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# $\eta^1$-Alkynylplatinum(II) complexes with cycloocta-1,5-diene and tri(1-cyclohepta-2,4,6-trienyl)phosphane ligands

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Dedicated to Professor Rolf Gleiter on the occasion of his 65th birthday

**Abstract**

$\eta^1$-Alkynylplatinum(II) complexes of the type (cod)Pt(C≡C–R)$_2$ (**1**, cod = $\eta^4$-cycloocta-1,5-diene; R = Me (**a**), $^t$Bu (**b**), Ph (**c**), Fc (**d**), SiMe$_3$ (**e**)) were prepared in good yields from the reaction of (cod)PtCl$_2$ with either HC≡C–R and NaOEt (R = $^t$Bu, Ph, Fc) or di(1-alkynyl)dimethyltin, Me$_2$Sn(C≡C–R)$_2$ (R = Me, SiMe$_3$). The analogous reaction of [P]PtCl$_2$ ([P] = tri(1-cyclohepta-2,4,6-trienyl)phosphane, {P(C$_7$H$_7$)$_2$($\eta^2$-C$_7$H$_7$)}) with Me$_2$Sn(C≡C–R)$_2$ (R = Me, $^t$Bu, Ph, Fc, SiMe$_3$), afforded selectively the complexes [P]PtCl(C≡C–R) **2a**–**e** in high yield, in which the 1-alkynyl group is in *cis* position with respect to the phosphorus atom, and one of the C$_7$H$_7$ rings is $\eta^2$-coordinated to platinum through the central C=C bond. Complexes **3a**–**e** of the type [P]Pt(C≡C–R)$_2$ could not be prepared by the reaction of **2** with an excess of the 1-alkynyltin reagents. However, the reaction of **1** with the phosphane P(C$_7$H$_7$)$_3$ gave compounds **3a**–**e** in quantitative yield by substitution of the cod ligand. The molecular structures of **2b** and **3d** were determined by X-ray structure analysis, and complexes **1**–**3** were characterised in solution by multinuclear magnetic resonance spectroscopy ($^1$H-, $^{13}$C-, $^{29}$Si-, $^{31}$P-, $^{195}$Pt-NMR). The structures of **2** and **3** in solution were found to be fluxional with respect to coordination of the C$_7$H$_7$ rings to platinum. 

*Keywords:* Platinum; Tin; Alkynes; Cycloocta-1,5-diene; Phosphanes; NMR; X-ray

## 1. Introduction

Metal complexes containing different π-systems in the coordination sphere are of particular interest with respect to intramolecular ligand–ligand interactions. We have studied platinum(II) compounds in which the π-coordinated ($\eta^2$) olefinic double bond of a cyclic chelate ligand — such as cycloocta-1,5-diene, C$_8$H$_{12}$ (cod) in **1** or tri(1-cyclohepta-2,4,6-trienyl)phosphane, P(C$_7$H$_7$)$_3$ [P] in **2** and **3** — is connected through the metal with σ-coordinated ($\eta^1$) **1**-alkynyl ligands in either *cis*- or *trans*-position.

Complexes of platinum(II) in which 1-alkynyl groups are $\eta^1$-linked to platinum are known mainly as anionic species, [Pt(C≡C–R)$_4$]$^{2-}$, or as bis(phosphane) complexes of the type *trans*-[(PR$_3$)$_2$Pt(C≡C–R)$_2$] and *cis*-[(PR$_3$)$_2$Pt(C≡C–R)$_2$] [1–3]. In the latter cases, the use of chelating diphosphanes such as dppe [4], dppm [5] or dmpe and depe helps to increase the stability (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$; dppm = Ph$_2$PCH$_2$PPh$_2$; dmpe = Me$_2$PCH$_2$CH$_2$PMe$_2$; depe = Et$_2$PCH$_2$CH$_2$PEt$_2$). A few complexes of the type (cod)Pt(C≡C–R)$_2$ have been described which, however, have not been fully characterised in solution by NMR spectroscopy [6,7]. With respect to the reactivity of the Pt–C≡ and the C≡C bonds, all these complexes are attractive starting materials for further syntheses, as has been shown in various research areas (cf. Refs. [2,8–11]). However, little is known about such platinum(II) complexes, in which one or both phosphane donor functions are replaced by $\eta^2$ bonded alkene ligands. The phosphane [P] [12] offers unique potential as a chelating ligand since it can use C=C bonds for π complexation in addition to the metal–phosphorus bond [13]. Considering the already existing large NMR data set of $\eta^1$-alkynylplatinum complexes [3–5,14], the new complexes should also be

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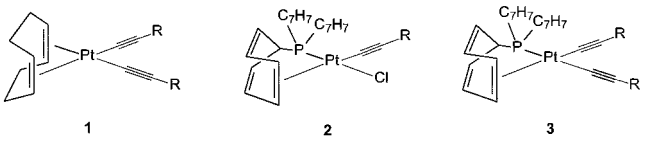
of interest from the NMR point of view. So far little direct structural information is available on $\eta^1$-alkynylplatinum complexes [3b,15–17]. In the present work, we have therefore determined the crystal structures of **2b** and **3d** by X-ray analysis.




| R | Me | $^t$Bu | Ph | Fc | SiMe$_3$ |
|---|---|---|---|---|---|
| | a | b | c | d | e |

(Fc = ferrocenyl, CpFe($C_5H_4$–))

## 2. Results and discussion

### 2.1. Synthesis of the cyclooctadiene complexes (cod)Pt(C≡C–R)$_2$ (1a–e)

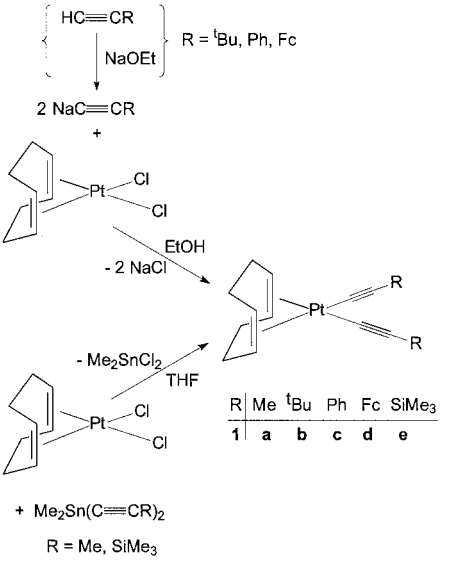
In principle, complexes of the type **1** can be prepared from (cod)$PtCl_2$ and the respective lithium alkynide, which is formed from the corresponding alkyne and $^n$BuLi. However, the procedures shown in Scheme 1 are more convenient and give the desired compounds **1** in essentially quantitative yield, and the complexes **1** can be used without further purification. Separation from dimethyltin dichloride is easily achieved by precipitation of **1** from the reaction mixture; repeated washing with hexane and drying under high vacuum leads to pure products **1a** and **1e**. The complexes **1** are colourless (**1a**, **b**, **e**), yellow (**1c**) or orange solids (**1d**) which can be stored indefinitely under an inert atmosphere.

### 2.2. Synthesis of the phosphane complexes [P]PtCl(C≡C–R) (2a–e) and [P]Pt(C≡C–R)$_2$ (3a–e)

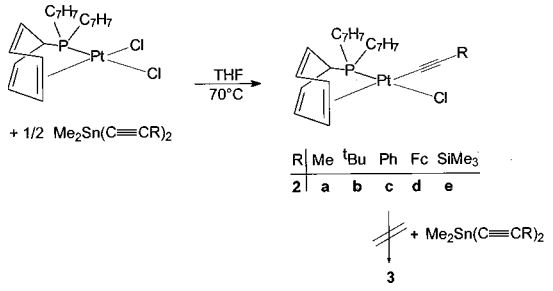
The reaction of the platinum dichloride [P]$PtCl_2$ with $Me_2Sn(C{\equiv}C{-}R)_2$ in a molar ratio of 2:1 provides a surprisingly clean method to obtain selectively the monochloro complexes **2** (Scheme 2), after separation from dimethyltin dichloride in the same way as described in Section 2.1. This is remarkable, since the analogous reactions of, e.g. (dppe)$PtCl_2$ [4] or (dppm)$PtCl_2$ [5] afford exclusively the di(1-alkynyl) compounds corresponding to **3**, and attempts to prepare the platinum chlorides analogous to **2** have not been successful. Unexpectedly, the complexes **2** do not react with an excess of the 1-alkynyltin compound to give **3**. The compounds **2** are yellow (**2a**–**c** and **e**) or orange (**2d**) solids, of which **2b** could be crystallised to give single crystals suitable for X-ray structural analysis (vide infra).

For the preparation of the di(1-alkynyl)platinum(II) complexes **3**, the cod compounds **1** are excellent starting materials. The reactions of **1** with the phosphane $P(C_7H_7)_3$ lead quantitatively to **3** by replacement of the cod ligand (Scheme 3). Again the complexes **3** are yellow (**3a**–**c** and **e**) or orange (**3d**) solids, and single crystals were obtained in the case of **3d**, for which an X-ray structural analysis was carried out (vide infra). All compounds **2a**–**e** and **3a**–**e** are stable under an inert atmosphere and can be stored for extended periods without decomposition.

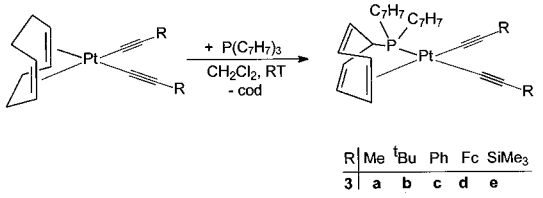
The complexes **2** and **3** are fluxional with respect to the bonding of the cyclohepta-2,4,6-trienyl rings to platinum [18,19]. The dynamic processes involved cannot be simply dissociative reducing the coordination



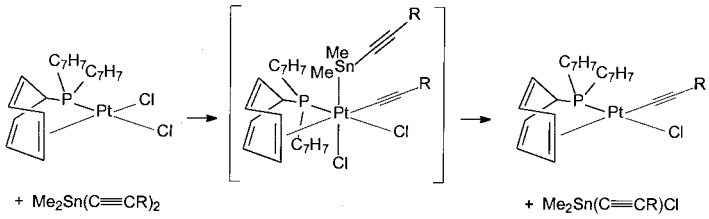

Scheme 1.




Scheme 2.




Scheme 3.




Scheme 4.

Table 1
$^{195}$Pt-, $^{13}$C- and $^{29}$Si-NMR data [a] of the (cod)platinum(II)di(1-alkynyl) complexes **1a–e**

| | $\delta^{195}$Pt | $\delta^{13}$C (Pt–C≡) | $\delta^{13}$C (≡C–) | $\delta^{13}$C (R) | $\delta^{13}$C (cod) |
|---|---|---|---|---|---|
| **1a** | 614.6 | 82.2 [1413.8] | 103.0 [371.1] | 6.8 [25.4] | 102.7, 30.2 [80.8] |
| **1b** | 605.6 | 80.7 [1410.7] | 117.3 [367.0] | 32.1 [b] | 102.5, 30.2 [79.8] |
| **1c** | 592.1 | 92.7 [1412.0] | 103.5 [362.3] | 130.9 (i) [c] [36.6] | 104.2, 30.4 [79.5] |
| **1d** | 602.3 | 90.7 [1352.0] | 105.0 [374.7] | 69.4 (C-1(Fc)) [d] [30.9] | 103.5, 29.5 [79.8] |
| **1e** | 610.1 | 112.1 [1350.1] | 112.6 [316.0] | 0.9 [e] | 104.2, 30.2 [75.2] |

[a] Solutions in $CD_2Cl_2$ (saturated; at 23 °C); coupling constants $J(^{195}Pt,^{13}C)$ are given in brackets ($\pm 1$ Hz).
[b] Overlapping signals.
[c] Other $\delta^{13}$C: 131.8 (*o*), 127.8 (*m*), 126.5 (*p*).
[d] Other $\delta^{13}$C: 67.7, 71.2 (C-3,4(Fc), C-2,5(Fc)), 71.2 (Cp).
[e] $^1J(^{29}Si,^{13}C) = 55.5$ Hz; $\delta^{29}Si = -21.6$; $^3J(^{195}Pt,^{29}Si) = 30.4$ Hz; $^1J(^{29}Si,^{13}C\equiv) = 83.9$ Hz; $^2J(^{29}Si,\equiv^{13}C) = 13.4$ Hz; $^1\Delta\ ^{12/13}C(^{21}Si) = -3$(Me), $-15$(C≡) ppb.

number of platinum, since this would lead to a three-coordinate intermediate, in which *cis*/*trans* scrambling of the ligands is expected to take place. However, the coupling constants $^2J(^{31}P, \equiv^{13}C)$ do not change their values with temperature in the case of **2**, and the alkynyl groups remain different in **3** when the exchange of the $C_7H_7$ rings in coordination to platinum is fast with respect to the NMR time scale. This indicates that the $C_7H_7$ exchange probably passes through a transition state, in which a leaving $C_7H_7$ group is immediately replaced by the incoming next one. Since this process blocks coordination sites at the platinum centre, it could explain why the replacement of the remaining chloro ligand in **2** by an alkynyl ligand cannot be achieved using the alkynyltin compound as a transfer reagent. It has been proved definitely in the case of palladium that the Pd–Cl/alkynyltin exchange proceeds via oxidative addition and reductive elimination [3b,20], and the same mechanism (see Scheme 4) is likely to account for Pt–Cl/alkynyltin exchange. Thus, it appears that the first step leading from [P]$PtCl_2$ to **2** is possible, whereas the second step, which would lead to **3**, is no longer favourable.

### 2.3. NMR spectroscopic results

$^{13}$C-, $^{29}$Si- and $^{195}$Pt-NMR data of the complexes **1** are given in Table 1, whereas Tables 2 and 3 contain $^{13}$C-, $^{29}$Si-, $^{31}$P- and $^{195}$Pt-NMR data of the complexes **2** and **3**, respectively.

$^{195}$Pt-NMR spectra can be conveniently recorded at moderate field strengths $B_0$ (e.g. 5.87 T, corresponding to the $^1$H-NMR frequency of 250 MHz). At higher field strengths $B_0$, the $^{195}$Pt-NMR signals broaden significantly as a result of increasingly efficient (dependent on $B_0^2$) chemical shift anisotropy induced nuclear spin relaxation [21]. This becomes evident not only for the $^{195}$Pt-NMR signals but also for the $^{195}$Pt satellites in the $^{13}$C- (Fig. 1), $^{31}$P- or $^{29}$Si-NMR spectra (Fig. 2). The $\delta^{195}$Pt data for each class of compounds are spread over a narrow range (**1**: 23 ppm; **2**: 11 ppm; **3**: 14 ppm), and conclusions beyond the identification of the type of complex cannot be reached, considering the huge range of $\delta^{195}$Pt-NMR data in general [22]. On the other hand, these narrow ranges of $\delta^{195}$Pt data indicate that the influence of the various groups R in the C≡C–R ligands is either small (more likely) or that shielding or deshielding effects on the $^{195}$Pt nuclei compensate each other (less likely in these cases). On going from **2** to **3** the $^{195}$Pt nuclear shielding increases by $\approx 105 \pm 5$ ppm, due to the presence of a second alkynyl group instead of a chloro ligand.

The $\delta^{31}$P data of the compounds **2** and **3** also cover a small range for each type of compound (only $\approx 2$ ppm) which again points towards rather small effects exerted by the different groups R on the electronic structure in the vicinity of the platinum or phosphorus atom. The $^{31}$P nuclear shielding decreases by $\approx 10 \pm 1$ ppm on going from **2** to **3**. Small changes due to different groups R in **2** and **3** are also confirmed by the small range of the respective coupling constants

$^1J(^{195}Pt,^{31}P)$ of **2** (3915–3979 Hz) and **3** (2523–2578 Hz). The marked decrease in the magnitude of $^1J(^{195}Pt,^{31}P)$ values on going from **2** to **3** ($\approx 1396 \pm 30$ Hz; i.e. 35%) indicates the stronger polarising ability of the chloro ligand in **2** as compared to the second alkynyl group in **3**.

A typical $^{13}$C-NMR spectrum is shown in Fig. 1. The $\delta^{13}$C(alkyne) values of **1** and **2** are similar (slight shift

Table 2
$^{195}$Pt-, $^{31}$P-, and $^{13}$C-NMR data [a] of the [P]Pt(chloro)1-alkynyl complexes **2a–d**

| No | $\delta^{195}$Pt | $\delta^{31}$P | $\delta^{13}$C(Pt–C≡) | $\delta^{13}$C(≡C–) | $\delta^{13}$C(R) | $\delta^{13}$C(Pt–(C=C)) | $\delta^{13}$C(C-1′) | $\delta^{13}$C (C-1) |
|---|---|---|---|---|---|---|---|---|
| **2a** | 70.2 {3966} | 92.0 {3966} | 77.8 [1525.9] (17.2) | 105.4 [416.6] (<2) | 5.7 [27.0] | 95.7 [60.1] (<2) | 34.4 [b] (25.9) | 34.1 [c] [55.3] (43.1) |
| **2b** | 59.4 {3979} | 91.2 {3979} | 78.2 [1594.8] (17.0) | 117.9 [396.9] (<2) | 28.9 (C), 31.3 (Me) | 95.9 [58.7] (<2) | 33.6 [d] (26.0) | 34.0 [e] [56.3] (43.4) |
| **2c** | 67.2 {3915} | 93.6 {3915} | 92.2 [1515.1] (16.9) | 108.8 [409.3] (<2) | 125.3 (i) [f] | 96.9 [58.4] (<2) | 33.7 [g] (28.6) | 34.2 [h] [56.0] (42.8) |
| **2d** | 64.9 {3945} | 92.7 {3945} | 88.6 [1524.7] (17.3) | 106.5 [412.3] (<2) | 67.7 [i] (C-1(Fc)) | 95.8 [61.8] (<2) | 33.8 [j] (27.1) | 34.1 [k] [54.4] (39.2) |
| **2e** | 69.4 {3943} | 91.6 {3943} | 109.8 [1419.6] (15.8) | 114.2 [350.6] (<2) | 0.0 [l] | 98.0 [51.5] (<2) | 34.1 [m] (29.3) | 34.0 [n] [58.1] (42.8) |

[a] Solutions in $CD_2Cl_2$ (saturated; at $-20$ °C); coupling constants $J(^{31}P,^{13}C)$ are given in parentheses, $J(^{195}Pt,^{13}C)$ in brackets, and $^1J(^{195}Pt,^{31}P)$ in braces.
[b] Coordinated ring; other $\delta^{13}$C: 127.7 [51.4] (C-2′,7′), 130.0 (9.7) (C-3′,6′).
[c] Non-coordinated rings; other $\delta^{13}$C: 112.6, 113.0 (C-2,7), 126.6 (11.5), 126.9 (11.5) (C-3,6), 130.4, 130.5 (C-4,5).
[d] Coordinated ring; other $\delta^{13}$C: 127.6 [53.2] (C-2′,7′), 130.4 (10.4) (C-3′,6′).
[e] Non-coordinated rings; other $\delta^{13}$C: 111.9, 112.8 (C-2,7), 126.5 (12.1), 126.8 (11.3) (C-3,6), 130.5, 130.7 (C-4,5).
[f] Other $\delta^{13}$C: 130.5 (*o*), 128.0 (*m*), 126.5 (*p*).
[g] Coordinated ring; other $\delta^{13}$C: 127.9 [54.1] (C-2′,7′), 130.1 (9.2).
[h] Non-coordinated rings; other $\delta^{13}$C: 113.4, 113.6 (C-2,7), 126.6 (11.8), 126.8 (11.8) (C-3,6), 130.6, 130.8 (C-4,5).
[i] Other $\delta^{13}$C: 67.9, 70.6 (C-2,5(Fc), C-3,4(Fc)), 69.3 (Cp).
[j] Coordinated ring; other $\delta^{13}$C: 127.7 [52.7] (C-2′,7′), 130.0 (9.5) (C-3′,6′).
[k] Non-coordinated rings; other $\delta^{13}$C: 113.8, 113.9 (C-2,7), 126.3 (11.7), 126.5 (11.7) (C-3,6), 130.6, 130.7 (C-4,5).
[l] $^1J(^{29}Si,^{13}C) = 55.9$ Hz; $\delta^{29}Si = -21.9$; $^3J(^{195}Pt,^{29}Si) = 33.1$ Hz; $^4J(^{31}P,^{29}Si) = 0.6$ Hz.
[m] Coordinated ring; other $\delta^{13}$C: 128.0 [50.4] (C-2′,7′), 130.2 (9.4) (C-3′,6′).
[n] Non-coordinated rings; other $\delta^{13}$C: 112.4, 112.7 (C-2,7), 126.6 (11.8), 126.7 (11.2) (C3,6), 130.5, 130.7 (C-4,5).

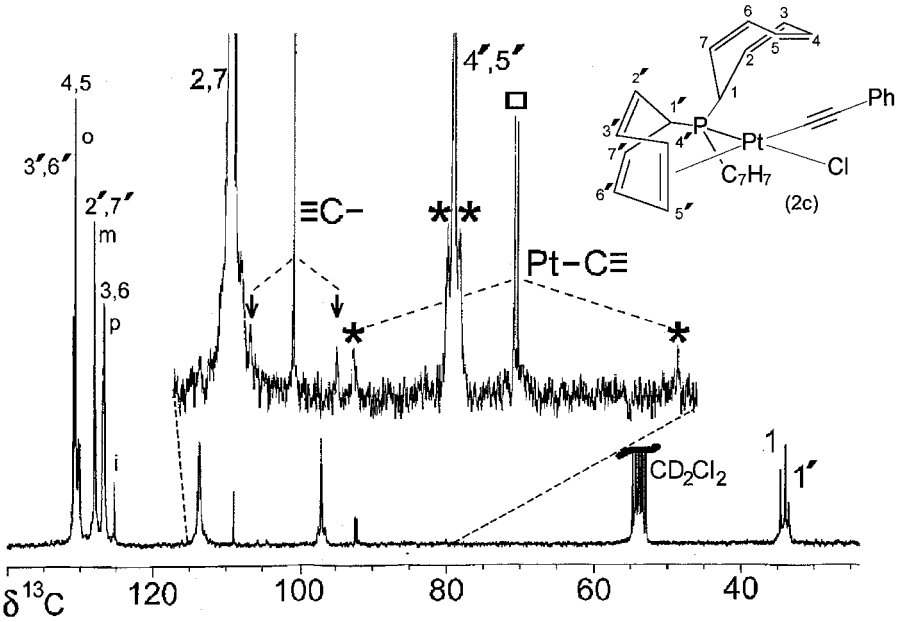



Fig. 1. $^{13}$C-NMR (62.8 MHz) spectrum of **2c** (saturated solution in $CD_2Cl_2$, measured at $-20 \pm 1$ °C to slow down the dynamic process involving the ligand [P]). The expansion shows the region of the alkynyl $^{13}$C resonances, for which the $^{195}$Pt satellites (marked by asterisks) corresponding to the coupling constants $^nJ(^{195}Pt,^{13}C)$ are clearly visible.

Table 3
$^{195}$Pt-, $^{31}$P-, and $^{13}$C-NMR data [a] of the [P]Pt(1-alkynyl)$_2$ complexes **3a–d**

| No | $\delta^{195}$Pt | $\delta^{31}$P | $\delta^{13}$C(Pt–C≡) | $\delta^{13}$C(≡C–) | $\delta^{13}$C(R) | $\delta^{13}$C(Pt–(C≡C)) | $\delta^{13}$C(C-1′) | $\delta^{13}$C (C-1) |
|---|---|---|---|---|---|---|---|---|
| **3a** | −28.7 {2560} | 101.7 {2560} | n.m. | n.m. | n.m. | n.m. | n.m. | n.m. |
| **3b** | −39.7 {2554} | 101.2 {2554} | 78.6 [b] [1525.7] (15.9); 95.9 [c] [1126.7] (163.1) | 121.0 [b] [416.1] (<2); 112.9 [c] [284.9] (32.6) | 28.5, 28.9 (C), 31.9, 31.2 (Me) | 90.1 [59.4] | 34.0 [d] (21.6) (<2) | 32.8 [e] [34.5] (36.7) |
| **3c** | −38.9 {2578} | 103.2 {2578} | 90.1 [b] [1538.1] (15.8); 112.5 [c] [1129.0] (159.5) | 112.6 [b] [428.3] (<2); 104.7 [c] [293.0] (33.0) | 126.0 126.3 (i) [f] | 91.7 [56.9] (<2) | 34.5 [g] (19.5) | 33.5 [h] [38.5] (36.7) |
| **3d** | −40.6 {2576} | 102.2 {2576} | 87.6 [b] [1537.7] (15.9); 108.9 [c] [1135.0] (161.7) | 110.3 [b] [434.4] (<2); 100.7 [c] [297.7] (33.9) | 66.0, 68.9 (C-1(Fc)) [i] | 90.3 [58.9] (<2) | 34.7 [j] (22.0) | 33.5 [k] [36.6] (36.3) |
| **3e** | −26.5 {2523} | 101.6 {2523} | 108.3 [b] [1444.2] (14.7); 133.5 [c] [1072.2] (146.7) | 117.0 [b] [365.7] (<2); 108.2 [c] [264.4] (26.7) | −0.3, 0.5 [l] | 93.1 [53.1] (<2) | 34.6 [m] (21.5) | 33.1 [n] [35.2] (36.4) |

[a] Solutions in $CD_2Cl_2$ (saturated; at −40 °C); coupling constants $J(^{31}P,^{13}C)$ are given in parentheses, $J(^{195}Pt,^{13}C)$ in brackets, and $^1J(^{195}Pt,^{31}P)$ in braces; n.m. means not measured.
[b] Alkynyl group C≡C–R *cis* to phosphorus atom.
[c] Alkynyl group C≡C–R *trans* to phosphorus atom.
[d] Coordinated ring; other $\delta^{13}$C: 128.4 [45.0] (C-2′,7′), 130.4 (10.1) (C-3′,6′).
[e] Non-coordinated rings; other $\delta^{13}$C: 111.4, 112.0 (C-2,7), 125.8 (11.1), 126.1 (10.2) C(3,6), 130.0, 130.2 (C-4,5).
[f] Other $\delta^{13}$C: 131.1, 131.2 (*o*), 127.8, 128.0 (*m*), 126.5, 126.6 (*p*).
[g] Coordinated ring; other $\delta^{13}$C: 129.1 [45.9] (C-2′,7′), 130.4 (9.0) (C-3′,6′).
[h] Non-coordinated rings; other $\delta^{13}$C: 112.9, 113.1 (C-2,7), 125.9 (10.9), 126.2 (10.8) (C-3,6), 130.3, 130.4 (C-4,5).
[i] Other $\delta^{13}$C: 67.4, 67.7, 70.8, 71.0 (C-2,5(Fc), C-3,4(Fc)), 69.6, 70.0 (Cp).
[j] Coordinated ring; other $\delta^{13}$C: 128.8 [46.7] (C-2′,7′), 130.5 (9.3) (C-3′,6′).
[k] Non-coordinated rings; other $\delta^{13}$C: 112.9, 113.9 (C-2,7), 126.2 (10.8), 126.6 (10.0) (C-3,6), 130.3, 130.4 (C-4,5).
[l] In *cis* position with respect to the phosphorus atom: $\delta^{29}Si = -21.6$; $^3J(^{195}Pt,^{29}Si) = 36.4$ Hz; $^4J(^{31}P,^{29}Si) = 1.4$ Hz; in *trans* position with respect to the phosphorus atom: $\delta^{29}Si = -23.1$; $^3J(^{195}Pt,^{29}Si) = 23.9$ Hz; $^4J(^{31}P,^{29}Si) = 3.5$ Hz.
[m] Coordinated ring; other $\delta^{13}$C: 129.1 [44.2] (C-2′,7′), 130.6 (9.7) (C-3′,6′).
[n] Non-coordinated rings; other $\delta^{13}$C: 112.2, 112.3 (C-2,7), 126.1 (9.2), 126.3 (8.9) (C-3,6), 130.2, 130.3 (C-4,5).

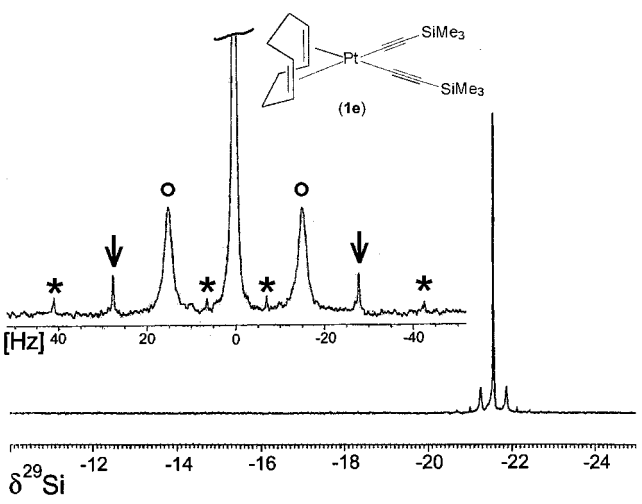



Fig. 2. $^{29}$Si-NMR (99.6 MHz) spectrum of **1e** (saturated solution in $CD_2Cl_2$, at $23 \pm 1$ °C), recorded by the refocused INEPT pulse sequence with $^1$H decoupling [24]. $^{195}$Pt (open circles) and $^{13}$C satellites (arrows and asterisks) are indicated. The broadening of the $^{195}$Pt satellite signals results from fast $^{195}$Pt nuclear spin relaxation owing to the chemical shift anisotropy mechanism.

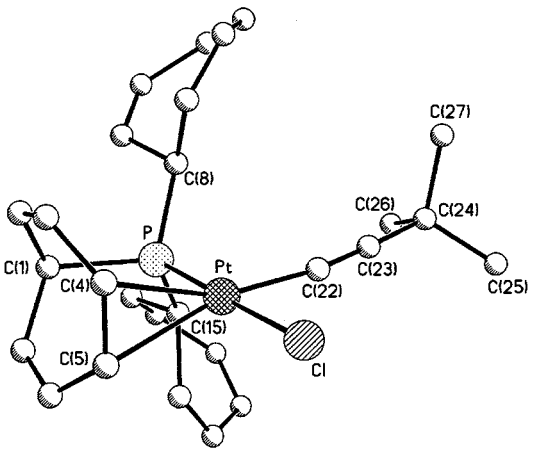



Fig. 3. Molecular structure of $[P(C_7H_7)_2(\eta^2\text{-}C_7H_7)]PtCl(C{\equiv}C\text{-}^tBu)$ (**2b**) cf. Table 4.

to lower frequencies of the $^{13}$C(Pt–C≡) and to higher frequencies of the $^{13}$C(≡C) resonances in **2**), in agreement with the expectation that the nature of the ligand in *trans* position will determine major changes. In both **1** and **2**, an $\eta^2$ C=C bond is coordinated to Pt in *trans* position to the alkynyl groups. The magnitude of $^2J(^{31}P,{=}^{13}C)$ in **2** is small, which confirms the *cis* position of the alkynyl group with respect to the phosphorus atom. In the cases of $^1J(^{195}Pt,^{13}C{\equiv})$, the magnitude in general is somewhat smaller in **1** than in **2**, although there is no agreement in the trends of $^1J(^{195}Pt,^{13}C{\equiv})$ as a function of R, except that the smallest value is always observed for R = $SiMe_3$ (this also holds for the alkynyl groups in *cis* position to phosphorus in the complexes **3**). The $^{13}$C-NMR parameters of the alkynyl groups in *trans* position to phosphorus are significantly different from those in *cis* position, as becomes apparent from the data in Tables 2 and 3. The $^{13}C(Pt–C{\equiv}_{trans})$ resonances move to much higher frequencies, and the $^{13}C(\equiv C_{trans})$ resonances are shifted significantly to lower frequencies. The magnitude of the coupling constants $^1J(^{195}Pt,^{13}C{\equiv}_{trans})$ of **3** is reduced by $\approx 25\%$ with respect to that of $^1J(^{195}Pt,^{13}C{\equiv}_{cis})$, which also indicates the different effects exerted by the phosphane and the C=C bond in *trans* positions to the alkynyl group. The influence of the phosphane ligand on the $^{13}$C-NMR parameters observed here corresponds closely to the effects measured previously for $(dppe)Pt(C{\equiv}C\text{–}R)_2$, $(dppm)Pt(C{\equiv}C\text{–}R)_2$ and $(depe)Pt(C{\equiv}C\text{–}R)_2$ [4,5,14a]. A more detailed discussion of the $^{13}$C-NMR parameters in context with other data for organometallic-substituted alkynes (see Ref. [23] for a collection of data) will be presented elsewhere [24].

$^{29}$Si-NMR spectra of alkynyl(methyl)silanes can be recorded most efficiently [25] by applying the refocused INEPT pulse sequences with $^1$H decoupling [26], as shown in Fig. 2 for the determination of all coupling constants $J(^{29}Si,^{13}C)$ in **1e**. Changes in the electronic structure of the $C{\equiv}C\text{–}SiMe_3$ group are indicated by the shift of the $^{29}$Si-NMR signals of **1e**–**3e** to lower frequencies ($\approx 3.5$ ppm for the $C{\equiv}C\text{–}SiMe_3$ groups in *cis* and $\approx 5$ ppm for $C{\equiv}C\text{–}SiMe_3$ in *trans* position with respect to the phosphorus atom) relative to alkynyl(trimethyl)silanes without Pt–C≡bonds. The trend in the changes of the magnitude of $^3J(^{195}Pt,^{29}Si_{cis/trans})$ follows the $^{195}Pt-^{13}C$ couplings: in **3e** the *trans* position of the $C{\equiv}C\text{–}SiMe_3$ with respect to phosphorus causes a decrease in the magnitude of $^3J(^{195}Pt,^{29}Si)$ (23.9 Hz) of 34% when compared with the value 36.4 Hz for the $C{\equiv}C\text{–}SiMe_3$ group in *trans* position to the C=C bond. The magnitude of $^1J(^{29}Si,^{13}C{\equiv})$ in **1e** (83.9 Hz) has increased slightly with respect to $Me_3Si\text{–}C{\equiv}C\text{–}Me$ (80.9 Hz [26]) and markedly with respect to $Me_3Si\text{–}C{\equiv}C\text{–}SiMe_3$ (76.5 Hz [24]), whereas the magnitude of $^2J(^{29}Si,{=}^{13}C)$ in **1e** (13.4 Hz) is smaller than that in $Me_3Si\text{–}C{\equiv}C\text{–}Me$ (15.6 Hz [26]) and similar to that in $Me_3Si\text{–}C{\equiv}C\text{–}SiMe_3$ (12.6 Hz [23]). For a meaningful discussion of these parameters and of isotope-induced chemical shifts $\Delta^{12/13}$ ($^{29}$Si) [26,27], there are still not enough data of this type available.

### 2.4. X-ray structure determinations of *2b* and *3d*

The molecular structures of two characteristic examples, $[P]PtCl(C{\equiv}C\text{–}^tBu)$ (**2b**) and $[P]Pt(C{\equiv}C\text{–}Fc)_2$ (**3d**), were determined by X-ray structure analysis (Figs. 3 and 4). Selected bond lengths and angles are collected in Tables 4 and 5. Both **2b** and **3d** are square-planar 16e complexes which contain a chelating $P(C_7H_7)_2(\eta^2\text{-}C_7H_7)$ ligand, coordinated through both the phosphorus atom and the central double bond of one cyclohepta-2,4,6-trienyl substituent. In the crystal lat-

tice the two pending $C_7H_7$ ligands have no connection with the Pt(II) atom to which the $P(C_7H_7)_3$ ligand is attached, in contrast to the situation in solution. The C=C bond axis of the $\eta^2$-coordinated double bond is arranged perpendicular to the coordination plane; the angle of the C(4)–C(5) vector relative to the best (coordination) plane is 88.6° in **2b** and 88.4° in **3d**. As expected, the bond length of this C=C bond (138.0(10) in **2b** and 140.3(10) in **3d**) is found between those of typical single (154 pm) and typical double (134 pm) bonds (Tables 4 and 5); it compares well with the bond distance of the $\eta^2$-coordinated C=C double bonds in (cod)$PtCl_2$ (137.5(8) and 138.7(8) pm [28]) or (cod)$PtBr(C_6H_2Me_3$-2,4,6) (142(3) *trans* to the bromo and 134(3) pm *trans* to the mesityl ligand [29]).

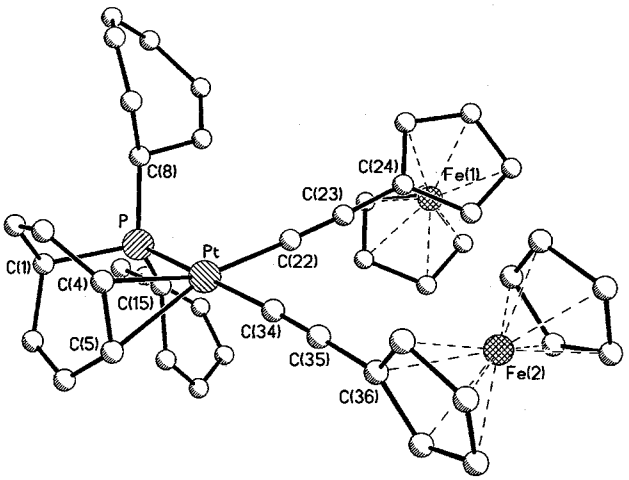



Fig. 4. Molecular structure of $[P(C_7H_7)_2(\eta^2\text{-}C_7H_7)]Pt(C{\equiv}C\text{–}Fc)_2$ (**3d**) cf. Table 5.

Table 4
Selected bond lengths (pm) and bond angles (°) for [P]PtCl(C≡C–$^t$Bu) (**2b**)

| | | | |
|---|---|---|---|
| *Bond lengths* | | | |
| Pt–P | 220.89(14) | Pt–Cl | 236.78(15) |
| Pt–C(4) | 225.7(6) | Pt–C(22) | 196.2(6) |
| Pt–C(5) | 226.2(6) | C(22)–C(23) | 120.3(9) |
| Pt–Z(C4,5) | 215.2 | C(23)–C(24) | 148.0(9) |
| C(1)–C(2) | 148.7(11) | P–C(1) | 185.6(7) |
| C(2)–C(3) | 134.2(11) | P–C(8) | 183.2(6) |
| C(3)–C(4) | 145.1(10) | P–C(15) | 182.2(6) |
| C(4)–C(5) | 138.0(10) | | |
| C(5)–C(6) | 145.0(9) | | |
| C(6)–C(7) | 131.4(11) | | |
| C(1)–C(7) | 149.4(11) | | |
| *Bond angles* | | | |
| C(4)–Pt–C(5) | 35.6(2) | Pt–C(22)–C(23) | 172.6(6) |
| P–Pt–Z(C4,5) | 93.1 | C(22)–C(23)–C(24) | 178.2(7) |
| P–Pt–C(22) | 85.72(18) | Pt–P–C(1) | 107.9(2) |
| P–Pt–Cl | 178.91(5) | Pt–P–C(8) | 114.9(2) |
| C(22)–Pt–Cl | 93.26(18) | Pt–P–C(15) | 115.3(2) |
| Cl–Pt–Z(C4,5) | 87.9 | C(1)–P–C(8) | 107.5(3) |
| C(22)–Pt–Z(C4,5) | 177.9 | C(8)–P–C(15) | 102.6(3) |
| | | C(1)–P–C(15) | 108.3(3) |
| *Dihedral angle* | | | |
| PPt(Z(C4,5)/C(22) | 1.8 | | |
| PtCl | | | |
| *Coordination plane* | | | |
| PtPZ(C4,5)C(22)Cl | $\overline{\Delta} = 1.2$ | | |

Z(C4,5) is the centre of the coordinated double bond C(4)–C(5). $\overline{\Delta}$ is the average deviation from the best (coordination) plane (pm).

The Pt–C distance *trans* to the coordinated double bond (i.e. *cis* to the phosphorus atom) in both **2b** (196.2(6) pm) and **3d** (195.0(8) pm) is observed in the normal range of 193–198 pm, expected for such compounds [15–17] (cf. (bipy)$Pt(C{\equiv}C\text{–}Ph)_2$ 195.9(5) and 196.2(4) pm [17b]). In the di(ferrocenylethynyl)platinum complex **3d**, the Pt–C bond length *trans* to phosphorus is significantly enlarged to 202.4(7) pm (vs. 195.0(8) pm *cis* to P), indicating a stronger *trans*-influence [30] of the phosphorus atom which is only slightly compensated by a shorter C≡C bond length (118.6(9) pm vs. 120.8(10) pm). This may be compared with the structures of the *cis* and *trans* isomers of $(Ph_3P)_2Pt(C{\equiv}C\text{–}^tBu)(\eta^1\text{-}C(Me){=}CH_2)$ [16b], where the Pt–C(alkinyl) bond is longer if the $\eta^1$-alkenyl group stands *trans* to the *tert*-butylethynyl ligand (204(1) pm) than in the *cis* arrangement (197(2) pm), indicating the stronger *trans*-influence of the $\eta^1$-alkenyl group. The strong *trans*-influence of organyl ligands may also be deduced from (cod)PtBr(1-mesityl) where the olefinic bond *trans* to mesityl is pushed back (Pt–C 228(2) and 231(2) pm) as compared with that *trans* to Br (Pt–C 213(2) pm) [29].

The Pt–P bond length (220.89(14) pm in **2b** and 227.21(18) pm in **3d**) is comparatively short (cf. various 1-alkynylplatinum complexes [15–17]), although it still reflects the higher *trans*-influence [30] of the 1-alkynyl as compared to the chloro ligand. In the case of **3d**, the short Pt–P bond appears to be accompanied by an elongated Pt–C(alkinyl) bond (202.4(7) pm) in the *trans* position. Different Pt–P bond lengths have also been observed in *cis*-$[(Ph_3P)_2Pt(\eta^1\text{-}C{\equiv}C^tBu)(\eta^1\text{-}C(Me){=}CH_2)]$ (228.6(4) pm *trans* to *tert*-butylethynyl, 234.0(4) pm *trans* to methylvinyl), whereas the Pt–P bond distances are equal (229.3(3) and 229.6(3) pm) in the *trans*-isomer [16b]).

The C≡C alkynyl bond vectors deviate slightly from the coordination plane (C(22)–C(23) in **2b** by 5.7°); in the case of the di(ferrocenylethynyl)platinum complex **3d** the angles of the vectors C(22)–C(23) (6.2°) and C(34)–C(35) (6.8°) are similar, but the ferrocenyl-substituted C≡C triple bonds protrude from the coordination plane into different directions, being arranged either above or below.

Considering the large amount of structural data which is available for ferrocene derivatives, it is inter-

Table 5
Selected bond lengths (pm) and bond angles (°) for [P]Pt(C≡C–Fc)$_2$ (**3d**)

| | | | |
|---|---|---|---|
| *Bond lengths* | | | |
| Pt–P | 227.21(18) | Pt–C(22) | 195.0(8) (*cis* to P) |
| Pt–C(4) | 226.5(8) | C(22)–C(23) | 120.8(10) |
| Pt–C(5) | 227.0(7) | C(23)–C(24) | 142.8(10) |
| Pt–Z(C4,5) | 215.6 | Pt–C(34) | 202.4(7) (*trans* to P) |
| | | C(34)–C(35) | 118.6(9) |
| C(1)–C(2) | 148.8(11) | C(35)–C(36) | 143.5(10) |
| C(2)–C(3) | 134.8(11) | | |
| C(3)–C(4) | 144.0(11) | | |
| C(4)–C(5) | 140.3(10) | | |
| C(5)–C(6) | 144.1(10) | P–C(1) | 186.0(7) |
| C(6)–C(7) | 132.4(11) | P–C(8) | 184.4(8) |
| C(1)–C(7) | 150.0(11) | P–C(15) | 183.4(7) |
| *Bond angles* | | | |
| C(4)–Pt–C(5) | 36.0(3) | Pt–C(22)–C(23) | 173.8(6) (*cis* to P) |
| P–Pt–Z(C4,5) | 91.6 | C(22)–C(23)–C(24) | 178.2(7) |
| P–Pt–C(22) | 92.2(2) | Pt–C(34)–C(35) | 174.1(7) (*trans* to P) |
| P–Pt–C(34) | 177.4(2) | C(34)–C(35)–C(36) | 178.9(8) |
| C(22)–Pt–C(34) | 86.2(3) | Pt–P–C(1) | 108.6(3) |
| C(22)–Pt–Z(C4,5) | 175.2 | Pt–P–C(8) | 118.4(2) |
| C(34)–Pt–Z(C4,5) | 90.1 | Pt–P–C(15) | 115.2(2) |
| | | C(1)–P–C(8) | 105.0(4) |
| | | C(8)–P–C(15) | 101.0(4) |
| | | C(1)–P–C(15) | 107.8(4) |
| *Dihedral angle* | | | |
| PPt(Z(C4,5)/C(22)PtC(34) | 3.7 | | |
| *Coordination plane* | | | |
| PtPZ(C4,5)C(22)C(34) | $\overline{\Delta} = 3.8$ | | |

Z(C4,5) is the centre of the coordinated double bond C(4)–C(5). $\overline{\Delta}$ is the average deviation from the best (coordination) plane (pm).

esting to note that the cyclopentadienyl rings of the ferrocenyl substituents in [P]Pt(C≡C–Fc)$_2$ (**3d**) are almost exactly eclipsed — the deviation of the conformational angle $\tau$ from the ideal eclipsed arrangement ($\tau = 0°$) is only 1.9° at Fe(1) and 2.9° at Fe(2).

## 3. Conclusions

Complexes of platinum(II) bearing both π-bonded $\eta^2$-alkene ligands and σ-bonded $\eta^1$-alkynyl ligands are readily available, stable, and easy to characterise by multinuclear magnetic resonance in solution, and by X-ray structural analysis in the solid state. The 1-alkynyltin compounds are attractive alkynyl transfer reagents, although any prediction about the product distribution is speculative. In the present cases, the highly selective transfer of only one alkynyl group is particularly noteworthy, opening the access to the complexes **2**, in which the alkynyl group takes the place solely in *trans*-position with respect to the $\eta^2$-coordinated C=C unit of the tri(1-cyclohepta-2,4,6-trienyl)phosphane ligand. According to the solution-state NMR parameters, the group R (Me, $^t$Bu, Ph, Fc, SiMe$_3$) in C≡C–R have very little influence on the electronic structure of all complexes **1**–**3**, whereas the electronic structure of the alkynyl groups appears to be markedly influenced by the nature of the ligand in *trans*-position. This could be demonstrated here for the first time by NMR parameters for alkynyl groups in the series of the complexes **1**–**3**, in comparison with data reported for corresponding bis(phosphane)platinum(II) complexes [3–5].

## 4. Experimental

### 4.1. General and starting materials

Preparation and handling of all compounds were carried out in an atmosphere of dry Ar, and carefully dried solvents were used throughout. Starting materials were prepared according to literature procedures, e.g. (cod)PtCl$_2$ [31], [P]PtCl$_2$ [32], Me$_2$Sn(C≡C–R)$_2$ [33], CpFe(C$_5$H$_4$–C≡CH) [34], or were used as commercial products without further purification, e.g. Me–C≡CH, $^t$Bu–C≡CH, Ph–C≡CH, Me$_3$Si–C≡CH and $^n$BuLi (1.6 M in hexane).

NMR spectroscopy: Bruker ARX 250 or DRX 500 ($^1$H-, $^{13}$C-, $^{29}$Si-, $^{31}$P-, $^{195}$Pt-NMR); direct single pulse measurements, or in the case of some $^{13}$C- and $^{29}$Si-NMR spectra by using the refocused INEPT pulse sequence with $^1$H decoupling [25], based on $^nJ(^{13}C,^1H) \approx 3–5$ Hz, and $^2J(^{29}Si,^1H) \approx 7$ Hz. Chemical

shifts are given with respect to $Me_4Si$ [$\delta^1H$ ($CD(H)Cl_2$) = 5.33; $\delta^{13}C$ ($CD_2Cl_2$) = 50.3; $\delta^{29}Si = 0$ for $\Xi(^{29}Si) = 19.867184$ MHz]; external aqueous $H_3PO_4$ (85%) with $\delta^{31}P = 0$ for $\Xi(^{31}P) = 40.480747$ MHz, and $\delta^{195}Pt = 0$ for $\Xi(^{195}Pt) = 21.400000$ MHz. IR spectra: Perkin–Elmer, Spectrum 2000 FTIR. EIMS: Finnigan MAT 8500 (ionisation energy 70 eV).

### 4.2. General procedures for the synthesis of complexes (cod)Pt(C≡C–R)$_2$ (1)

#### 4.2.1. R = Me, $SiMe_3$ (1a and 1e)

Di(1-alkynyl)dimethyltin, $Me_2Sn(C{\equiv}C{-}R)_2$ (R = Me, $SiMe_3$), (0.6 mmol) was added to a suspension of (cod)$PtCl_2$ (0.187 g; 0.5 mmol) in THF (20 ml). The reaction mixture was stirred for 3 h at room temperature (r.t.), and became a clear brown solution. This solution was concentrated under vacuum to 5 ml, before hexane (40 ml) was added. A pale brown precipitate was formed which was separated and washed several times with small portions of hexane. Recrystallisation from $CH_2Cl_2$–hexane and drying under a high vacuum gave colourless or pale yellow powders.

*4.2.1.1. (cod)Pt(C≡C–Me)$_2$ (1a).* M.p. (dec.) 156 °C. Yield 166 mg (87%), $C_{14}H_{18}Pt$. $^1$H-NMR ($CD_2Cl_2$, 23 °C): $\delta = 1.98$ (s, 6H, $^4J(^{195}Pt,^1H) = 17.6$ Hz, $H^{Me}$), 2.42 (m, 8H, $H^{CH_2}$), 5.43 (s, 4H, $^2J(^{195}Pt,^1H) = 47.3$ Hz, $H^{CH}$). IR (CsI, cm$^{-1}$): $\nu$(C≡C) 2052. EIMS; *m/e* (%): 381 (100) [$M^+$], 366 (4) [$M^+ - Me$], 350 (8) [$M^+ - 2Me$], 303 (41) [(cod)$Pt^+$], 272 (59) [$M^+ - cod$].

*4.2.1.2. (cod)Pt(C≡C–SiMe$_3$)$_2$ (1e).* M.p. (dec.) 142 °C. Yield 206 mg (83%), $C_{18}H_{30}PtSi_2$. $^1$H-NMR ($CD_2Cl_2$, 23 °C): $\delta = 0.09$ (s, 18H, $^2J(^{29}Si,^1H) = 119.2$ Hz, $H^{Me}$), 2.46 (m, 8H, $H^{CH_2}$), 5.52 (s, 4H, $^2J(^{195}Pt,^1H) = 44.9$ Hz, $H^{CH}$). IR (CsI, cm$^{-1}$): $\nu$(C≡C) 2061. EIMS; *m/e* (%): 497 (100) [$M^+$], 482 (66) [$M^+ - Me$], 389 (13) [$M^+ - cod$], 375 (30) [$M^+ - cod - Me$], 303 (20) [(cod)$Pt^+$].

#### 4.2.2. R = $^t$Bu, Ph, Fc (1b–1d)

The respective terminal alkyne, HC≡C–R (R = $^t$Bu, Ph, Fc) (1.30 mmol) was added to a freshly prepared NaOEt solution (30 mg (1.30 mmol) Na and 5 ml EtOH), and this mixture was stirred for 20 min at r.t. Then it was cooled to 0 °C and slowly transferred to a suspension of (cod)$PtCl_2$ (243 mg; 0.65 mmol) in EtOH (20 ml), and the reaction mixture was stirred several hours at r.t. The solvent was removed in vacuo and the residue extracted with $CH_2Cl_2$. The combined extracts were reduced in vacuo to 3 ml, then 50 ml of hexane was added. The precipitate was filtered off and washed with small portions of hexane. Recrystallisation from $CH_2Cl_2$–hexane and drying under a high vacuum gave a white (**1b**), yellow (**1c**) or orange (**1d**) powder.

*4.2.2.1. (cod)Pt(C≡C–$^t$Bu)$_2$ (1b).* Reaction time 2 h. M.p. (dec.) 133 °C. Yield 224 mg (74%), $C_{20}H_{30}Pt$. $^1$H-NMR ($CD_2Cl_2$, 23 °C): $\delta = 1.17$ (s, 18H, $H^{tBu}$), 2.41 (m, 8H, $H^{CH_2}$), 5.40 (s, 4H, $^2J(^{195}Pt,^1H) = 45.4$ Hz, $H^{CH}$). IR (CsI, cm$^{-1}$): $\nu$(C≡C) 2031. EIMS; *m/e* (%): 465 (100) [$M^+$], 450 (8) [$M^+ - Me$], 408 (10) [$M^+ - {}^t$Bu], 357 (12) [$M^+ - cod$], 342 (16) [$M^+ - cod - Me$], 303 (34) [(cod)$Pt^+$].

*4.2.2.2. (cod)Pt(C≡C–Ph)$_2$ (1c).* Reaction time 1 h. M.p. (dec.) 180 °C. Yield 299 mg (91%), $C_{24}H_{22}Pt$. $^1$H-NMR ($CD_2Cl_2$, 23 °C): $\delta = 2.55$ (m, 8H, $H^{CH_2}$), 5.68 (s, 4H, $^2J(^{195}Pt,^1H) = 43.9$ Hz, $H^{CH}$), 7.10–7.24 (m, 6H, $H^{p,m}$), 7.37 (m, 4H, H°). IR (CsI, cm$^{-1}$): $\nu$(C≡C) 2125. EIMS; *m/e* (%): 505 (1) [$M^+$], 397 (1) [$M^+ - cod$], 303 (1) [(cod)$Pt^+$], 204 (88) [$PhC_4Ph^+$], 78 (83) [$C_6H_6^+$], 65 (99) [$C_5H_5^+$], 54 (100) [$C_4H_6^+$].

*4.2.2.3. (cod)Pt(C≡C–Fc)$_2$ (1d).* Reaction time 1.5 h. M.p. (dec.) 158 °C. Yield 380 mg (81%), $C_{32}H_{30}Fe_2Pt$. $^1$H-NMR ($CD_2Cl_2$, 23 °C): $\delta = 2.52$ (m, 8H, $H^{CH_2}$), 4.05 (vt, 4H, $H^{3,4(Fc)}$), 4.18 (s, 10H, $H^{Cp}$), 4.34 (vt, 4H, $H^{2,5(Fc)}$), 5.59 (s, 4H, $^2J(^{195}Pt,^1H) = 45.0$ Hz, $H^{CH}$). IR (CsI, cm$^{-1}$): $\nu$(C≡C) 2139. EIMS; *m/e* (%): 488 (1) [$M^+ - C_2Fc$], 418 (22) [$FcC_4Fc^+$], 186 (8) [$FcH^+$], 78 (100) [$C_6H_6^+$].

### 4.3. General procedure for the synthesis of the complexes [P]PtCl(C≡C–R) (2)

The complex {$P(C_7H_7)_2(\eta^2$-$C_7H_7)$}$PtCl_2$ (114 mg; 0.20 mmol) was suspended in THF (15 ml), then $Me_2Sn(C{\equiv}C{-}R)_2$ (R = Me, $^t$Bu, Ph, Fc, $SiMe_3$) (0.12 mmol) was added, and the mixture was heated under reflux for 45 min. During this time a clear yellow solution was formed. The volume of the solution was reduced under vacuum to 3 ml, and hexane (50 ml) was added. The precipitate was separated, recrystallised from $CH_2Cl_2$–hexane, and dried in a high vacuum to give the products as yellow (**2a**–**c** and **e**) or orange (**2d**) powders.

#### 4.3.1. {$P(C_7H_7)_2(\eta^2$-$C_7H_7)$}PtCl(C≡C–Me) (2a)

M.p. (dec.) 176 °C. Yield 97 mg (86%), $C_{24}H_{24}ClPPt$. $^1$H-NMR ($CD_2Cl_2$, −20 °C): $\delta = 1.83$ (s, 3H, $^4J(^{195}Pt,^1H) = 18.2$ Hz, $H^{Me}$), 2.45 (dt, 2H, $^2J(^{31}P,^1H) = 10.0$ Hz, $^3J(^1H,^1H) = 6.5$ Hz, $H^1$), 4.59 (dt, 1H, $^2J(^{31}P,^1H) = 11.7$ Hz, $^3J(^1H,^1H) = 9.1$ Hz, $H^{1'}$), 5.20 (m, 2H, $H^{2,7}$), 5.26 (m, 2H, $H^{2,7}$), 5.70 (m, 2H, $H^{2',7'}$), 5.92 (m, 2H, $^2J(^{195}Pt,^1H) = 37.5$ Hz, $H^{4',5'}$), 6.29 (m, 4H, $H^{3,6}$), 6.49 (m, 2H, $H^{3',6'}$), 6.61 (m, 4H, $H^{4,5}$). IR (CsI, cm$^{-1}$): $\nu$(C≡C) 2149. EIMS; *m/e* (%): 574 (1) [$M^+$], 537 (2) [$P(C_7H_7)_3Pt(C{\equiv}CMe)^+$], 481 (1) [$P(C_7H_7)_2Pt(C{\equiv}CMe)Cl^+$], 446 (2) [$P(C_7H_7)_2Pt$-$(C{\equiv}CMe)^+$], 304 (3) [$P(C_7H_7)_3^+$], 91 (100) [$C_7H_7^+$], 78 (34) [$C_6H_6^+$].

#### 4.3.2. {P(C$_7$H$_7$)$_2$(η$^2$-C$_7$H$_7$)}PtCl(C≡C–$^t$Bu) (2b)

M.p. (dec.) 195 °C. Yield 97 mg (79%), $C_{27}H_{30}ClPPt$. $^1$H-NMR ($CD_2Cl_2$, −20 °C): δ = 1.01 (s, 9H, H$^{tBu}$), 2.41 (dt, 2H, $^2J(^{31}P,^1H) = 10.1$ Hz, $^3J(^1H,^1H) = 6.5$ Hz, H$^1$), 4.69 (dt, 1H, $^2J(^{31}P,^1H) = 12.0$ Hz, $^3J(^1H,^1H) = 8.6$ Hz, H$^{1'}$), 5.18 (m, 2H, H$^{2,7}$), 5.38 (m, 2H, H$^{2,7}$), 5.73 (m, 2H, H$^{2',7'}$), 5.94 (m, 2H, $^2J(^{195}Pt,^1H) = 36.9$ Hz, H$^{4',5'}$), 6.30 (m, 4H, H$^{3,6}$), 6.51 (m, 2H, H$^{3',6'}$), 6.63 (m, 4H, H$^{4,5}$). IR (CsI, cm$^{-1}$): ν(C≡C) 2127. EIMS; m/e (%): 616 (7) [M$^+$], 579 (8) [P(C$_7$H$_7$)$_3$Pt(C≡C$^t$Bu)$^+$], 534 (5) [P(C$_7$H$_7$)$_3$PtCl$^+$], 525 (5) [P(C$_7$H$_7$)$_2$Pt(C≡C$^t$Bu)Cl$^+$], 499 (5) [P(C$_7$H$_7$)$_3$Pt$^+$], 488 (10) [P(C$_7$H$_7$)$_2$Pt(C≡C$^t$Bu)$^+$], 443 (3), [P(C$_7$H$_7$)$_2$PtCl$^+$], 408 (5) [P(C$_7$H$_7$)$_2$Pt$^+$], 317 (5) [P(C$_7$H$_7$)Pt$^+$], 304 (2) [P(C$_7$H$_7$)$_3^+$], 91 (100) [C$_7$H$_7^+$].

#### 4.3.3. {P(C$_7$H$_7$)$_2$(η$^2$-C$_7$H$_7$)}PtCl(C≡C–Ph) (2c)

M.p. (dec.) 181 °C. Yield 114 mg (90%), $C_{29}H_{26}ClPPt$. $^1$H-NMR ($CD_2Cl_2$, −20 °C): δ = 2.49 (dt, 2H, $^2J(^{31}P,^1H) = 10.1$ Hz, $^3J(^1H,^1H) = 6.6$ Hz, H$^1$), 4.74 (dt, 1H, $^2J(^{31}P,^1H) = 11.7$ Hz, $^3J(^1H,^1H) = 8.9$ Hz, H$^{1'}$), 5.25 (m, 2H, H$^{2,7}$), 5.35 (m, 2H, H$^{2,7}$), 5.76 (m, 2H, H$^{2',7'}$), 6.08 (m, 2H, $^2J(^{195}Pt,^1H) = 37.4$ Hz, H$^{4',5'}$), 6.29 (m, 4H, H$^{3,6}$), 6.58 (m, 2H, H$^{3',6'}$), 6.62 (m, 4H, H$^{4,5}$), 7.10–7.20 (m, 5H, Ph). IR (CsI, cm$^{-1}$): ν(C≡C) 2128. EIMS; m/e (%): 636 (71) [M$^+$], 454 (1) [P(C$_7$H$_7$)Pt(C≡CPh)Cl$^+$], 304 (1) [P(C$_7$H$_7$)$_3^+$], 91 (66) [C$_7$H$_7^+$], 78 (100) [C$_6$H$_6^+$].

#### 4.3.4. {P(C$_7$H$_7$)$_2$(η$^2$-C$_7$H$_7$)}PtCl(C≡C–Fc) (2d)

M.p. (dec.) 173 °C. Yield 130 mg (92%), $C_{33}H_{30}FePPt$. $^1$H-NMR ($CD_2Cl_2$, −20 °C): δ = 2.50 (dt, 2H, $^2J(^{31}P,^1H) = 10.2$ Hz, $^3J(^1H,^1H) = 6.5$ Hz, H$^1$), 4.05 (s, 5H, H$^{Cp}$), 4.07 (m, 2H) and 4.14 (m, 2H) (H$^{Fc}$), 4.68 (dt, 1H, $^2J(^{31}P,^1H) = 11.9$ Hz, $^3J(^1H,^1H) = 8.8$ Hz, H$^{1'}$), 5.27 (m, 2H, H$^{2,7}$), 5.42 (m, 2H, H$^{2,7}$), 5.73 (m, 2H, H$^{2',7'}$), 6.00 (m, 2H, $^2J(^{195}Pt,^1H) = 36.6$ Hz, H$^{4',5'}$), 6.29 (m, 4H, H$^{3,6}$), 6.58 (m, 2H, H$^{3',6'}$), 6.67 (m, 4H, H$^{4,5}$). IR (CsI, cm$^{-1}$): ν(C≡C) 2118. EIMS; m/e (%): 418 (38) [FcC$_4$Fc$^+$], 186 (9) [Fc$^+$], 91 (100) [C$_7$H$_7^+$], 78 (70) [C$_6$H$_6^+$].

#### 4.3.5. {P(C$_7$H$_7$)$_2$(η$^2$-C$_7$H$_7$)}PtCl(C≡C–SiMe$_3$) (2e)

Reaction time 60 min. M.p. (dec.) 202 °C. Yield 91 mg (72%), $C_{26}H_{30}ClPPtSi$. $^1$H-NMR ($CD_2Cl_2$, −20 °C): δ = −0.03 (s, 9H, $^2J(^{29}Si,^1H) = 119.5$ Hz, $^5J(^{195}Pt,^1H) = 6.9$ Hz, H$^{Me}$), 2.45 (dt, 2H, $^2J(^{31}P,^1H) = 10.2$ Hz, $^3J(^1H,^1H) = 6.4$ Hz, H$^1$), 4.68 (dt, 1H, $^2J(^{31}P,^1H) = 11.8$ Hz, $^3J(^1H,^1H) = 8.6$ Hz, H$^{1'}$), 5.17 (m, 2H, H$^{2,7}$), 5.39 (m, 2H, H$^{2,7}$), 5.73 (m, 2H, H$^{2',7'}$), 6.06 (m, 2H, $^2J(^{195}Pt,^1H) = 36.3$ Hz, H$^{4',5'}$), 6.30 (m, 4H, H$^{3,6}$), 6.54 (m, 2H, H$^{3',6'}$), 6.65 (m, 4H, H$^{4,5}$). IR (CsI, cm$^{-1}$): ν(C≡C) 2062. EIMS; m/e (%): 631 (2) [M$^+$], 616 (2) [P(C$_7$H$_7$)$_3$Pt(C≡CSiMe$_2$)Cl$^+$], 595 (4) [P(C$_7$H$_7$)$_3$-Pt(C≡CSiMe$_3$)$^+$], 504 (5) [P(C$_7$H$_7$)$_2$Pt(C≡CSiMe$_3$)$^+$], 408 (2) [P(C$_7$H$_7$)$_2$Pt$^+$], 317 (2) [P(C$_7$H$_7$)Pt$^+$], 304 (2) [P(C$_7$H$_7$)$_3^+$], 91 (100) [C$_7$H$_7^+$].

### 4.4. General procedure for the synthesis of the complexes [P]Pt(C≡C–R)$_2$ (3)

The phosphane P(C$_7$H$_7$)$_3$ (65 mg; 0.21 mmol), dissolved in $CH_2Cl_2$ (10 ml), was added dropwise to a solution of (cod)Pt(C≡C–R)$_2$ (**1a**–**e**) (0.20 mmol) in $CH_2Cl_2$ (15 ml). The reaction mixture was stirred at r.t. and then brought to dryness in a high vacuum. The remaining solid was washed with hexane (50 ml). Recrystallisation from $CH_2Cl_2$–hexane and drying under high vacuum gave yellow (**3a**–**c** and **e**) or orange (**3d**) powders.

#### 4.4.1. {P(C$_7$H$_7$)$_2$(η$^2$-C$_7$H$_7$)}Pt(C≡C–Me)$_2$ (3a)

Reaction time 15 min. M.p. (dec.) 139 °C. Yield 95 mg (82%), $C_{27}H_{27}PPt$. $^1$H-NMR ($CD_2Cl_2$, −40 °C): δ = 1.93 (d, 3H, $^4J(^{195}Pt,^1H) = 10.9$ Hz, $^5J(^{31}P,^1H) = 2.4$ Hz, H$^{trans\text{-}Me}$), 1.95 (d, 3H, $^4J(^{195}Pt,^1H) = 12.4$ Hz, $^5J(^{31}P,^1H) = 2.0$ Hz, H$^{cis\text{-}Me}$), 2.20 (dt, 2H, $^2J(^{31}P,^1H) = 11.2$ Hz, $^3J(^1H,^1H) = 6.7$ Hz, H$^1$), 4.53 (dt, 1H, $^2J(^{31}P,^1H) = 13.2$ Hz, $^3J(^1H,^1H) = 8.0$ Hz, H$^{1'}$), 5.18 (m, 2H, H$^{2,7}$), 5.23 (m, 2H, H$^{2,7}$), 5.51 (m, 2H, H$^{2',7'}$), 5.63 (m, 4H, H$^{3,6}$), 6.05 (m, 2H, $^2J(^{195}Pt,^1H) = 37.5$ Hz, H$^{4',5'}$), 6.24 (m, 4H, H$^{4,5}$), 6.37 (m, 2H, H$^{3',6'}$). IR (CsI, cm$^{-1}$): ν(C≡C) 2149.

#### 4.4.2. {P(C$_7$H$_7$)$_2$(η$^2$-C$_7$H$_7$)}Pt(C≡C–$^t$Bu)$_2$ (3b)

Reaction time 30 min. M.p. (dec.) 149 °C. Yield 122 mg (92%), $C_{33}H_{39}PPt$. $^1$H-NMR ($CD_2Cl_2$, −40 °C): δ = 1.01/1.19 (s/s, 9H/9H, H$^{cis/trans\text{-}^t Bu}$), 2.17 (dt, 2H, $^2J(^{31}P,^1H) = 8.3$ Hz, $^3J(^1H,^1H) = 6.9$ Hz, H$^1$), 4.62 (dt, 1H, $^2J(^{31}P,^1H) = 12.6$ Hz, $^3J(^1H,^1H) = 8.8$ Hz, H$^{1'}$), 5.13 (m, 2H, H$^{2,7}$), 5.33 (m, 2H, H$^{2,7}$), 5.66 (m, 2H, H$^{2',7'}$), 6.03 (m, 2H, $^2J(^{195}Pt,^1H) = 39.8$ Hz, H$^{4',5'}$), 6.25 (m, 4H, H$^{3,6}$), 6.40 (m, 2H, H$^{3',6'}$), 6.60 (m, 4H, H$^{4,5}$). IR (CsI, cm$^{-1}$): ν(C≡C) 2114. EIMS; m/e (%): 661 (9) [M$^+$], 580 (61) [P(C$_7$H$_7$)$_3$Pt(C≡C$^t$Bu)$^+$], 570 (14) [P(C$_7$H$_7$)$_2$Pt(C≡C$^t$Bu)$_2^+$], 499 (68) [P(C$_7$H$_7$)$_3$Pt$^+$], 408 (2) [P(C$_7$H$_7$)$_2$Pt$^+$], 304 (1) [P(C$_7$H$_7$)$_3^+$], 91 (100) [C$_7$H$_7^+$].

#### 4.4.3. {P(C$_7$H$_7$)$_2$(η$^2$-C$_7$H$_7$)}Pt(C≡C–Ph)$_2$ (3c)

Reaction time 90 min. M.p. (dec.) 147 °C. Yield 132 mg (94%), $C_{37}H_{31}PPt$. $^1$H-NMR ($CD_2Cl_2$, −40 °C): δ = 2.31 (dt, 2H, $^2J(^{31}P,^1H) = 9.9$ Hz, $^3J(^1H,^1H) = 6.6$ Hz, H$^1$), 4.74 (dt, 1H, $^2J(^{31}P,^1H) = 10.2$ Hz, $^3J(^1H,^1H) = 7.8$ Hz, H$^{1'}$), 5.25 (m, 2H, H$^{2,7}$), 5.34 (m, 2H, H$^{2,7}$), 5.73 (m, 2H, H$^{2',7'}$), 6.08 (m, 2H, $^2J(^{195}Pt,^1H) = 41.4$ Hz, H$^{4',5'}$), 6.29 (m, 4H, H$^{3,6}$), 6.52 (m, 2H, H$^{3',6'}$), 6.61 (m, 4H, H$^{4,5}$), 7.14–7.42 (m, 10H, Ph$^{cis/trans}$). IR (CsI, cm$^{-1}$): ν(C≡C) 2117. EIMS; m/e (%): 601 (2) [P(C$_7$H$_7$)$_3$Pt(C≡CPh)$^+$], 499 (1) [P(C$_7$H$_7$)$_3$Pt$^+$], 408 (1) [P(C$_7$H$_7$)$_2$Pt$^+$], 91 (100) [C$_7$H$_7^+$], 78 (40) [C$_6$H$_6^+$].

#### 4.4.4. $\{P(C_7H_7)_2(\eta^2\text{-}C_7H_7)\}Pt(C{\equiv}C\text{–}Fc)_2$ (3d)

Reaction time 90 min. M.p. (dec.) 132 °C. Yield 178 mg (96%), $C_{46}H_{39}Fe_2PPt$. $^1$H-NMR ($CD_2Cl_2$, −40 °C): $\delta = 2.30$ (dt, 2H, $^2J(^{31}P,^1H) = 9.2$ Hz, $^3J(^1H,^1H) = 6.8$ Hz, $H^1$), 4.05/4.23 (s/s, 5H/5H, $H^{Cp}$), 4.08/4.11 (m/m, 2H/2H) and 4.19/4.38 (m/m, 2H/2H) ($H^{Fc}$), 4.63 (dt, 1H, $^2J(^{31}P,^1H) = 9.0$ Hz, $^3J(^1H,^1H) = 8.1$ Hz, $H^{1'}$), 5.34 (m, 2H, $H^{2,7}$), 5.43 (m, 2H, $H^{2,7}$), 5.69 (m, 2H, $H^{2',7'}$), 6.19 (m, 2H, $^2J(^{195}Pt,^1H) = 38.5$ Hz, $H^{4',5'}$), 6.32 (m, 4H, $H^{3,6}$), 6.46 (m, 2H, $H^{3',6'}$), 6.70 (m, 4H, $H^{4,5}$). IR (CsI, $cm^{-1}$): $\nu$(C≡C) 2130.

#### 4.4.5. $\{P(C_7H_7)_2(\eta^2\text{-}C_7H_7)\}Pt(C{\equiv}C\text{–}SiMe_3)_2$ (3e)

Reaction time 15 min. M.p. (dec.) 158 °C. Yield 125 mg (90%), $C_{31}H_{39}PPtSi_2$. $^1$H-NMR ($CD_2Cl_2$, −40 °C): $\delta = -0.03/0.05$ (s/s, 9H/9H, $H^{Me}$), 2.21 (dt, 2H, $^2J(^{31}P,^1H) = 9.3$ Hz, $^3J(^1H,^1H) = 6.1$ Hz, $H^1$), 4.67 (dt, 1H, $^2J(^{31}P,^1H) = 11.9$ Hz, $^3J(^1H,^1H) = 9.0$ Hz, $H^{1'}$), 5.12 (m, 2H, $H^{2,7}$), 5.31 (m, 2H, $H^{2,7}$), 5.68 (m, 2H, $H^{2',7'}$), 6.23 (m, 4H, $H^{3,6}$), 6.26 (m, 2H, $^2J(^{195}Pt,^1H) = 46.8$ Hz, $H^{4',5'}$), 6.47 (m, 2H, $H^{3',6'}$), 6.62 (m, 4H, $H^{4,5}$). IR (CsI, $cm^{-1}$): $\nu$(C≡C) 2058.

Table 6
Crystal data and structure refinement parameters for the complexes **2b** and **3d**

| | **2b** | **3d** |
|---|---|---|
| Empirical formula | $C_{27}H_{30}ClPPt$ | $C_{45}H_{39}PFe_2Pt\cdot(CH_3)_2CO$ |
| Crystal | Yellow prism | Dark red plate |
| Temperature (°C) | 23 | 23 |
| Crystal size (mm) | $0.20\times0.16\times0.12$ | $0.18\times0.14\times0.08$ |
| Crystal system | Triclinic | Monoclinic |
| Space group | $P\bar{1}$ | $P2_1/c$ |
| Unit cell parameters | | |
| $a$ (pm) | 901.92(1) | 1192.14(12) |
| $b$ (pm) | 1022.83(14) | 1376.08(13) |
| $c$ (pm) | 1390.66(13) | 2438.1(4) |
| $\alpha$ (°) | 84.296(10) | |
| $\beta$ (°) | 85.699(10) | 94.574(5) |
| $\gamma$ (°) | 78.302(12) | |
| $Z$ | 2 | 4 |
| Absorption coefficient, $\mu$ ($mm^{-1}$) | 5.804 | 4.290 |
| Diffractometer | Siemens P4 (Mo–$K_\alpha$, $\lambda = 71.073$ pm) graphite monochromator | |
| Measuring range ($\vartheta$) | 2–25 | 2–25 |
| Reflections collected | 5241 | 8739 |
| Independent reflections ($I>2\sigma(I)$) | 4350 | 6962 |
| Absorption correction | Empirical ($\Psi$-scans) | |
| Min./max. transmission | 0.2805/0.9672 | 0.3420/0.9584 |
| Refined parameters | 272 | 479 |
| $wR_2/R_1$ value ($I>2\sigma(I)$) | 0.083/0.035 | 0.104/0.040 |
| Max. and min. residual electron density ($e\,pm^{-3}\times10^{-6}$) | 1.29 and −1.70 | 1.55 and −0.80 |

### 4.5. X-ray structural analyses of complexes 2b and 3d

Single crystals of **2b** and **3b** were sealed in Lindemann capillaries. Relevant experimental details on the crystal structure analyses are given in Table 6.

The intensity data were collected on a Siemens P4 diffractometer with Mo–$K_\alpha$ radiation ($\lambda = 71.073$ pm, graphite monochromator) at r.t. The hydrogen atoms are in calculated positions. All non-hydrogen atoms were refined with anisotropic temperature factors. The hydrogen atoms were refined applying the riding model with fixed isotropic temperature factors.

## 5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 168419 and 168420 for **2b** and **3d**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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