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Reactivity of 1-alkynylplatinum(II) complexes towards trialkylboranes

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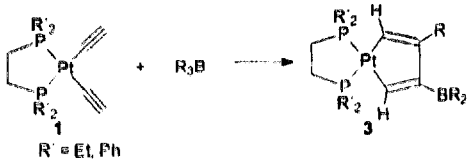
Abstract

1-Alkynylplatinum(II) complexes of the type *cis*-[(dppe)Pt(C≡C–R^1)$_2$] [**4**, R^1 = Me (**a**), ^{t}Bu (**b**), C(Me)=CH$_2$ (**c**), Ph (**d**), SiMe$_3$ (**e**)], *cis*-[(dmpe)Pt(C≡C–Me)$_2$] (**5a**), *cis*-[(depe)Pt(C≡C–Ph)$_2$] (**6d**), *cis*-[(Et$_3$P)$_2$Pt("Bu)(C≡C–R^1)] [**7**, R^1 = Me (**a**), Ph (**d**)] and *trans*-[(Et$_3$P)$_2$Pt((E)-2-pentenyl)(C≡C-Me)] (**8a**) react with trialkylboranes R$_3$B [**2**, R = Me (**a**), Et (**b**), ^{i}Pr (**c**)] by 1,1-organoboration. This involves cleavage of a Pt–C≡ bond, and formation of an alkynylborate-like intermediate in which a positively charged platinum fragment is coordinated to the C≡C bond. In most cases, the alkenylplatinum complexes of the type **9–13**, **28**, **30** which result from 1,1-organoboration are not stable, and either η^2-alkyne platinum(0) (**15–21**, **29**) or η^3-borylalkene platinum(0) complexes (**22–27**) or both are the next products. The proposed structures of all new platinum complexes in solution are based on ^{11}B, ^{31}P, ^{195}Pt NMR data, and in some cases also on complete ^{13}C NMR data sets. © 1997 Elsevier Science S.A.

Keywords: Boron; Phosphorus; Platinum; Alkynes; Organoboration; NMR

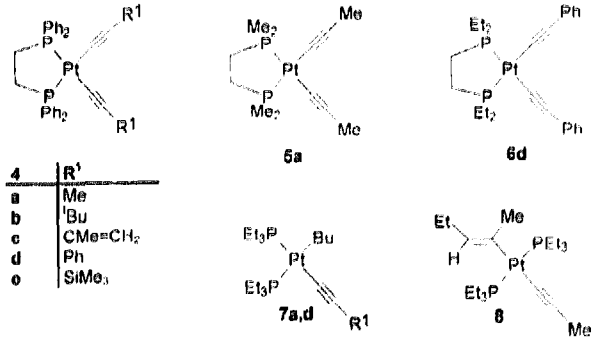
1. Introduction

Diethynylplatinum(II) complexes **1** react smoothly with the trialkylboranes **2** to give platina-2,4-cyclopentadienes **3** Eq. (1) [1,2]. This has been interpreted as the result of two consecutive 1,1-organoboration reactions [3], in which one Pt–C≡ bond is cleaved first in the course of an intermolecular 1,1-alkyloboration, followed by cleavage of the second Pt–C≡ bond prior to the final intramolecular 1,1-vinyloboration [1,2].



(1)

The mechanistic study and the extension of the reaction shown in Eq. (1) to di-1-alkynylplatinum(II) complexes **4–6** in general seemed attractive. If substituents other than hydrogen are linked to the C≡C bond, the 1,1-organoboration is expected to become slower, and intermediates may be detected by NMR spectroscopy. Therefore, in this work we report on an NMR spectroscopic study of the reactivity of **4–6** towards trialkylboranes **2**. In order to assess the influence of the phosphane ligands in *cis* and *trans* positions, the complexes **7** and **8** were also prepared and included in this study.



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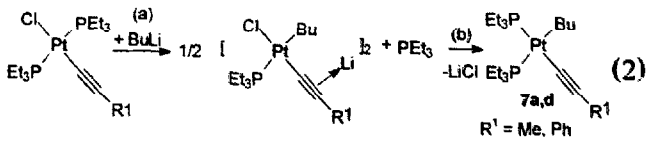
2. Results and discussion

2.1. Synthesis of the di-1-alkynylplatinum(II) complexes 4–6 and the mono-1-alkynylplatinum(II) complexes 7 and 8

The complexes **4b,c** and **6d** were prepared by the reaction of $[(dppe)PtCl_2]$ with the corresponding di-1-alkynyl(dimethyl)stannane, following the literature procedure for the other compounds **4** and **5a** [4,5].

The complexes **7** were obtained from the reaction of *trans*-$[(Et_3P)_2Pt(C{\equiv}C{-}R^1)Cl]$ [6] with ^{n}BuLi. Only the *cis*-complexes **7** were isolated. This can be explained if one considers the reaction of *trans*-$[(Et_3P)_2Pt(C{\equiv}C{-}R^1)_2]$ with ^{n}BuLi which leads to the formation of a Pt–C(^{n}Bu) bond by elimination of Et_3P to give a lithium-bridged dimer [7]. It is conceivable that the same type of reaction takes place in the case of *trans*-$[(Et_3P)_2Pt(C{\equiv}C{-}R^1)Cl]$ (Eq. (2a)), followed by abstraction of LiCl and reentry of Et_3P (Eq. (2b)).



(2)

It has been shown previously that 1,1-ethyloboration of *trans*-$[(Et_3P)_2Pt(C{\equiv}C{-}Me)_2]$ takes place only at one of the two 1-propynyl groups [8] (Eq. (3a)). Protodeborylation by hydrolysis on alumina affords the desired complex **8a** with *trans*-configuration (Eq. (3b))

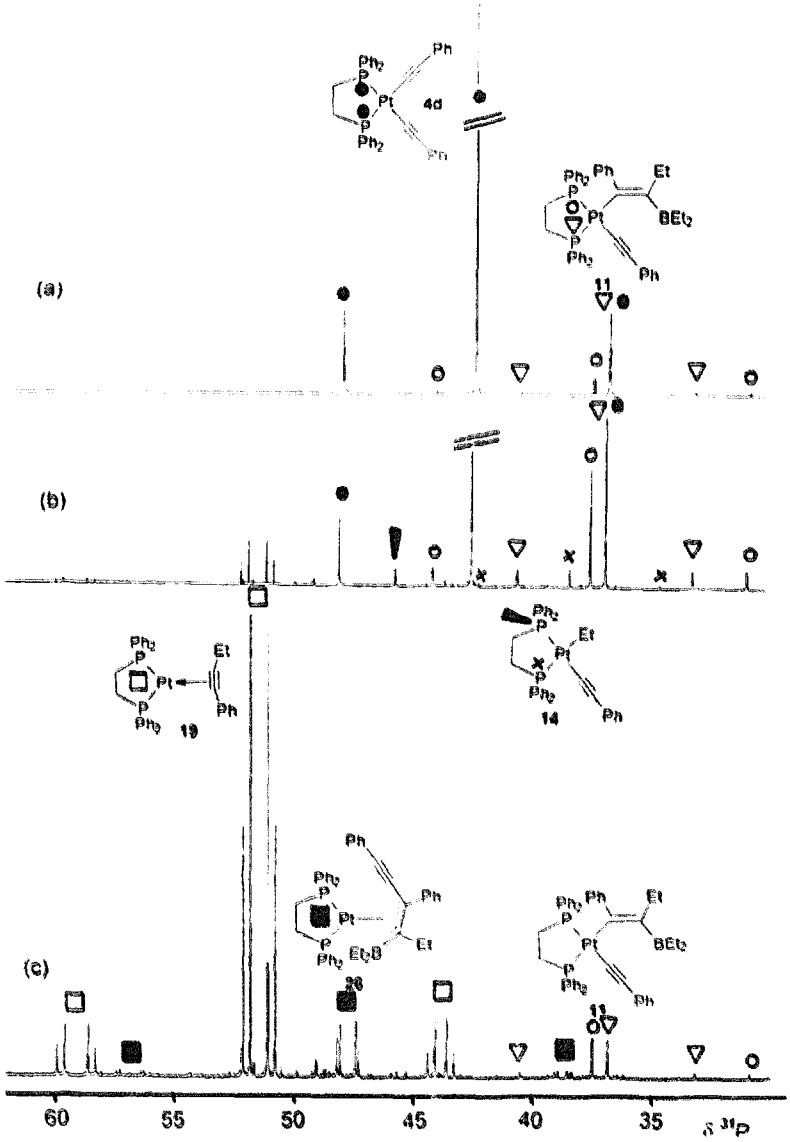
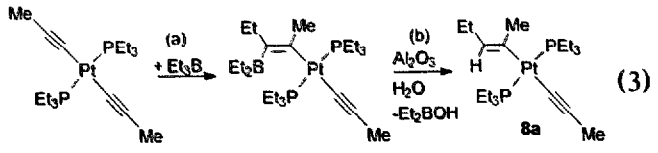


Fig. 1. 200.4 MHz $^{31}P\{^1H\}$ NMR spectra showing the progress of the reaction of *cis*-$[(dppe)Pt(C{\equiv}C{-}Ph)_2]$ (**4d**) with an excess of Et_3B (**2b**) at room temperature; (a) after 1 h, (b) after 5 h, and (c) after 24 h.

(see Section 4 for spectroscopic data of **4b,c 6d**, **7a,d** and **8a**).



(3)

2.2. Reactions of the di-1-alkynylplatinum(II) complexes 4–6 with trialkylboranes 2

The reactions of the di-1-alkynylplatinum(II) complexes **4–6** with trialkylboranes were monitored by ^{11}B, ^{31}P NMR (see Figs. 1 and 3), and partly also by ^{195}Pt NMR spectroscopy (see Fig. 2), and the results are summarized in Scheme 1. According to ^{31}P NMR spectra (see Table 1; supported by evidence from ^{195}Pt and ^{13}C NMR) of the reaction solutions, the first products such as **9–11** (and in an analogous way **12** and **13**) result from intermolecular 1,1-organoboration of one of the 1-alkynyl groups (Scheme 1b). A minor product is the complex of type **14** ($\delta^{31}P$ [$^1J(^{195}Pt\ ^{31}P)$] = 45.6 [2573.0] and 38.3 [1540.0]; $\delta^{195}Pt = -218.0$ [2573.0 and 1540.0]) (Scheme 1c) which was observed only in the case of the reaction of **4d** with **2d**, most likely as the result of a side-reaction of the zwitterionic intermediate **A** (Scheme 1a). Such zwitterionic intermediates have been observed in the course of the 1,1-organoboration of di-1-alkynyltin [3,9–12] or di-1-alkynyllead compounds [3,13,14]. In analogy it is suggested that the complexes of type **9–13** undergo an intramolecular rearrangement by migration of the 1-alkynyl group from platinum to boron to give the zwitterionic intermediate **B** (Scheme 1e). Cationic platinum(II) complexes with an η^2-alkyne ligand have been described [15–19] but ap-

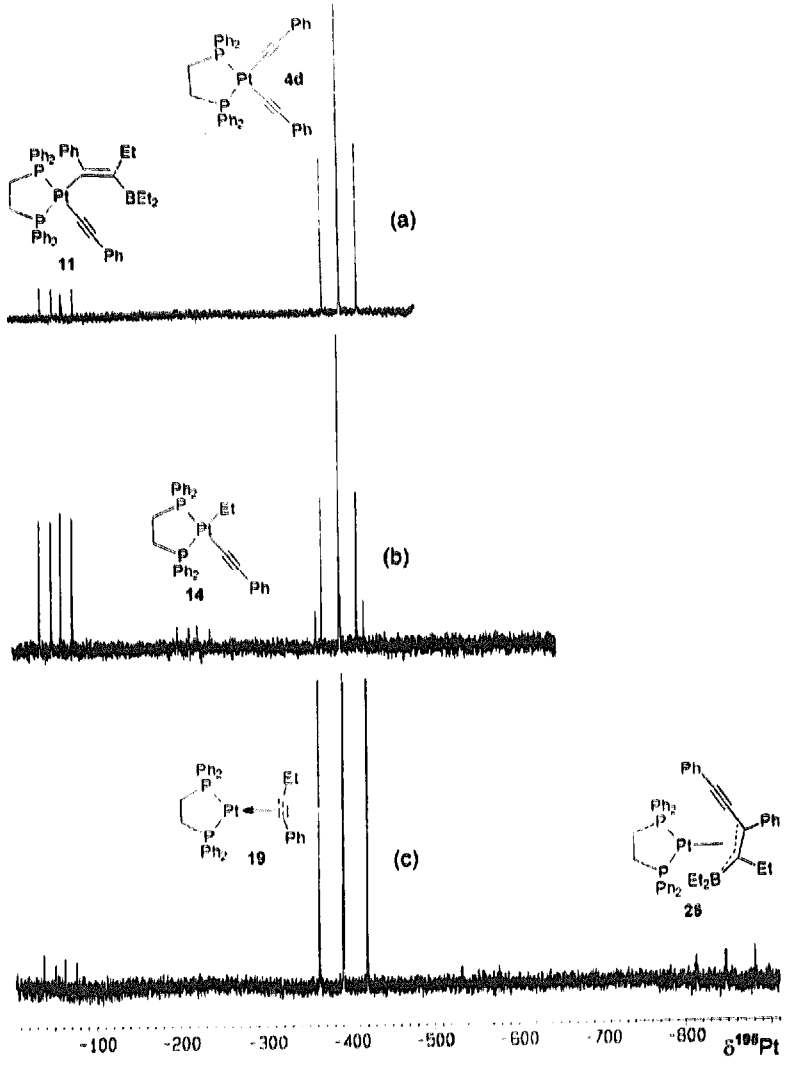


Fig. 2. 107.0 MHz ^{195}Pt NMR spectra of the reaction of *cis*-[(dppe)Pt(C≡C–Ph)$_2$] (**4d**) with an excess of Et_3B (**2b**) at room temperature corresponding to the ^{31}P NMR spectra shown in Fig. 1: (a) after 2 h, (b) after 6 h, and (c) after 24 h.

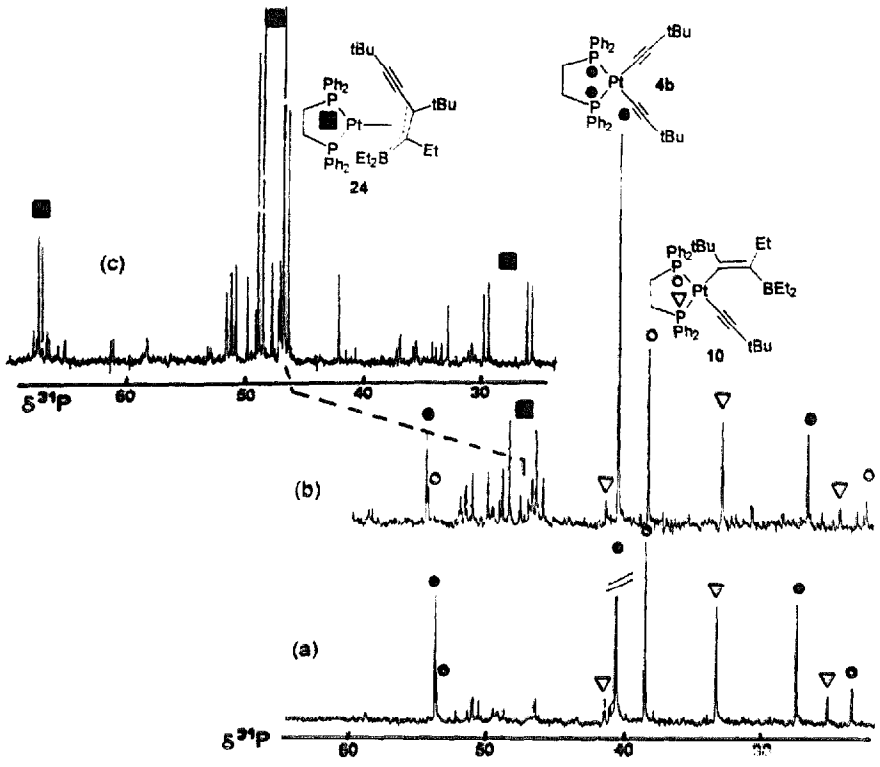


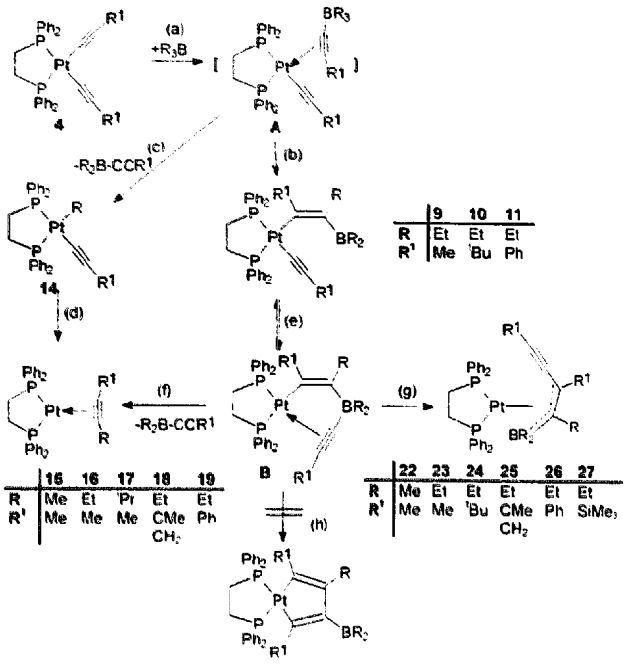
Fig. 3. 80.2 MHz $^{31}P\{^1H\}$ NMR spectra showing the progress of the reaction of *cis*-[(dppe)Pt(C≡C-^{t}Bu)$_2$] (**4b**) with an excess of Et_3B (**2b**) in C_6H_6/C_6D_6 at 55 °C: (a) after 24 h, (b) after 4 days, (c) after 3 weeks (after four weeks extensive decomposition is observed).

pear to be fairly unstable in the absence of electronegative substituents at the C≡C bond. The intermediate **B**, although a potential precursor of platina-2,4-cyclopentadienes [1,2] (Scheme 1h), gives instead either η^2-alkyne platinum(0) complexes **15–19** (and analogously **20** and **21**) by elimination of dialkyl(alkynyl)borane (detected in the ^{11}B NMR spectra: $\delta^{11}B$ 72.0 [20]; Scheme 1f) or η^3-alkenylboryl platinum(0) complexes **22–27** by oxidative C–C coupling (Scheme 1g), or mixtures containing both types of complexes. The proposed principal structure of **15–21** is based on typical [21–24] ^{31}P and ^{195}Pt NMR data, together with ^{13}C NMR evidence [25] in several cases (Table 2). There is also a consistent ^{31}P and ^{195}Pt NMR data set for **22–27** (Table 3) together with some evidence from ^{11}B and ^{13}C NMR in support of the proposed structure with an η^3-alkenylborane ligand. The shift of the ^{11}B NMR signals by 40–50 ppm to lower frequencies with respect to alkenylboranes indicates that the B–C≡C group is involved in the coordination to platinum [2,26]. All NMR data of **22–27**

Table 1
^{31}P NMR data [a] of the complexes **9–13**

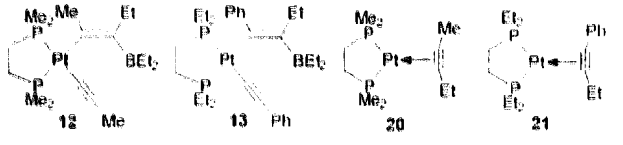
No.	R	R^1	$\delta^{31}P$ [b] [$^1J(^{195}Pt, ^{31}P)$]	($^2J(^{31}P, ^{31}P)$)	$\delta^{31}P$ [c] [$^1J(^{195}Pt, ^{31}P)$]
9	Et	Me	35.4 [1346]	(< 5)	38.8 [2678]
10	Et	^{t}Bu	33.4 [1377]	(< 5)	38.8 [2233]
11 [d]	Et	Ph	38.4 [1495]	(6.0)	38.9 [2681]
12	Et	Me	21.2 [1392]	(< 5)	19.9 [2566]
13	Et	Ph	48.4 [1517]	(< 5)	42.0 [2587]

[a] In CD_2Cl_2; coupling constants $^1J(^{195}Pt, ^{31}P)$ are accurate to ±2 Hz.
[b] Phosphorus atom in *trans*-position to the alkenyl group.
[c] Phosphorus atom in *trans*-position to the alkynyl group.
[d] $\delta^{195}Pt$ = −157.0; $\delta^{13}C$ [$^1J(^{195}Pt, ^{13}C)$] ($J(^{31}P, ^{13}C)$) = 106.3 (144.7, 13.9) ≡CPt; 111.2 (31.6, 2.5) ≡C; 27.4 [50.5] (11.4) CH_2–C≡; 14.1 CH_3–CH_2–C≡; 20.7 broad CH_2B; 8.8 CH_3–CH_2B.



Scheme 1.

are comparable with those obtained previously for similar complexes [2].

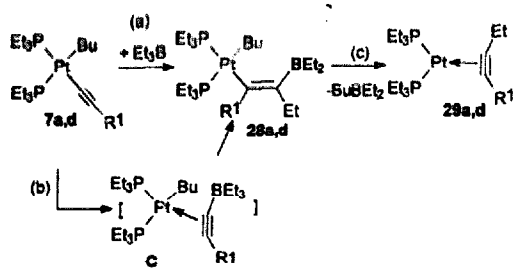


Trimethylborane (**2a**) reacts much faster than triethylborane (**2b**), and the reaction of triisopropylborane (**2c**) with **4a** is extremely slow (> 7 days) at room temperature (prolonged heating of mixtures of **2c** and **4** causes extensive decomposition). It appears from ^{31}P NMR spectra of reaction mixtures containing **2b** and **5a** or **5d** that these complexes are somewhat more reactive than **4a** or **4d**. Within the series of compounds **4**, **4a** is more reactive than **4c** and **4d**. The least reactive complexes are **4b** and **4e**; thus mixtures of **2b** and **4b** or **4e** require several days of heating at 50–100°C in order to observe partial conversion into **10** or further reactions to **24** or **27**. Again, prolonged heating at > 50°C is accompanied by decomposition. In the absence of an excess of the trialkylborane **2**, a complex mixture of numerous unidentified compounds is formed. This is due to the presence of $R_2B-C\equiv C-R^1$ (Scheme 1c, f) which is more reactive than R_3B, and therefore may compete effectively with R_3B in the initial stage of the 1,1-organoboration reaction. In the presence of a large excess of **2** and in the case of the fairly reactive starting complexes, one observes mainly the reactions with **2**. Nevertheless, the presence of the unstable, reactive boranes $R_2B-C\equiv C-R^1$ always gives rise to decomposition and side-reactions, leading to unidentified impurities, and hampering the isolation of pure products. However, ^{31}P NMR spectra indicate that the products shown in Scheme 1 represent at least 70% of the reactions, although it appears that the ratio of the complexes **15–21/22–27** depends critically on reaction conditions (solvent, temperature, concentration). Even careful attempts to keep such factors unchanged did not always lead to a constant product distribution in repetitive experiments.

Table 2
^{13}C, ^{31}P and ^{195}Pt NMR data [a] of the complexes **15–21**

No.	R	R^1	$\delta^{31}P[^1J(^{195}Pt, ^{31}P)]$	$(^2J(^{31}P, ^{31}P))$	$\delta^{31}P[^1J(^{195}Pt, ^{31}P)]$	$\delta^{195}Pt$
15 [b]	Me	Me	52.3 [3062]	n.m.	52.3 [3062]	−282.6
16 [c]	Et	Me	52.3 [3071]	(60.0)	51.2 [3069]	n.m.
17	^{i}Pr	Me	52.4 [3071]	(69.6)	50.7 [3075]	n.m.
18 [d]	Et	$CMe=CH_2$	51.8 [3124]	(65.4)	59.5 [3052]	−380.7
19 [e]	Et	Ph	51.9 [3146]	(62.0)	50.9 [3043]	−382.2
20	Et	Me	19.3 [2891]	(63.5)	17.6 [2886]	n.m.
21	Et	Ph	52.7 [2985]	(48.0)	51.1 [2888]	435.8

[a] In CD_2Cl_2; coupling constants $^1J(^{195}Pt, ^{31}P)$ are accurate to ± 2 Hz; n.m. means not measured; $\delta^{31}P$ values are not assigned.
[b] ^{13}C NMR: $\delta^{13}C$ ($J(^{31}P, ^{13}C)$) = 121.9 (63.0 Σ $^2J(^{31}P, ^{13}C)_{trans}$ + $^2J(^{31}P, ^{13}C)_{cis}$) C≡C; 16.0 (12.0 Σ $^3J(^{31}P, ^{13}C)_{trans}$ + $^3J(^{31}P, ^{13}C)_{cis}$) $CH_3C\equiv$.
[c] ^{13}C NMR: $\delta^{13}C$ ($J(^{31}P, ^{13}C)$) = 120.5 (47.5, 4.0), 120.9 (51.0, 11.5) C≡C; 24.2 (11.5, 10.2) $CH_2-C\equiv$; 18.0 (10.0, 10.0) $CH_3-C\equiv$; 16.0 $CH_3CH_2C\equiv$.
[d] ^{13}C NMR: $\delta^{13}C$ [$J(^{195}Pt, ^{13}C)$] ($J(^{31}P, ^{13}C)$) = 139.4 (65.0, 5.0) $\equiv C-C=$; 127.4 (60.0, 5.0) $\equiv CEt$; 138.2 (10.0, 9.0,) $=C-C\equiv$; 116.8 [44.3] (4.4) $=CH_2$; 23.7 [35.7] (6.0) $CH_3C=$; 24.7 (9.7, 7.7) $CH_2C\equiv$; 16.7 [34.9] (5.1) $CH_3CH_2C\equiv$; some ^{195}Pt satellites could not be assigned with certainty due to overlap with other ^{13}C NMR signals.
[e] ^{13}C NMR: $\delta^{13}C$ [$J(^{195}Pt, ^{13}C)$] ($J(^{31}P, ^{13}C)$) = 140.7 [310.0] (70.1, 5.0) $\equiv CPh$; the $^{13}C(\equiv CEt)$ NMR signal is not assigned due to overlap with signals of the phenyl groups; 135.5 [< 3] (10.8, 8.1) i, 131.9 [46.0] (6.1) o, 128.4 m, 125.6 p *Ph*–C≡; 135.8 [49.8] (29.6, 5.4) i, 136.1 [49.8] (31.0, 6.1) i, 133.2 [25.0] (14.2, 2.0) o, 128.6 [< 3] (9.4), 128.8 [< 3] (8.4) m, 130.1 [< 3] (2.0) 130.2 [< 3] (2.0) PhP; 31.5 [12.0] (24.3, 16.8), 31.2 [12.0] (24.3, 16.8) CH_2P; 24.6 [16.0] (11.5, 8.8) $CH_2-C\equiv$; 16.5 [37.0] (5.4) $CH_3CH_2C\equiv$.



Scheme 2.

2.3. Reaction of the cis-mono-1-alkynyl-bis(triethylphosphane)platinum(II)complexes 7 with triethylborane 2b

The reaction of **7** with **2b** proceeds smoothly by 1,1-ethyloboration to give the alkenylplatinum(II) complexes **28** (Scheme 2a); the reaction is complete after warming the mixture from −78°C to room temperature. The alkynylborate-like intermediate **C**, analogous to **A** (Scheme 1) is shown in Scheme 2b. The proposed structure of **28a,d** is based on consistent ^{11}B, ^{13}C, ^{31}P and ^{195}Pt NMR data (Table 4). After several days, ^{31}P NMR spectra of the reaction solutions show growing signals typical of the complexes **29** (Scheme 2c) together with numerous smaller signals owing to decomposition.

2.4. Reaction of the trans-1-propynyl-bis(triethylphosphane)platinum(II) complex 8a with triethylborane 2b

The complex **8a** reacts very slowly with an excess of **2b** (see Fig. 4). Even after two weeks at room temperature almost half of the amount of **8a** is still present. The main new component of the mixture is the 1,1-ethyloboration product **30**, accompanied by two other complexes in a 1:1 ratio. The latter result from the symmetrization reaction of **8a**. The complex *trans*-$[(Et_3P)_2Pt(C{\equiv}C{-}Me)_2]$ thus formed reacts with **2b** as shown in Eq. (3a), whereas *trans*-$\{(Et_3P)_2Pt[C(Me){=}C(H)Et)_2\}$ does not react with **2b**. The structural assignment is based on $\delta^{31}P$ data, relative intensities in the ^{31}P NMR NMR spectra and coupling constants $^1J(^{195}Pt, ^{31}P)$ (see Fig. 4). Since **8a** reacts much

Table 3
^{11}B, ^{31}P and ^{195}Pt NMR data [a] of the complexes **22–27**

No.	R	R'	$\delta^{31}P$ [$^1J(^{195}Pt, ^{31}P)$]	($^2J(^{31}P, ^{31}P)$)	$\delta^{31}P$ [$^1J(^{195}Pt, ^{31}P)$]	$\delta^{195}Pt$
22 [b,d]	Me	Me	49.1 [3598]	(42.5)	48.6 [3686]	−787.0
23 [b,e]	Et	Me	49.1 [3612]	(44.0)	48.1 [3683]	n.m.
24 [f]	Et	^{t}Bu	49.1 [3497]	(37.8)	46.7 [3766]	n.m.
25	Et	CMe=CH_2	48.3 [3558]	(36.3)	47.7 [3658]	−843.0
26 [b,g]	Et	Ph	48.1 [3712]	(25.5)	47.3 [3615]	−839.0
27 [c]	Et	$SiMe_3$	38.4 [4000]	(39.5)	37.6 [3660]	−860.0

[a] In C_6D_6 (25 ± 1°C) if not noted otherwise; coupling constants $^1J(^{195}Pt, ^{31}P)$ are accurate to ±2 Hz n.m. means not measured; $\delta^{31}P$ values are not assigned.
[b] In CD_2Cl_2.
[c] In [D_8]toluene.
[d] $\delta^{11}B = 24.8$ ($h_{1/2} = 425$ Hz). ^{13}C NMR: $\delta^{13}C$: 92.2 broad, =C–B; 74.7 =*C*Me; 3.4 *CH*$_3$C=; 23.2, 21.9 *CH*$_3$C=; all other ^{13}C NMR signals overlap with resonances of **15** or impurities.
[e] $\delta^{11}B$ 31.0 ($h_{1/2} = 650$ Hz).
[f] $\delta^{11}B$ 28.5 ($h_{1/2} = 500$ Hz).
[g] ^{13}C NMR: $\delta^{13}C$ [$J(^{195}Pt, ^{13}C)$] = 98.8 broad, =C–B; 93.8 [240.0] =C–Ph; 96.1, 91.8 C≡C–Ph; all other ^{13}C NMR signals overlap with signals of the major component **19**.

Table 4
^{11}B, ^{13}C, ^{31}P and ^{195}Pt NMR data [a] of the complexes **28a,d**

No.	$\delta^{13}C$(=CPt)	$\delta^{13}C$(=CB)	$\delta^{13}C(CH_2Pt)$	$\delta^{31}P$ [b]	($^2J(^{31}P, ^{31}P)$)	$\delta^{31}P$ [c]	$\delta^{195}Pt$
28a [d,e]	191.6 [881.2] (114.4, 12.7)	148.6 [60] [f]	22.3 [335.7] (89.0, 7.3)	5.7 [1591]	(11.0)	−0.9 [1824]	25.9 [1591, 1824]
29 [d]	183.8 [895.0] (113.0, 11.7)	149.9 [45] [f]	[h]	5.8 [1731]	(11.6)	1.2 [1937]	16.5 [1731, 1837]

[a] In C_6D_6 at 25 ± 1°C; coupling constants $J(^{195}Pt, ^{13}C)$ (±1 Hz) and $^1J(^{195}Pt, ^{31}P)$ (±2 Hz) are given in square brackets, $J(^{31}P, ^{13}C)$ (±1 Hz) in parentheses.
[b] Phosphorus atom in *trans*-position to ^{n}Bu.
[c] Phosphorus atom in *cis*-position to ^{n}Bu.
[d] Other $\delta^{13}C$ data: 34.8 [15.2] (3.8, <1), 27.2 [76.0] (4.5,1.9), 14.5 [<3] (<1) –$CH_2CH_2CH_3$; 29.3 [108] (10.8, <1), 15.5 [<3] (<1) =C–CH_2CH_3; 26.1 [71.2] (10.8, <1) =C–CH_3; 19.3 [f], 9.5 B–CH_2CH_3.
[e] $\delta^{11}B$ 76.0 ± 0.5.
[f] Broad signal owing to partially relaxed ^{13}C–^{11}B coupling.
[g] $\delta^{11}B$ 78.0 ± 1.
[h] Assignment uncertain due to overlap with other ^{13}C NMR signals.

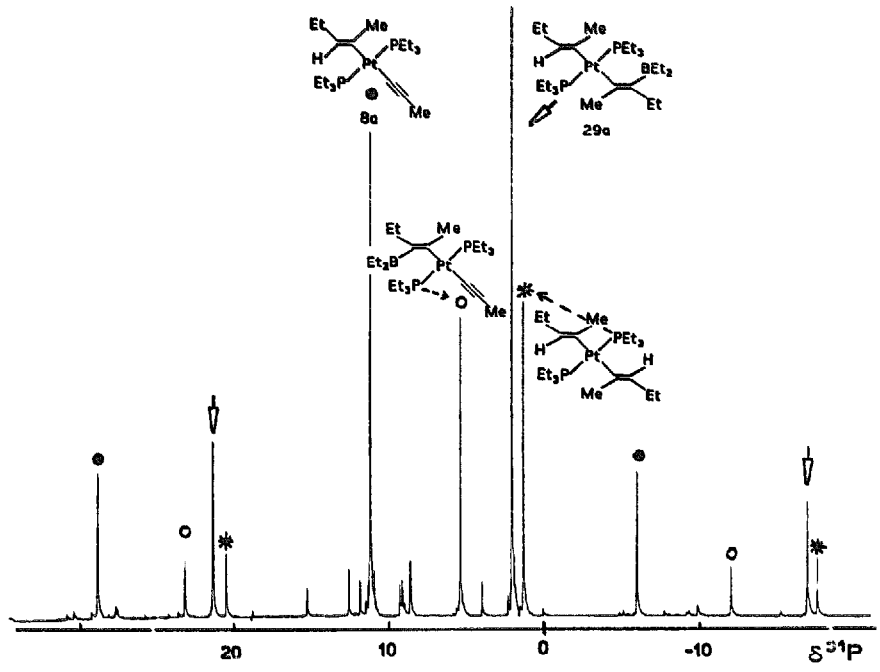


Fig. 4. 80.2 MHz $^{31}P\{^1H\}$ NMR spectrum of the reaction solution (C_6D_6) containing the complex **8a** and an excess of Et_3B after 2 weeks of reaction time at room temperature. The central ^{31}P NMR signals are assigned and ^{195}Pt satellites are marked by arrows, asterisks, filled and non-filled circles. Other weak signals belong to unidentified decomposition products.

slower with **2b** than comparable complexes **4–7** with *cis*-configuration, it is assumed that steric hindrance exerted by the phosphane ligands is responsible.

2.5. NMR spectroscopic results

The NMR data of the new 1-alkynylplatinum(II) complexes **4b,c**, **7a,d** and **8a** agree consistently with the known NMR data sets of similar compounds [4,5,27–29]. In the case of **8a**, the presence of the olefinic proton (see Fig. 5) invites for carrying out various 1D heteronuclear double resonance experiments [30] or 2D heteronuclear shift correlations (HETCOR) in order to determine absolute signs of coupling constants [31,32]. Thus, selective ^1H (^{31}P) experiments (^1H and ^{31}P are

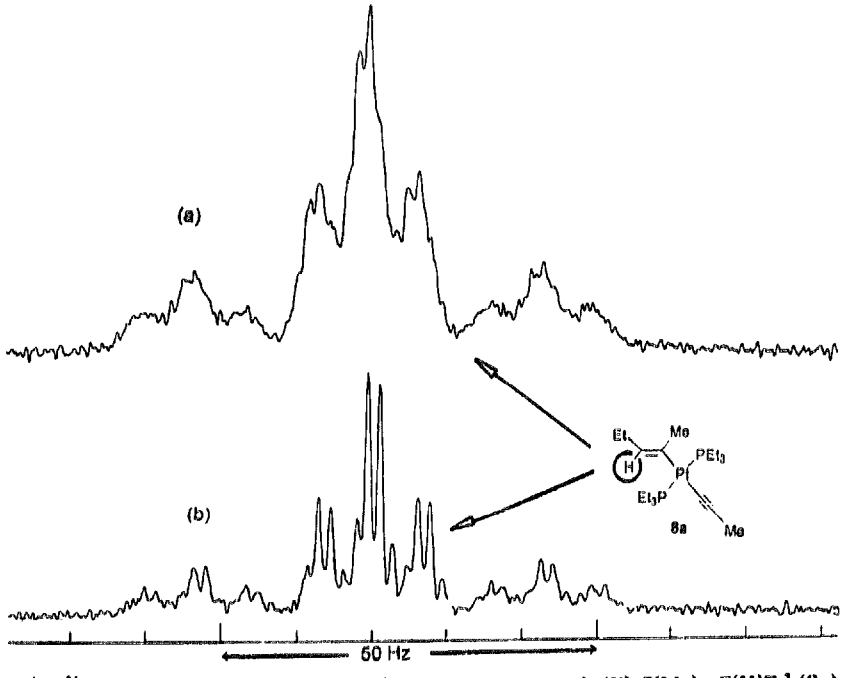


Fig. 5. 200 MHz ^1H (a) and $^1H\{^{31}P\}$ NMR spectrum (b) of *trans*-$[(Et_3P)_2Pt(C{\equiv}C\text{-}Me)\text{-}(E)\text{-}C(Me){=}C(H)Et]$ (**8a**), showing the signal of the olefinic proton; the coupling constants $^3J(^1H, ^1H) = 6.6$ Hz (t), $^4J(^1H\text{-}C{=}C\text{-}C^1H_3)$ 1.6 Hz (q) are clearly resolved, together with the ^{195}Pt satellites [$^3J(^{195}Pt, ^1H) = 46.3$ Hz].

the active spins and ^{195}Pt is the so-called passive spin) reveal that the signs of $^{1}J(^{195}Pt, ^{31}P)$ (> 0 [26]) and $^{3}J(^{195}Pt, ^{1}H)$ (across the C=C bond) are alike. The 2D $^{13}C/^{1}H$ HETCOR (based on $^{1}J(^{13}C, ^{1}H)$; ^{1}H and/or ^{13}C are the active spins, and ^{195}Pt is the passive spin) shows that the signs of $^{3}J(^{195}Pt, ^{1}H)$ (> 0, vide supra) and $^{2}J(^{195}PtC=^{13}C)$ are opposite. Other signs of coupling constants for 1-alkynylplatinum(II) complexes have been determined previously [33,34].

Although it was not possible to record meaningful ^{13}C NMR spectra of most of the mixtures formed in the course of the 1,1-organoboration reactions, some products were formed reasonably pure, allowing to extend the ^{31}P and ^{195}Pt data set by ^{13}C NMR data. Thus the proposed structure of the complex **11** is supported by diagnostic ^{13}C NMR data (Table 1). Similarly, the complexes **18** and **19** are formed almost selectively, and a fairly complete ^{13}C NMR data set could be obtained (Table 3).

3. Conclusions

The various products formed by 1,1-organoboration of 1-alkynylplatinum(II) complexes result primarily from cleavage of a Pt–C≡ bond, similar to the findings for 1-alkynylsilicon, -germanium, -tin and -lead compounds [3]. This confirms the previously proposed mechanism [1,2] for the reaction of 1-ethynylplatinum(II) complexes with trialkylboranes [1,2]. In contrast to 1,1-organoboration of 1-alkynyltin or -lead compounds, zwitterionic intermediates with Pt(II) coordinated to the C≡C bond of an alkynylborate (**A**, **B**, or **C**) could neither be isolated nor detected by NMR measurements. However, the intermediacy of such unstable species can be deduced from the nature of the products such as η^2-alkyne platinum(0) or η^3-alkenylborane platinum(0) complexes.

4. Experimental

All compounds were prepared and handled in an atmosphere of Ar or N_2, observing necessary precautions to exclude traces of oxygen or moisture. Starting materials such as terminal alkynes or ^{n}BuLi (1.6 M in hexane) were obtained commercially or prepared following literature procedures: [(dppe)$PtCl_2$] [35], [(depe)$PtCl_2$] [36] [1], *trans*-[$(Et_3P)_2Pt(Cl)C{\equiv}C$–Me] [5], **4a,d,e**, **5a** [4], $Me_2Sn(C{\equiv}C$–$^{t}Bu)_2$, $Me_2Sn(C{\equiv}C$–$CMe{=}CH_2)_2$ [37], Me_3B [38], Et_3B [39], $^{i}Pr_3B$ [40], NMR measurements were carried out at 25°C using Bruker WP 200, AC 300, ARX 250 and DRX 500 instruments, all equipped with multinuclear units. Chemical shifts are given with respect to Me_4Si [δ^1H (C_6D_5H) = 7.15, ($CHCl_3/CDCl_3$ = 7.24, ($CHDCl_2$) = 5.33; $\delta^{13}C$ (C_6D_6) = 128.0, ($CDCl_3$) = 77.0, (CD_2Cl_2) = 53.8], Et_2O–BF_3 [$\delta^{11}B = 0$, $\Xi(^{11}B) = 32.083971$ MHz], H_3PO_4 (85%, aq.) [$\delta^{31}P = 0$, $\Xi(^{31}P) = 40.480747$ MHz] and to $\delta^{195}Pt = 0$ with $\Xi(^{195}Pt) = 21.4$ MHz.

4.1. *Cis*-di-1-alkynyl[1,2-bis(diorganylphosphino)ethane]platinum(II) 4b,c and 6d

The complexes were prepared and isolated in 95% yield in the same way as reported previously [4] by the reaction of *cis*-[(dppe)$PtCl_2$ or *cis*-[(depe)$PtCl_2$] with the respective di-1-alkynyl(dimethyl)stannane in THF.

4b: m.p. 235°C decomp. ^{13}C NMR (50.3 MHz, CD_2Cl_2): $\delta^{13}C$ [$J(^{195}Pt, ^{13}C)$] ($J(^{31}P, ^{13}C) = 90.3$ [1130.5] (149.0, 16.0) dd ≡–CPt; 120.5 [302.5] (33.7, 1.4) dd C≡, 29.4 [< 4] (< 1) C–C≡; 32.2 [8.2] (< 1) Me–C 28.6, 130.2, 134.1, 128.8, 131.3 dppe. ^{31}P NMR (80.9 MHz, CD_2Cl_2): $\delta^{31}P$ [$^{1}J(^{195}Pt, ^{31}P)$] = 41.1 [2258.0]. ^{195}Pt NMR (42.8 MHz, CD_2Cl_2): $\delta^{195}Pt$ [$^{1}J(^{195}Pt, ^{31}P)$] = −386.8 [2258.0] t.

4c: m.p. 210°C decomp.; IR (CH_2Cl_2): $\nu(C{\equiv}C)$ = 2110 (m), 2075 (w) cm^{-1}. ^{13}C NMR (50.3 MHz, CD_2Cl_2): $\delta^{13}C$ [$J(^{195}Pt, ^{13}C)$] ($J(^{31}P, ^{13}C) = 105.4$ [1137.0] (146.5, 15.5) dd ≡CPt; 113.5 [305.2] (34.1, 1.0] dd C≡; 131.1 [25.8] (< 1) ≡C; 115.6 [12.4] (< 1) $=CH_2$; 24.8 [7.7] (< 1) Me–C=; 28.8 [40.4] (38.3, 10.9) dd CH_2P; 130.4 [24.3] (54.8), 133.9, 129.1, 131.5 PhP. ^{31}P NMR (80.9 MHz, CD_2Cl_2): $\delta^{31}P$ [$^{1}J(^{195}Pt, ^{31}P)$] = 41.3 [2264.0]. ^{195}Pt NMR (42.8 MHz, CD_2Cl_2): $\delta^{195}Pt$ [$^{1}J(^{195}Pt, ^{31}P)$] = 382.0 [2264.0] t.

6d: m.p. 180°C decomp.; IR (CH_2Cl_2): $\nu(C{\equiv}C)$ = 2114 (m), 2108 (m) cm^{-1}. ^{13}C NMR (50.3 MHz, CD_2Cl_2): $\delta^{13}C$ [$J(^{195}Pt, ^{13}C)$] ($J(^{31}P, ^{13}C) = 109.8$ [1084.8] (139.8, 16.7) dd ≡CPt; 110.8 [197.3] (34.4,1.5) dd C≡; 128.9 [25.6], 131.4 [8.8], 128.2, 125.5 Ph–C≡; 24.5, 18.8, 8.8 depe. ^{31}P NMR (80.9 MHz, CD_2Cl_2): $\delta^{31}P$ [$^{1}J(^{195}Pt, ^{31}P)$] = 51.6 [2209.0]. ^{195}Pt NMR (42.8 MHz, CD_2Cl_2): $\delta^{195}Pt$ [$^{1}J(^{195}Pt, ^{31}P)$] = −387.2 [2209.0] t.

4.2. *Cis*-1-alkynyl(n-butyl)[bis(triethylphosphane)]platinum(II) 7a,d

A solution of 2.0 mmol each of *trans*-[$(Et_3P)_2Pt(Cl)C{\equiv}C$–$R^1$] [$R^1$ = Me (**a**), Ph (**d**)] in 30 ml of hexane and 5 ml of benzene was cooled at −78°C, and 1.25 ml of a solution of ^{n}BuLi in hexane (1.6 M) was added to the stirred suspension within 5 min. After

[1] See also Ref. [2].

warming to room temperature all insoluble material was filtered off and the solvents were removed in vacuo. The colourless residues turned out to be the pure (> 97% according to ^{31}P NMR) complexes **7a,d** in ca. 65% yield.

7a: m.p. 65°C decomp.; ^{13}C NMR (50.3 MHz, CD_2Cl_2): $\delta^{13}C$ [$J(^{195}Pt, ^{13}C)$] ($J(^{31}P, ^{13}C)$ = 103.9 [1226.3] (147.0, 21.6) dd ≡CPt; 96.1 [341.8] (33.3, < 1) d C≡; 6.8 [25.6] (< 1) Me–C≡–; 16.8 [535.4] (91.6, 7.2) dd, 36.3 [13.9] (3.9, < 1) d, 28.9 [88.2] (8.9, < 1) d, 14.8 [< 3] (< 1) Pt–$CH_2CH_2CH_2CH_3$. ^{31}P NMR (80.9 MHz, CD_2Cl_2): $\delta^{31}P$[$^1J(^{195}Pt, ^{31}P)$] ($^2J(^{31}P, ^{31}P)$ = 10.3 [1426.0] (14.3); 10.3 [2587.0] (14.3). ^{195}Pt NMR (42.8 MHz, CD_2Cl_2): $\delta^{195}Pt$ [$^1J(^{195}Pt, ^{31}P)$] = −278.0 [2587.0, 1426.0] dd.

7d: m.p. 55°C decomp.; NMR (50.3 MHz, CD_2Cl_2): $\delta^{13}C$ [$J(^{195}Pt, ^{13}C)$] ($J(^{31}P, ^{13}C)$ 120.5 (146.7, 21.9) dd ≡CPt; 105.8 [338.0] (31.0, < 1) d C≡; 131.4, 128.1, 124.8 Ph–C≡; 16.7 [526.6] (88.4, 6.4) dd, 36.2 [9.0] (4.6, < 1) d, 28.8 [83.8] (10.0, < 1) d, 14.8 [< 3] (< 1) Pt–$CH_2CH_2CH_2CH_3$. ^{31}P NMR (80.9 MHz, CD_2Cl_2): $\delta^{31}P$ [$^1J(^{195}Pt, ^{31}P)$] [$^2J(^{31}P, ^{31}P)$] = 9.3 [1430.0] (15.5); 9.8 [2627.0] (16.6)). ^{195}Pt NMR (42.8 MHz, CD_2Cl_2): $\delta^{195}Pt$ [$^1J(^{195}Pt, ^{31}P)$] = −262.4 [2627.0,1430.0] dd.

4.3. Trans-(E)-2-pentenyl(1-propynyl)[bis(triethylphosphane)]platinum(II) 8a

Triethylborane (3 ml, 21.4 mmol) was added in one portion to a solution of 1.27 g (2.5 mmol) of *trans*-[$(Et_3P)_2Pt(C{\equiv}C{-}Me)_2$] in 20 ml of benzene, and the mixture was kept in the dark at room temperature for two weeks. ^{31}P NMR spectra indicated that ca. 90% of the starting platinum complex was converted into the alkenylborane (Eq. (3a)) by 1,1-ethyloboration. Then the reaction mixture was added to a column (length 20 cm, diameter 3 cm) filled with neutral alumina and benzene. After elution with 150 ml of benzene, all volatile material was removed in vacuo, and 0.94 g (70%) of **8a** was left as a colourless oil. IR (hexane): ν(C≡–C) 2121(m) cm^{-1}; ν(C=C) 1585 (broad) cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ^1H [$J(^{195}Pt, ^1H)$] ($J(^{31}P, ^1H)$) = 2.02 [−13.2] (2.0) t CH_3–C≡; 5.41 [+46.3] (0.5), $^3J(^1H, ^1H)$ = 6.6 Hz, $^4J(^1H, ^1H)$ = 1.6 Hz, m (see Fig. 5) H–C=; 2.03 m CH_3–C=; 2.20 m, 1.08 $^3J(^1H, ^1H)$ = 7.5 Hz, t, =C–CH_2–CH_3; 1.8 m, 1.0 m P–CH_2CH_3; ^{13}C NMR (50.3 MHz, C_6D_6): $\delta^{13}C$ [$J(^{195}Pt, ^{13}C)$] ($J(^{31}P, ^{13}C)$ = 96.6 [796.0] (15.3) t ≡CPt; 100.7 [210.0] (< 1) C≡; 6.7 [17.8] (< 1) Me–C≡; 146.3 [643.5] (10.8) t ≡CPt; 131.8 [33.0] (4.1) C=; 25.3 [44.5] (< 1) Me–C=; 23.3 [51.5] (< 1) CH_3–C=; 16.8 [< 3] (< 1) CH_3–CH_2–C=; 15.5, 8.2 EtP. ^{31}P NMR (80.9 MHz, CD_2Cl_2): $\delta^{31}P$ [$^1J(^{195}Pt, ^{31}P)$] = 11.3 [2797.0]. ^{195}Pt NMR (42.8 MHz, C_6D_6): $\delta^{195}Pt$ [$^1J(^{195}Pt, ^{31}P)$] = −87.1 [2797.0] t.

4.4. Reactions of the 1-alkynylplatinum(II) complexes 4–8 with trialkylboranes 2 (general procedure)

The respective 1-alkynylplatinum(II) complex (ca. 0.1 to 0.3 mmol) was dissolved in 2.0 ml of CD_2Cl_2 (if heating was required [D_8]toluene served as solvent) at room temperature. These solutions were transferred into NMR tubes and cooled at −78°C. An excess of the respective trialkylborane (ca. 2–3 mmol) was added in one portion through a syringe (or in the case of Me_3B, the borane was condensed into the NMR tube which then was sealed after several pump–freeze circles). The reaction mixtures were warmed to room temperature, and the progress of the reactions was always monitored by ^{31}P NMR spectroscopy, in favourable cases also by ^{195}Pt NMR spectroscopy. In general, the colour of the mixtures turned dark but the solutions stayed clear for several days at room temperature. After heating at > 50°C or after more than 10 d at room temperature extensive decomposition started, indicated by precipitation of insoluble material and by the appearance of numerous unassigned ^{31}P NMR signals.

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