II) acetylides (**1**), shown in eq. 3, was extremely gratifying [7]. In this work, we give more detailed information about this reaction as well as about the NMR spectroscopic properties of **3**. Furthermore we report on the behaviour of the platinacyclopentadiene complexes (**3**) in solution and on the identification of the rearranged products.

Results and discussion

The convenient synthesis of diethynylplatinum(II) complexes with $R^2_2P(CH_2)_nPR^2_2$ ligands has been described for $n = 2$, $R^2 = Me$, Ph and for $n = 1$, $R^2 = Ph$ [8,9]. We have used these procedures for compounds **1a** ($R^2 = Ph$) and **1b** ($R^2 = Et$) (eq. 2).

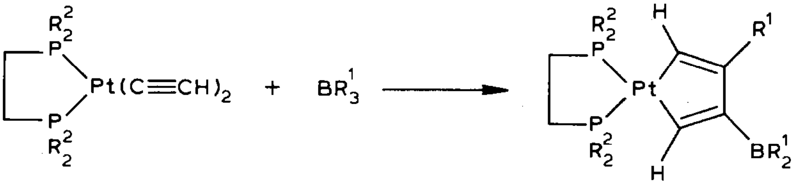


(2)

1 a b

R^2 = Ph, Et

Complex **1a** reacts with trialkylboranes, BR^1_3, (**2**) in CH_2Cl_2 to give pure platinacyclopentadienes **3a–c** in essentially quantitative yield, eq. 3.



(3)

1

2 a b c

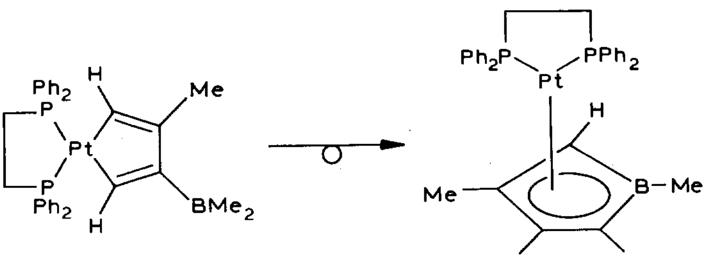
R^1 = Me, Et, Pr^i

3,**4**

R^2 = Ph, Et

Compounds **3a–c** can be isolated as yellow extremely air-sensitive solids and stored in the dark for several years. They decompose slowly within several days in CD_2Cl_2 or toluene. The decomposition is faster in CD_2Cl_2 than in toluene, and **3c** appears to be more stable than **3b** and **3a**.

The products of decomposition of **3b**,**c** in solution have not so far been identified (except for $dppePtCl_2$ in CD_2Cl_2 solution). However, compound **3a** ($R^1 = Me$) in CD_2Cl_2 rearranges into a new borol complex **5a** (50%) along with other, unidentified, products (eq. 4).



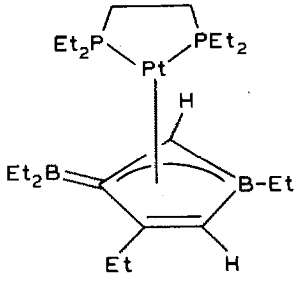
(3a)

(5a)

(4)

The conversion into **5a** is more efficient when the reaction between **1a** and **2a** is carried out in toluene. The slow dissolution of **1a** (over 48 h) to form **3a** in the presence of an excess of trimethylborane is accompanied by rearrangement into **5a** (~ 75%). However, it was not possible to isolate pure **5a** from any of these mixtures, by chromatography or fractional crystallization.

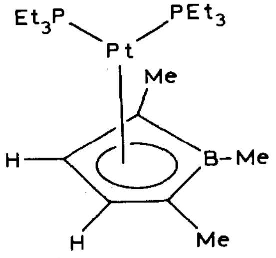
The very large influence of the groups R^1, R^2 on product distribution and stability is reflected by the results for the complex **1b** (R^2 = Et). With an excess of trimethylborane (**2a**) immediate reaction and decomposition is observed at room temperature; the same conditions but with triethylborane (**2b**) lead readily to **4b**, which is also unstable, and rearranges and/or reacts with **2b** to give mainly (~ 70%) another type of borol complex (**6b**), along with other unidentified products. Finally, with an excess triisopropylborane (**2c**) complex **4c** is formed, and can be isolated as a dark yellow solid. Complex **4c** is stable in solution for several days. No reaction was observed between **4c** and excess of **2c**. Addition of triethylborane, (**2b**) to a solution of **4c**, did not induce further reactions or rearrangement.



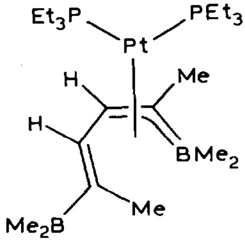
(6b)

Platinacyclopentadienes with =CH groups have been characterized for the first time, and the convenient synthesis of **3** (eq. 3) thus permits a study of the chemistry of this type of compound in more detail. The mechanism involved in the formation of compounds **3** is thought to be analogous to that proposed for the organoboration of alkynylstannanes [4], and has been outlined in the preliminary communication [7]. It is likely that the selective formation of **3** is the result of a favourable combination of various circumstances involving the dppe ligand, the alkynyl group ($C\equiv CH$ or $C\equiv CR$, $R \neq H$), and the nature of the organoborane. It has been shown that the reactions of trialkylboranes (**2**) with other Pt^{II} acetylides (dppePt $(C\equiv CR)_2$, $R \neq H$) do not give platinacyclopentadienes, and, even the reaction of **1a** with 9-ethyl-9-borabicyclo[3.3.1]nonane takes a completely different course [10]. This unpredictable behaviour of platinum(II) acetylides towards trialkylboranes justifies the study of the well-defined platinacyclopentadienes (**3a–c**, **4c**) in solution, as it may elucidate some of the problems involved.

Clearly, the replacement of R^2 = Ph by R^2 = Et increases the reactivity of the Pt–C bonds in **4** compared to **3**. The rearrangement of **3a** into **5a** shows that the size of R^1 is also important. This is also shown by the relative stability of the complexes **3** and **4**, which increases from R^1 = Me to R^1 = Pr^i. We suggest that most of the processes which lead to further reactions of **3** or **4** are initially caused by R_3B-induced opening of the C_4Pt ring in **3** or **4**. The presence of a small amount of unreacted trialkylborane in solution cannot be avoided, since the organoboration of metal acetylides must be regarded as a reversible reaction [4]. It is noteworthy that the borol ligand in **5a** is an isomer of the borol ligand in the platinum-borol complex **7a** which is formed along with other compounds (one of which is the olefin complex **7b**) by light and/or heat-induced rearrangement of the complex **A** (see eq. 1) [10].



(7a)



(7b)

At present we have no substantiated mechanistic explanation for the formation of **6b** from **4b** and **2b**, but the suggested structure of **6b** is consistent with all the NMR data. It is a new type of a borol complex since in it the exocyclic boryl group in the 3-position disturbs the symmetry of the borol ligand in such a way that the platinum coordinates to only one part of the borol system. At present the olefin complex **7b** [10] is the only compound available for comparison.

Although, many transition metal borol complexes are known [11] the results presented here provide a new synthetic route to these interesting compounds.

NMR measurements

The extreme sensitivity of the platinacyclopentadienes has so far prevented the isolation of suitable single crystals of **3** or **4**. We were also unable to isolate pure samples of the borol complexes **5a**, **6b** or **7a**. The characterization of the new compounds is thus based mainly on ^{1}H, ^{11}B, ^{13}C, ^{31}P, and ^{195}Pt NMR studies. Since there are no other elements present in the compounds in question, consistent information on their structure should be provided by chemical shift data and coupling constants. The NMR data (^{11}B, ^{13}C, ^{31}P, ^{195}Pt) for the platinacyclopentadienes **3**, **4** are shown in Table 1 and those for the platinum complexes **5a**, **6b**, **7a**, **7b** in Table 2.

The $\delta(^{11}B)$ values of the platinacyclopentadienes are found in the expected range for this type of three-coordinate boron [4,12]. The ^{11}B nuclear shielding in the borol complexes **5a** and **7a** is similar to that observed for *nido*-2,3,4,5-tetracarbahexaboranes(6) [12,13] and for borol complexes with other metals (range of $\delta(^{11}B)$ 4.0–24.0 [12]). The ^{11}B nuclei in **6b** and **7b** (B(1)) are less shielded than those in **5a**, **7a**, but the $\delta(^{11}B)$ values are in the same range as the value for the 16e complex, bis(1,3,5-tetraethyl-2-methyl-1,3-diborolenyl)platinum [14] ($\delta(^{11}B)$ 48.0).

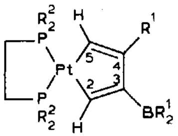
The structure of the platinacyclopentadienes **3**, **4** is proved by the ^{13}C NMR spectra [7,15,16], in particular by the values of $^{n}J(^{31}P^{13}C(2,4,5))_{cis,trans}$ ($n = 2,3$) and $^{n}J(^{195}Pt^{13}C(2,4,5))$ ($n = 1,2,3$) and by the broad resonances (C(3)) which arise from partially relaxed scalar coupling $^{1}J(^{13}C^{11}B)$ [12,17]. The conclusions from the ^{13}C NMR data are corroborated by details of the ^{31}P NMR and ^{1}H NMR spectra (see Fig. 1).

The ^{13}C NMR spectra are also extremely helpful in confirming the structures of the borol complexes. The ^{1}H coupled spectra help to distinguish between C(2,3,4,5),

(Continued on p. 278)

TABLE 1

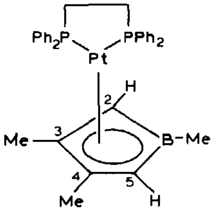
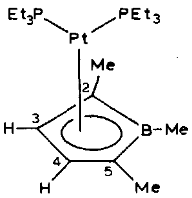
^{11}B, ^{13}C, ^{31}P AND ^{195}Pt NMR DATA [a] FOR THE PLATINACYCLOPENTADIENES **3a–c**, **4b**, **c**

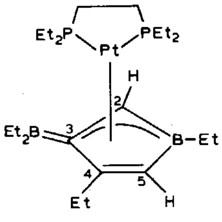
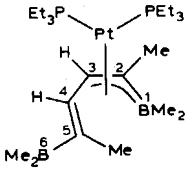
		$\delta(^{13}C)$						$\delta(^{11}B)$	$\delta(^{31}P)$		$\delta(^{195}Pt)$ [c]
		C(2)	C(3)	C(4)	C(5)	R^1	BR^1				
3a	$R^1 = Me$, $R^2 = Ph$	175.1 (103.3, 7.6) [853.3]	174.4 (br [b])	162.2 (11.2, 3.4) [133.2]	149.7 (105.6, 8.2) [885.0]	24.4 (8.2, < 1.0) [92.7]	12.8 (br [b])	77.1	48.9 (6.1) [1779.8]	49.0 (6.1) [1778.5]	−436.4
3b	$R^1 = Et$, $R^2 = Ph$	166.4 (105.0, 8.3) [854.6]	175.3 (br [b])	168.8 (13.4, 3.8) [132.2]	147.2 (106.8, 8.9) [898]	29.7 (8.3, < 1.0) [85.0] 14.5	18.5 (br [b]) 8.2	77.7	48.6 (6.1) [1777.4]	49.1 (6.1) [1782.0]	−434.9
3c	$R^1 = Pr^i$, $R^2 = Ph$	154.2 (107.0, 7.6) [851.0]	176.2 (br [b])	174.8 (14.1, 4.1) [138.5]	145.3 (107.4, 8.8) [913.2]	32.0 (8.2, 1.0) [74.4] 23.6	23.5 (br [b]) 19.5	77.5	48.0 (6.1) [1779.8]	49.4 (6.1) [1794.4]	−428.6
4b	$R^1 = Et$, $R^2 = Et$	not measured [d]						77.5	52.0 [1736]	52.0 [1736]	−434.7
4c	$R^1 = Pr^i$, $R^2 = Et$	153.7 (106.8, 8.9)	176.2 (br [b])	174.6 (14.0, 3.8)	142.6 (108.1, 8.9)	31.8 (7.6, < 1.0) [71.2] 23.5	24.8 (br [b]) 19.4	77.5	50.9 (1.5) [1736]	52.2 (1.5) [1739]	−430.4

[a] $J(^{31}P^{13}C)$, $J(^{31}P^{31}P)$ in parentheses and $J(^{195}Pt^{13}C)$, $J(^{195}Pt^{31}P)$ in square brackets, ±0.7 Hz. [b] Resonances are broad owing to partially relaxed scalar coupling $^1J(^{13}C^{11}B)$. [c] All the ^{195}Pt resonances appear as broad (chemical shift anisotropy relaxation) triplets because the magnitudes of the two coupling constants $^1J(^{195}Pt^{31}P)$ are very similar. [d] Decomposes rapidly in solution.

TABLE 2

^{11}B, ^{13}C, ^{31}P AND ^{195}Pt NMR DATA [a] FOR PLATINUM-BOROL COMPLEXES **5a**, **6b**, **7a** AND FOR THE OLEFIN COMPLEX **7b**, FOR COMPARISON

	δ(^{13})						δ(^{11}B)	δ(^{31}P)		δ(^{195}Pt)
	C(2)	C(3)	C(4)	C(5)	BR^1	R^1				
 (5a)	90.9 [b] (br [c]) [32.7]	111.5 (2.7) [28.3]	111.5	90.9 [b]	−4.1 (br [c])	14.6	18.0	42.5 [d], (18.5) [4922]	33.7 [d] (18.5) [4535]	−1897.0
 (7a)	108.1 (br [c]) [62.0]	89.3 [e] (4.9) [24.4]	89.3 [e] (4.9) [24.4]	108.1 (br [c]) [62.0]	−4.1 (br [c])	16.9	19.1	6.4, (<1.5) [5182]	1.2 (<1.5) [4274]	−1724.0

 (6b)	83.5 [f,g] (10.8, 4.8) [95.5]	96.3 [f] (10.8, 3.6) [72]	147.3 [h]	132.9 [f,i] [50.0]	– [j]	35.5 (4.8, < 2.0) [19.1]	46.0	51.8 [k] (13.5) [3604.7]	54.9 [k] (13.5) [3310.5]	−987.0
 7b	82.4 (br [c])	68.7 (29.3, 4.9) [190.4]	157.1 [41.5]	133.4 (br [c])	11.5 (br [c])	– [j] 27.4 (3.7, < 2.0) [27.0]	40.0(1) 73.4(6)	18.0 (15.0) [3808.0]	20.1 (15.0) [3502.0]	−749.0

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[a] $J(^{31}P^{13}C)$, $J(^{31}P^{31}P)$ in parentheses and $J(^{195}Pt^{13}C)$, $J(^{195}Pt^{31}P)$ in square brackets, ±0.7 Hz. [b] $^1J(^{13}C^1H)$ 146.0 ± 1 Hz. [c] Resonances are broad owing to partially relaxed scalar coupling $^1J(^{13}C^{11}B)$. [d] ^{31}P resonance at room temperature (br); data given are from ^{31}P NMR spectra at −80°C in $CDCl_2$. [e] $^1J(^{13}C^1H)$ 158.7 ± 0.7 Hz. [f] Broad resonances at room temperature (see [c]) which are sharpened at lower temperature; data given are obtained at −30°C in CD_2Cl_2. [g] $^1J(^{13}C^1H)$ 120 ± 5 Hz. [h] Sharp signal, both at room temperature and at −30°C, quaternary carbon atom. [i] $J(^{13}C^1H)$ 125 ± 5 Hz. [j] Dubious assignment owing to overlap with signals of the depe ligand and with resonances of unidentified products. [k] No change between −30 to +40°C.

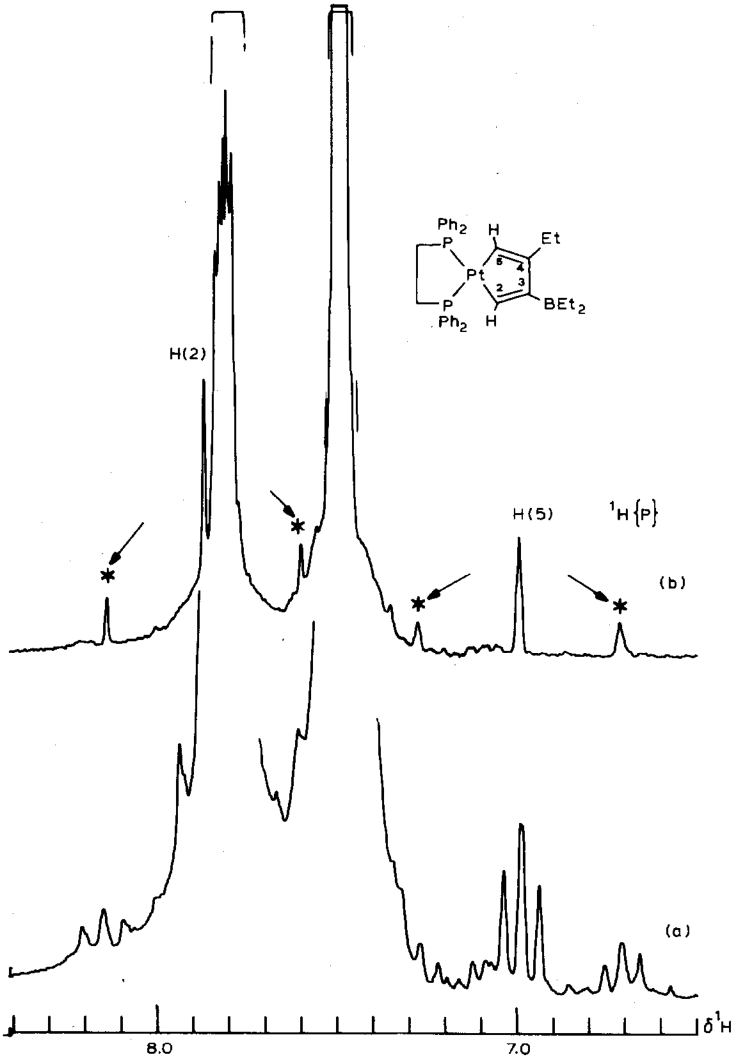

Fig. 1. 200 MHz ^{1}H NMR spectra of **3b**; range of olefinic and aromatic protons, showing the ^{1}H resonances of protons in 2,5-position. (a) Normal ^{1}H NMR; (b) ^{1}H{^{31}P} NMR spectrum; the ^{1}H resonances of the 2,5-protons can now be assigned (H(5) shows an allylic coupling $^4J(^1\mathrm{HCCC}^1\mathrm{H})$ 1.3 Hz) together with their ^{195}Pt satellites (marked by asterisks).

and the assignments are confirmed by the observation of broad ($^1J(^{13}\mathrm{C}^{11}\mathrm{B})$, C(2,5)) or sharp ^{13}C resonances (C(3,4)). In the case of mixtures additional information stems from selective ^{11}B decoupling. The fairly small magnitude of the coupling constants $|^nJ(^{31}\mathrm{P}^{13}\mathrm{C})|$ and $|^nJ(^{195}\mathrm{Pt}^{13}\mathrm{C})|$ supports the proposed structures (see data $^nJ(^{195}\mathrm{Pt}^{13}\mathrm{C})$ given in Ref. 14). Like the $\delta(^{11}\mathrm{B})$ values for **5a**, **7a** the $\delta(^{13}\mathrm{C}(2,3,4,5)$ values for **5a**, **7a** are very close to those found for *nido*-2,3,4,5-tetracarbahexaboranes (6) [13]. Again the structures are in accord with ^{1}H NMR data, for which, in the case of mixtures, selective ^{31}P decoupling serves to correlate ^{1}H and ^{31}P resonances.

In the case of complex **6b** the information from ^{13}C and ^{1}H NMR is also extremely valuable in confirming the proposed new structure. The ^{13}C resonances of the borol ring are found as one sharp (C(4)) and three broad signals. The latter are sharpened either by ^{11}B decoupling or by measurement at low temperature (thermal decoupling of ^{11}B). Two of the broad ^{13}C signals (C(2,5)) show coupling $^{1}J(^{13}C^{1}H)$ in the ^{1}H-coupled spectra. The ^{13}C(4,5) resonances appear in olefinic region, whereas the ^{13}C(2,3) resonances are in the same range as the C(2,3,4,5) resonances in the borol complexes **5a**, **7a**. Furthermore, the ^{13}C(4,5) resonances show no coupling to phosphorus. Similarly, the ^{1}H(5) resonance appears in the olefinic region (δ(H(5)) 5.45 (br); $J(^{195}Pt^{1}H) \leqslant 3$ Hz, $J(^{31}P^{1}H) \leqslant 2$ Hz, $^{4}J(^{1}HCCC^{1}H) \leqslant 1.5$ Hz) and the ^{1}H(2) resonance is found in the typical region for π-bonded olefin (δ(H(2)) 3.30 (d); $^{2}J(^{195}Pt^{1}H)$ 39.9 Hz, $J(^{31}P(\delta(^{31}P)\ 54.9)\ ^{1}H)$ 8.3, $J(^{31}P(\delta(^{31}P)\ 51.8)^{1}H) \leqslant 1.5$; sign of $^{2}J(^{195}Pt^{1}H)$ is negative with respect to a positive sign of $^{1}J(^{195}Pt^{31}P)$). All these data, together with ^{11}B, ^{31}P and ^{195}Pt NMR data are fully consistent with the proposed structure of **6b**.

The $\delta(^{31}P)$ resonances (AB-spin system) of the platinacyclopentadienes **3a–c** are shifted to high frequence ($\sim$ 8–9 ppm) with respect to **1a**, whereas those of **4a**, **b** are almost identical to those of **1b**. However, there is an almost identical decrease in the magnitude of $^{1}J(^{195}Pt^{31}P)$ going from **1a** to **3a–c**, and from **1b** to **4b**, **c**, respectively ($\sim$ 490 Hz).

The ^{31}P NMR data for the borol complexes **5a**, **7a** and **6b** are very instructive, as they reveal the dynamic behaviour of these complexes more clearly than ^{1}H or ^{13}C NMR data. In **5a** and **7a** rotation of the $(R_3P)_2Pt$ fragment about the axis perpendicular to the C_4B plane is rapid on the NMR time scale [18]. The energy of activation for this process was estimated [19] as $\Delta G^{\ddagger}_{(70^{\circ}C)}$ 63 ± 1 kJ M^{-1} for **7a** and $\Delta G^{\ddagger}_{(-40^{\circ}C)}$ 42.5 ± 1 kJ M^{-1} for **5a** from the coalescence signals in the ^{31}P NMR. As there are AB-spin systems for **5a** and **7a**, at low temperature the borol complexes prefer the conformation with the Pt_2Pt-plane bisecting the C(3)–C(4) bond. This is in agreement with predictions based on extended Hückel MO calculations [20].

The ^{31}P NMR spectrum (AB-spin system) of the borol complex **6b** remains unchanged between -30 to $+40$°C, and that of **7b** between $+27$ to $+80$°C.

The change in the $\delta(^{195}Pt)$ values is very similar for **1a** ($\delta(^{195}Pt)$ -410.4), **3a–c** ($\delta(^{195}Pt) \sim -430$) and **1b** ($\delta(^{195}Pt)$ -412.1), **4b**, **c** ($\delta(^{195}Pt)$ -432). The ^{195}Pt shielding in **3a–c** is greater than in comparable noncyclic and cyclic Pt^{II}-organyl complexes (range of $\delta(^{195}Pt)$: -50 to -200 [22]).

There is a large increase in ^{195}Pt shielding in the Pt^{0} complexes (Table 2) compared with that in the platinacyclopentadienes **3**. The ^{195}Pt-shielding for the borol complexes **5a**, **7a** is extremely high [23]. A d^{10} electron configuration would account for reduced paramagnetic contributions to the ^{195}Pt shielding. The situation with respect to the ^{195}Pt shielding is thus comparable to that for bis(allyl)platinum ($\delta(^{195}Pt)$ -1639, -1410 [22]). In **7b** and the borol complex **6b** the ^{195}Pt resonances are shifted to lower frequency by $\sim$ 70 and $\sim$ 300 ppm, respectively, compared with those in dRpePt-C_4H_6 (R = Bu^{t}, cyclohexyl) [22]. The ^{195}Pt shielding in **6b** suggests that the electronic situation for the platinum nucleus is somewhere between that for an olefin complex with d^{8} electron configuration and that for a borol complex with formally d^{10} electron configuration. The greater electron density at platinum in the borol complexes is also reflected in the significant increase in the values $J(^{195}Pt^{31}P)$ in **5a**, **7a** compared with those for **6b**, **7b**.

Experimental

All manipulations involving the platinum acetylides and the organoboron compounds were carried out under nitrogen. The platinum starting materials, the organotin compound, and the trialkylboranes were prepared by published procedures: dppePtCl$_2$ [23]; depePtCl$_2$ [24]; dppePt(C≡CH)$_2$ (**1a**) [8]; depePt(C≡CH)$_2$ (**1b**) [8], vide infra; Me$_2$Sn(C≡CH)$_2$ [25]; BMe$_3$ (**2a**) [26]; BEt$_3$ (**2b**) [27], BPr$_3^i$ (**2c**) [28].

All NMR spectra were recorded with a Bruker WP 200 NMR spectrometer, equipped with a multinuclear unit, a modified selective ^{13}C-probe (for ^{13}C{^{1}H,^{11}B} heteronuclear triple experiments) and a double-tuned ^{1}H-probe (for ^{1}H{X} double resonance or ^{1}H{^{1}H,X} triple resonance experiments; X =^{31} P, ^{11}B or ^{195}Pt). Dried, oxygen-free deuterated solvents were used to prepare solutions ranging from ~ 3 to ~ 10%. C–H connectivities in ^{13}C NMR spectra were checked by using various pulse sequences based on ^{1}H-spin polarization transfer [29].

IR spectra were recorded with a Perkin–Elmer 325 spectrometer in CH$_2$Cl$_2$ solutions.

Bis(diethylphosphino)ethane-platinum(II)-diacetylide (1b)

In a two-necked flask equipped with a magnetic stirring bar 4.72 g (10 mmol) of bis(diethylphosphino)ethane-platinum(II) dichloride is suspended in 40 ml of THF. 2.2 g (11.1 mmol) of diethynyldimethylstannane are added. After 10 min at ambient temperature the brown solution obtained is poured into 200 ml of hexane. The solid precipitate is filtered off, washed with hexane, and dried in vacuo: 4.24 g (94%) of a pale yellow solid, m.p. ⩾ 130°C (dec.). IR (CH$_2$Cl$_2$): ν(C–H) 3285 cm^{-1}, ν(C≡C) 1972, 1979; NMR, in [ ] J(PtX), in ( ) J(PX) in Hz: ^{1}H NMR (in toluene-d_8): δ(^{13}C) (CDCl$_3$) 8.5, 18.2, 23.9, depe; 101.0 [1062.0], (137.3, 15.3) Pt–C≡; 95.2 [300.8], (33.8, ⩽ 1.2) ≡C–H; δ(^{31}P) (CDCl$_3$) 51.1 [2224]; δ(^{195}Pt) (CH$_2$Cl$_2$) −412.1. Found: C, 32.9; H, 6.0; C$_{12}$H$_{26}$P$_2$Pt calcd.: C, 33.7; H, 6.1%.

General method for the preparation of the platinacyclopentadienes 3a–c, 4c

A solution of 1 mmol of **1a**, **b** in 10 ml CH$_2$Cl$_2$ is cooled to −78°C and an excess of the trialkylborane (**2**) (~ 2 mmol) is added. (**2b**, **c** are added as liquids whereas **2a** is condensed to the degassed frozen solution at liquid nitrogen temperature.) In the case of **2a** the N$_2$ pressure is adjusted to ~ 600 Torr before the reaction flask is warmed to room temperature. The mixture is stirred for 6 h at room temperature then the volatile material is pumped off in vacuo, to leave, as yellow solids the pure compounds **3a–c** and **4c** (all decompose before melting at or above 70°C).

Borol complexes from platinacyclopentadienes (5a, 6b)

5a, in CH$_2$Cl$_2$. When the solution of **3a** in CH$_2$Cl$_2$ is kept for 72 h at room temperature decomposition occurs and ~ 50% (according to ^{31}P NMR) of the borol complex **5a** is formed. Slow cooling of the solution to −78°C or addition of hexane produces oily non-crystalline material. Chromatography on Al$_2$O$_3$ (neutral) with CH$_2$Cl$_2$/benzene gives no definite products.

5a, in toluene. 0.68 g (1.5 mmol) of **1a** is suspended in 60 ml of toluene in a 100 ml two-necked flask equipped with a magnetic stirring bar. The mixture is carefully degassed by several freeze-pump-thaw cycles, then 2 mmol of trimethylborane (measured by its pressure in a defined volume) is condensed into the flask. The N_2 pressure is adjusted to ~ 600 Torr before the mixture is warmed to room temperature. The progress of the reaction, which is accompanied by the appearance of a dark colour and dissolution of **1b**, is monitored by ^{31}P NMR (which reveals that **3a** appears as an intermediate). After 72 h no further change takes place. The ^{31}P NMR spectra of the clear brown solution shows that $\geqslant 75\%$ of **5a** has been formed, accompanied by several unidentified impurities. Pure **5a** is not obtained by fractional crystallization from various mixtures (toluene, toluene/hexane, CH_2Cl_2/hexane) or by chromatography on Al_2O_3 (neutral with toluene/CH_2Cl_2).

***6b**, in CH_2Cl_2.* A solution of 0.68 g (1.5 mmol) of **1b** in 20 ml CH_2Cl_2 in a 50 ml two-necked flask is cooled to $-78°C$. An excess, 0.29 g (3 mmol), of triethylborane is added from a syringe. The ^{31}P NMR spectrum taken immediately after the mixture is warmed to room temperature shows that **4b**, is still present, but it then reacts further to give (after 48 h) mainly ($> 70\%$) another compound, subsequently identified as the new borol complex **6b**. Attempts to crystallize **6b** from the reaction solution by addition of hexane or by cooling give oily brown material. Removal of CH_2Cl_2 and other volatile material in vacuo leaves a dark brown oil. Chromatography on Al_2O_3 (neutral) with benzene yields no definite compound.

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