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On the reactivity of platina-β-diketones: a straightforward synthesis of *trans*-acetylchlorobis-(phosphine)platinum(II) complexes and their reactivity

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The platina-β-diketone $[Pt_2\{(COMe)_2H\}_2(\mu\text{-}Cl)_2]$ (1) was found to react with monodentate phosphines to yield acetyl(chloro)platinum(II) complexes *trans*-$[Pt(COMe)Cl(PR_3)_2]$ (PR_3 = PPh_3, 2a; $P(4\text{-}FC_6H_4)_3$, 2b; $PMePh_2$, 2c; PMe_2Ph, 2d; $P(n\text{-}Bu)_3$, 2e; $P(o\text{-}tol)_3$, 2f; $P(m\text{-}tol)_3$, 2g; $P(p\text{-}tol)_3$, 2h). In the reaction with $P(o\text{-}tol)_3$ the methyl(carbonyl)platinum(II) complex $[Pt(Me)Cl(CO)\{P(o\text{-}tol)_3\}]$ (3a) was found to be an intermediate. On the other hand, treating 1 with $P(C_6F_5)_3$ led to the formation of $[Pt(Me)Cl(CO)\{P(C_6F_5)_3\}]$ (3b), even in excess of the phosphine. Phosphine ligands with a lower donor capability in complexes 2 and the arsine ligand in *trans*-$[Pt(COMe)Cl(AsPh_3)_2]$ (2i) proved to be subject to substitution by stronger donating phosphine ligands, thus forming complexes *trans*-$[Pt(COMe)Cl(L)L']$ (L/L′ = $AsPh_3/PPh_3$, 4a; $PPh_3/P(n\text{-}Bu)_3$, 4b) and *cis*-$[Pt(COMe)Cl(dppe)]$ (4c). Furthermore, in boiling benzene, complexes 2a–2c and 2i underwent decarbonylation yielding quantitatively methyl(chloro)platinum(II) complexes *trans*-$[Pt(Me)Cl(L)_2]$ (L = PPh_3, 5a; $P(4\text{-}FC_6H_4)_3$, 5b; $PMePh_2$, 5c; $AsPh_3$, 5d). The identities of all complexes were confirmed by ^1H, ^{13}C and ^{31}P NMR spectroscopy. Single-crystal X-ray diffraction analyses of $2a{\cdot}2CHCl_3$, 2f and 5b showed that the platinum atom is square-planar coordinated by two phosphine ligands (PPh_3, 2a; $P(o\text{-}tol)_3$, 2f; $P(4F\text{-}C_6H_4)_3$, 5b) in mutual *trans* position as well as by an acetyl ligand (2a, 2f) and a methyl ligand (5b), respectively, *trans* to a chloro ligand. Single-crystal X-ray diffraction analysis of 3b exhibited a square-planar platinum complex with the two π-acceptor ligands CO and $P(C_6F_5)_3$ in mutual *cis* position (configuration index: *SP*-4-3). **Copyright © 2005 John Wiley & Sons, Ltd.**

KEYWORDS: acyl complexes; platina-β-diketones; decarbonylation; X-ray diffraction analysis

INTRODUCTION

Since the synthesis and characterization of the first acyl complexes of a transition metal, $[Mn(COR)(CO)_5]$ (R = Me, Ph), in 1957[1] a plethora of acyl complexes has been prepared. The most widely used methods of preparation are the oxidative addition reactions of acyl halides to metal complexes in lower oxidation states (Scheme 1a), the acylations of metallate complexes, which can be regarded in a broader sense also as oxidative addition reactions (Scheme 1b), and migratory insertion reactions of carbon monoxide, which are induced by ligand L in many cases (Scheme 1c). To synthesize acyl platinum(II) complexes with phosphines as ancillary ligands via oxidative addition, phosphine platinum(0) complexes such as $[Pt(PR_3)_4]$ and $[Pt(PPh_3)_2(\eta^2\text{-}C_2H_4)]$ were mainly used as starting materials.[2] In the majority of cases the carbonylation of *trans*-$[Pt(R)X(PR'_3)_2]$ according to Scheme 1c requires a higher pressure of CO. Furthermore, dinuclear complexes $[\{Pt(R)(\mu\text{-}Cl)(CO)\}_2]$ were found to react with phosphines to yield acyl complexes.[3] Apart from the latter method, the appropriate starting phosphine complexes have to be prepared prior the synthesis of

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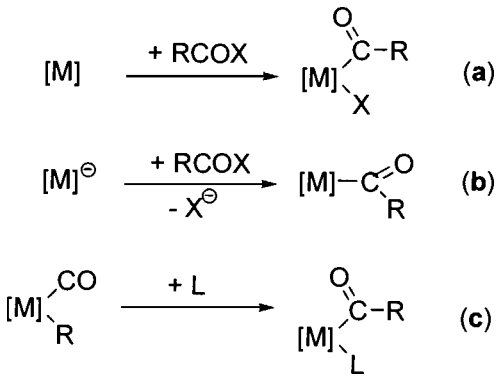
the acyl complexes. This may be laborious when a greater variety of phosphine ligands is necessary. Here we report on reactions of the dinuclear platina-β-diketone $[Pt_2\{(COMe)_2H\}_2(\mu\text{-}Cl)_2]$ (**1**)[4] with phosphines as a useful alternative to synthesize acetyl platinum complexes of the type *trans*-$[Pt(COMe)Cl(PR_3)_2]$ (**2**) with a wide variety of phosphine ligands. Furthermore, substitution reactions of the phosphine ligands and decarbonylation of type **2** complexes are described.

RESULTS AND DISCUSSION

Reactivity of platina-β-diketones towards monodentate *P*-donor ligands

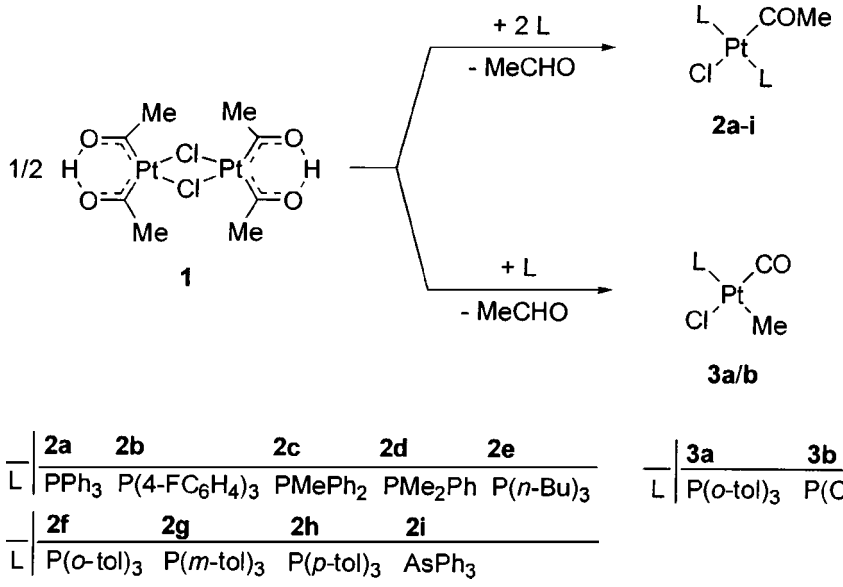
The platina-β-diketone **1** was found to react in methylene chloride with four equivalents of monodentate phosphines to yield acetyl(chloro)platinum(II) complexes **2a**–**2h**



Scheme 1. General methods of synthesis for acyl complexes (X = halide; square brackets symbolize the ligand sphere of M).

with cleavage of acetaldehyde (Scheme 2). The reactions proceeded with the alkylphosphine $P(n\text{-}Bu)_3$, arylphosphines [PPh_3, $P(o\text{-tol})_3$, $P(m\text{-tol})_3$, $P(p\text{-tol})_3$, $P(4\text{-}FC_6H_4)_3$] and alkylarylphosphines ($PMePh_2$, PMe_2Ph) at −20 °C within 2 h. These reactions proceeded via unseen intermediate acetyl(hydrido)platinum(IV) complexes $[Pt(COMe)_2Cl(H)(PR_3)_2]$ followed by reductive elimination of acetaldehyde.[5] As described in Ref. 5, triphenylarsine reacted in the same way to yield **2i**.

In the reaction of **1** with four equivalents of $P(o\text{-tol})_3$, the methyl carbonyl complex $[Pt(Me)Cl(CO)\{P(o\text{-tol})_3\}]$ (**3a**) was found to be an intermediate. As shown by ^{31}P NMR spectroscopy, after 5 min at room temperature the platina-β-diketone **1** was converted quantitatively into **3a** whereas after 30 min about 80% of the acetyl(chloro)platinum(II) complex **2f** was formed. Performing this reaction with a molecular ratio of $[\mathbf{1}]:[P(o\text{-tol})_3] = 1:2$, **3a** is the final product. In contrast to this, the analogous reaction of **1** with tris(perfluorophenyl)phosphine resulted in the formation of the methyl(carbonyl)platinum(II) complex $[Pt(Me)Cl(CO)\{P(C_6F_5)_3\}]$ (**3b**), even when **1** was reacted with four equivalents $P(C_6F_5)_3$ (Scheme 2). This different reactivity may be the consequence of the low donor capability of the perfluorinated triphenylphosphine (Tolman's electronic parameter is 2090.9 cm^{-1}; in comparison, for PPh_3 it is 2068.9 cm^{-1}).[6] Complexes **2** were obtained after chromatographic purification and reprecipitation from chloroform–*n*-pentane as colourless, air-stable crystals in good yields (42–85%). Complexes **3** were purified by dissolving in diethyl ether or methylene chloride and reprecipitation with *n*-pentane in 41% (**3a**) and 92% (**3b**) yield, respectively. The identities of these complexes were confirmed by ^1H, ^{13}C and ^{31}P NMR spectroscopy and for **2a, 2f** and **3b** also by single-crystal X-ray diffraction analysis.



Scheme 2.

Table 1. Selected NMR data (δ in ppm, J in Hz) for acetyl(chloro)platinum(II) complexes *trans*-[Pt(COMe)Cl(L)$_2$] (**2a**–**2i**)

L	$COCH_3$ $\delta(^1H)$ [^3J(Pt,H)]	$COCH_3$ $\delta(^{13}C)$ [^3J(P,C)]	$\delta(^{31}P)$	$^1J(^{195}Pt,^{31}P)$
PPh_3 (**2a**)[a]	1.17 [13.28]	44.2 [6.0]	21.3	3470
P(4-$FC_6H_4)_3$ (**2b**)[a]	1.23 [13.20]	44.4 [6.4]	19.1	3497
$PMePh_2$ (**2c**)	1.17 [13.23]	44.1 [5.6]	6.9	3322
PMe_2Ph (**2d**)	1.64 [14.06]	44.0 [5.9]	−5.7	3148
P(*n*-Bu)$_3$ (**2e**)[a]	2.14 [13.28]	47.1 [4.4]	8.6	3053
P(*o*-tol)$_3$ (**2f**)	[b]	39.0	16.9	3428
P(*m*-tol)$_3$ (**2g**)	1.19 [14.33]	43.9 [6.2]	22.1	3478
P(*p*-tol)$_3$ (**2h**)	1.17 [14.11]	44.0 [6.1]	19.9	3345
$AsPh_3$ (**2i**)[a]	1.32	45.8	—	—

[a] Own measurements; see also Ref. 5.
[b] Overlapped with *ortho*-tolyl group resonances.

Selected NMR spectroscopic data of the acetyl(chloro)-platinum complexes **2** are given in Table 1. The chemical equivalence of the phosphorus nuclei in **2a**–**2h** is evident from the singlet resonances in the ^{31}P NMR spectra as well as from the triplet pattern of the acetyl carbon resonances (^3J(P,C) = 4.4–6.4 Hz) in the ^{13}C NMR spectra. Thus, the *trans* configuration (configuration index: *SP*-4-3) of the complexes was proved unequivocally. The coordination-induced downfield shifts of the phosphorus resonances by 20–45 ppm and the values of the ^1J(Pt,P) coupling constants (3053–3497 Hz) are as expected.[7] The constitution of complexes **3** (configuration index: *SP*-4-3) follows not only from the single-crystal X-ray diffraction analysis of **3b** but also from the doublet pattern of the methyl carbon resonances (^2J(P,C) = 86.4/98.5 Hz, **3a**/**b**) and from the magnitude of the ^1J(Pt,P) coupling constants (1395/1073 Hz, **3a**/**b**), which are typically for a phosphorus *trans* to a methyl ligand.[8]

Complexes **2a, 2f** and **3b** crystallized from $CHCl_3$–*n*-pentane and CH_2Cl_2–*n*-pentane, respectively, as **2a**·2$CHCl_3$ and **3b** in well-shaped crystals that proved to be suitable for single-crystal X-ray diffraction analysis. The crystals of these complexes consist of discrete molecules without unusual intermolecular contacts. The asymmetric unit of **3b** contains two symmetry-independent molecules that are very similar in their structures. The molecular structures of the complexes **2a, 2f** and **3b** are shown in Figs 1–3; selected bond lengths and angles are given in the figure captions. In **2a** the coordination geometry about the platinum centre is in good approximation square-planar (sum of angles: 360.1°; angles between neighbouring ligands: 87.48(5)–92.8(2)°). In **2f** the deviations from the square-planar coordination are larger (sum of angles: 361.4°; angles between neighbouring ligands: 86.4(1)–92.86(3)°). The Pt–P bonds (2.308(1)/2.309(1) Å) in **2a** are in the typical range of those in other square-planar platinum(II) complexes having triarylphosphine ligands in mutual *trans* positions (median 2.308 Å; lower/upper quartile 2.297/2.321 Å; number of observations n = 414).[9] On the other hand, the relatively long Pt–P bonds (2.333(1)/2.3422(9) Å) in **2f** may be due to the bulkiness of the P(*o*-tol)$_3$ ligand (cf. cone angles: P(*o*-tol)$_3$ 194° versus PPh_3 145°).[6] In the two complexes the plane of the acetyl ligand is nearly perpendicular to the complex plane (interplanar angle: 89.2(6)°, **2a**; 86.1(4)°, **2f**). The platinum atom in **3b** is square-planar coordinated (sum of angles: 360.1°; angles between neighbouring ligands: 85.0(2)–101.1(2)°), having the two π-acceptor ligands (CO, P($C_6F_5)_3$) in mutual *cis* position (configuration index: *SP*-4-3) as expected because these ligands avoid sharing the same orbital.[10] In accordance with the high *trans*-influence of the methyl ligand,[11] the Pt–P bond (2.358(1)/2.369(1) Å) is longer

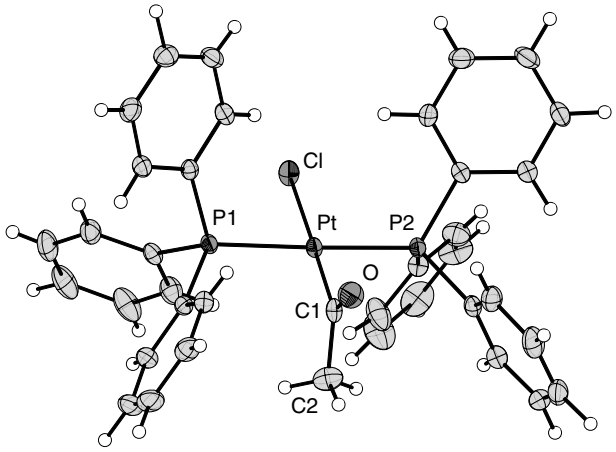


Figure 1. Molecular structure of *trans*-[Pt(COMe)Cl($PPh_3)_2$] in crystals of **2a**·2$CHCl_3$ showing the atom numbering (displacement ellipsoids at 30% probability). Selected bond lengths (in Å) and angles (in deg.): Pt–C1 2.010(5), Pt–Cl 2.442(1), Pt–P1 2.308(1), Pt–P2 2.309(1), C1–O 1.220(6), C1–C2 1.486(7); P1–Pt–C1 92.8(2), P1–Pt–Cl 87.48(5), P2–Pt–Cl 89.18(5), P2–Pt–C1 90.6(2), Cl–Pt–C1 178.6(1), O–C1–C2 120.0(5), P1–Pt–P2 176.64(4).

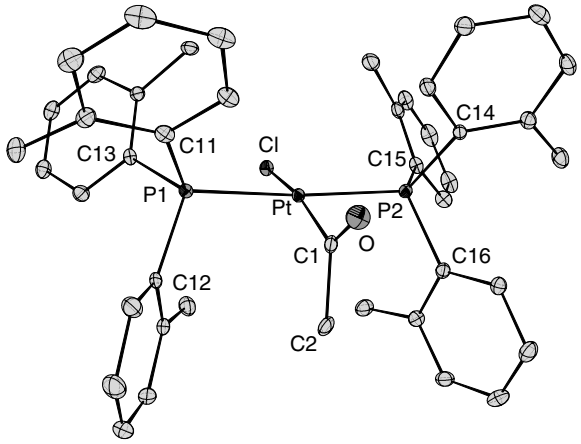


Figure 2. Molecular structure of *trans*-[Pt(COMe)Cl{P(*o*-tol)$_3$}$_2$] (**2f**) showing the atom numbering (displacement ellipsoids at 30% probability). Hydrogen atoms were omitted for clarity. Selected bond lengths (in Å) and angles (in deg.): Pt–C1 2.015(3), Pt–Cl 2.441(1), Pt–P1 2.3422(9), Pt–P2 2.333(1), C1–O 1.215(4), C1–C2 1.521(5); P1–Pt–C1 90.0(1), P1–Pt–Cl 92.10(3), P2–Pt–Cl 92.86(3), P2–Pt–C1 86.4(1), Cl–Pt–C1 168.0(1), O–C1–C2 118.2(3), P1–Pt–P2 172.37(3).

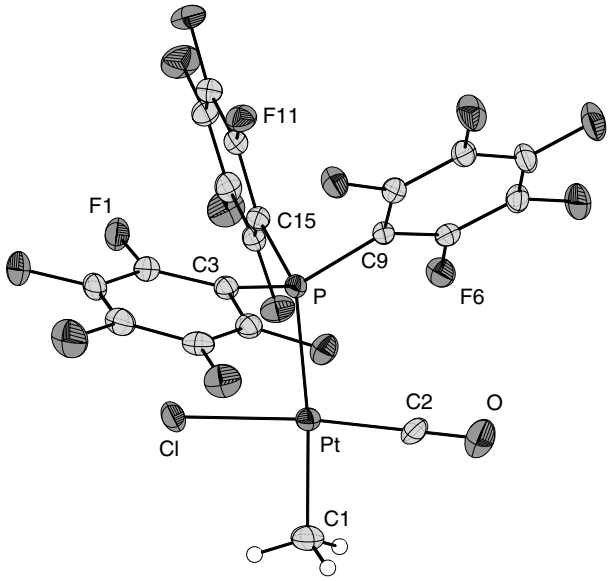
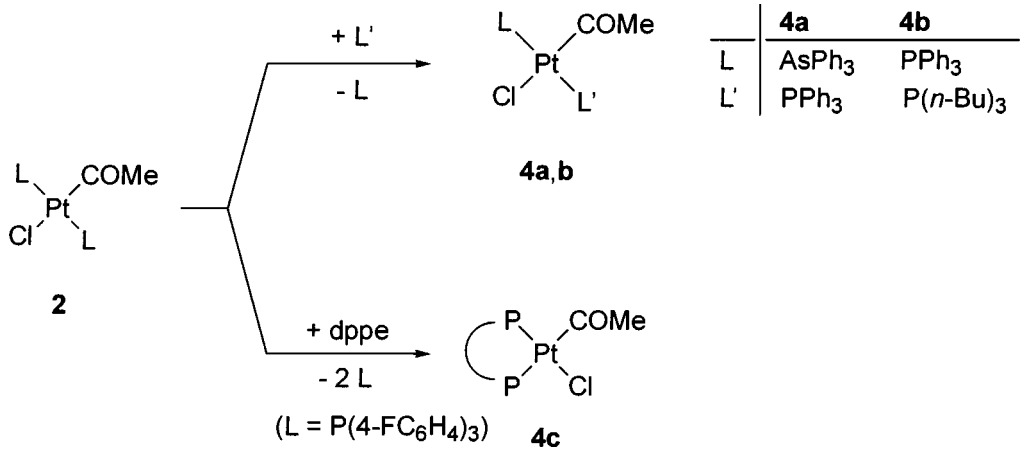


Figure 3. Molecular structure of [Pt(Me)Cl(CO){P(C$_6$F$_5$)$_3$}] (**3b**) showing the atom numbering (displacement ellipsoids at 30% probability). One of the two symmetry-independent molecules is shown. Selected bond lengths (in Å) and angles (in deg.); values for the two symmetry-independent molecules are given separated by a slash: Pt–C1 2.075(5)/2.078(5), Pt–C2 1.821(5)/1.838(5), Pt–P 2.358(1)/2.369(1), C2–O 1.121(6)/1.137(6); P–Pt–Cl 85.61(4)/85.19(5), P–Pt–C1 174.0(1)/173.6(2), P–Pt–C2 100.1(2)/101.2(2), C1–Pt–Cl 89.2(2)/88.7(2), C2–Pt–C1 85.2 (2)/85.0(2), Cl–Pt–C2 174.2(2)/173.6(2), Pt–C2–O 177.1(6)/ 177.7(5).

than those in *trans*-[PtX$_2${P(C$_6$F$_5$)$_3$}$_2$] (X = Cl: 2.280(1) Å; X = I: 2.292(6) Å).[12]

Ligand substitution reactions on acyl(chloro)platinum(II) complexes

The *P*- and *As*-ligands in the acetyl(chloro)platinum(II) complexes **2** proved to be susceptible to ligand substitution reactions according to Scheme 3. Thus, addition of one equivalent triphenylphosphine to a solution of the bis(triphenylarsine) complex **2i** in CH_2Cl_2 gave rise to the substitution of one triphenylarsine ligand. The mixed triphenylphosphine–triphenylarsine complex **4a** was isolated as white crystals in 65% yield. The reaction of the bis(triphenylphosphine) complex **2a** with one equivalent tri-*n*-butylphosphine afforded a mixture of complexes. The ^{31}P NMR spectroscopic measurements revealed that the reaction mixture contained, besides the starting complex **2a** (≈50%), the bis(tri-*n*-butylphosphine) complex **2e** as the main product (≈40%) and



Scheme 3.

the mixed tributylphosphine–triphenylphosphine complex *trans*-[Pt(COMe)Cl{P(*n*-Bu)$_3$}(PPh$_3$)] (**4b**) as the minor product (≈10%). Complex **2b**, having tris(4-fluorophenyl)-phosphine co-ligands, reacted with $Ph_2PCH_2CH_2PPh_2$ (dppe) to form *cis*-[Pt(COMe)Cl(dppe)] (**4c**) in 68% yield. Thus, all these reactions proceeded such that a phosphine/arsine ligand of lower donor capability was substituted by a phosphine with higher donor capability,[6] whereas the latter reaction is additionally driven by the formation of a chelate complex.

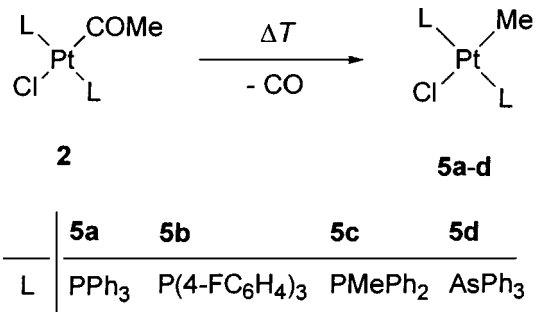
The constitution of complexes **4a**–**4c** was confirmed by NMR spectroscopic measurements (Table 2). The *trans* influence $AsPh_3 < PPh_3$ is clearly reflected in the ^1J(Pt,P) coupling constants in **4a** (4237 Hz) and **2a** (3470 Hz). The phosphorus nuclei in **4b** and **4c** are AX spin systems with coupling constants $^2J(P,P) = 15.6$ Hz in **4b** and $^{2/3}J(P,P) = 4.4$ Hz in **4c**. The greater coupling constant in **4b** compared with that in the *cis* complex **4c** is in accord with the proposed *trans* structure (configuration index: *SP*-4-4) of **4b**. In **4c** the inspection of the ^1J(Pt,P) coupling constants (1405 Hz vs. 4438 Hz) makes clear that the resonance at 32.5 ppm has to be assigned to the P-atom *trans* to the acetyl ligand and the resonance at 31.0 ppm to the P-atom *trans* to the chloro ligand.

Decarbonylation reactions of acyl(chloro)platinum(II) complexes

The acetyl(chloro)platinum(II) complexes with the PPh_3 (**2a**), P(4-FC_6H_4)$_3$ (**2b**), $PMePh_2$ (**2c**), and $AsPh_3$ (**2i**) co-ligands were found to decarbonylate in boiling benzene to yield methyl(chloro)platinum(II) complexes **5a**–**5d** (Scheme 4). The reactions were complete within 2 h. After recrystallization from chloroform–*n*-pentane the complexes **5** were obtained as white, air-stable crystals in nearly quantitative yields (89–97%).

Table 2. Selected NMR data (δ in ppm, J in Hz) for acetyl(chloro)platinum(II) complexes [Pt(COMe)Cl(L)L′] (**4a**–**4c**)

L/L′	COCH_3··δ(^{1}H) [^3J(Pt,H)]	L··δ(^{31}P) [^1J(Pt,P)]	L′··δ(^{31}P) [^1J(Pt,P)]
$AsPh_3$/PPh_3 (**4a**)	1.25	—	17.7 [4237]
PPh_3/P(*n*-Bu)$_3$ (**4b**)	—	14.2 [3833]	−1.4 [3346]
dppe (**4c**)	1.89 [7.28]	31.0 [4438]	32.5 [1405]



Scheme 4.

Selected NMR spectroscopic data of **5a**–**5d** that confirm their identities are given in Table 3. The methyl protons and methyl carbon atoms resonate at higher fields ($\delta_H = 0.08$ to -0.15, $\delta_C = -8.9$ to -17.1). Furthermore, the ^1J(Pt,C) coupling constants (664–678 Hz) give proof that the methyl group is directly bound to platinum. The singlet resonances in the ^{31}P NMR spectra give clear evidence for the *trans* configuration of the complexes. Compared with the analogous acetyl complexes **2**, the ^1J(Pt,P) coupling constants are lowered in complexes **5** by ∼300 Hz. On the basis of Bent's rules,[13] this lowering is in accord with the greater *s*-electron demand of the methyl ligand compared with the acetyl ligand.

From chloroform–*n*-pentane solutions *trans*-[Pt(Me)Cl{P(4-FC_6H_4)$_3$}$_2$] (**5b**) crystallized in well-shaped crystals whose structure was determined by single-crystal X-ray diffraction analysis. Complex **5b** crystallized in isolated molecules; the shortest intermolecular contact between non-hydrogen atoms is between fluorine atoms (2.658(4) Å). The molecular structure is shown in Fig. 4, along with selected geometrical parameters in the figure caption. The platinum atom in **5b** lies in a square-planar environment provided by one Cl, one C and two P atoms. All angles between neighbouring ligands are close to 90° (88.72(7)–91.31(6)°). The platinum–carbon bond (2.069(8) Å) and the platinum–chlorine bond (2.436(2) Å) in **5b** are as long as those in the other *trans*-[Pt(Me)Cl(PR_3)$_2$] complexes (PR_3 = PPh_3, $PMePh_2$, PEt_3, PCy_3): Pt–C, 2.018–2.18(1) Å, Pt–Cl, 2.346–2.440(4) Å.[14,15] In accordance with hybridization of the platinum-bound carbon atom, the Pt–C1(sp^3) distance in **5b** is longer than the Pt–C1(sp^2) distance in **2a** (2.069(8) vs. 2.010(5) Å).

Table 3. Selected NMR data (δ in ppm, J in Hz) for methyl(chloro)platinum(II) complexes *trans*-[Pt(Me)Cl(L)$_2$] (**5a**–**5d**)

L	δ(CH_3) [^2J(Pt,H)/^3J(P,H)]	δ(CH_3) [^1J(Pt,C)]	δ(^{31}P)	^1J(Pt,P)
PPh_3 (**5a**)	−0.10 [78.85/6.64]]	−9.5 [678.0]	30.4	3146
P(4-FC_6H_4)$_3$ (**5b**)	−0.15 [78.75/6.64]	−8.9 [666.2]	28.3	3158
$PMePh_2$ (**5c**)	−0.07 [81.34/6.64]	−13.7 [668.8]	14.8	3027
$AsPh_3$ (**5d**)	0.08 [76.64]	−17.1 [664.3]	—	—

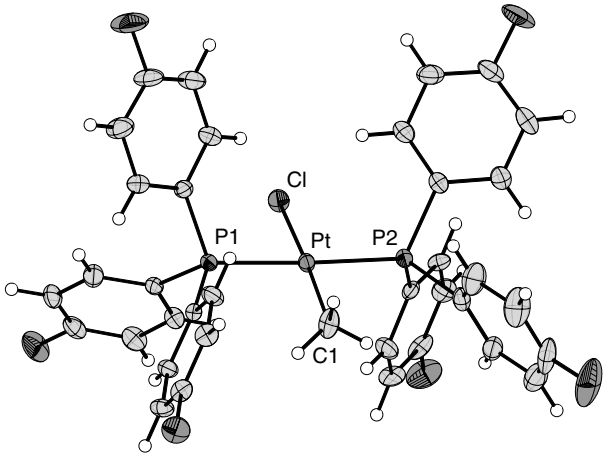


Figure 4. Molecular structure of *trans*-[Pt(Me)Cl-{P(4F-C_6H_4)$_3$}$_2$] (**5b**) showing the atom numbering (displacement ellipsoids at 30% probability). Selected bond lengths (in Å) and angles (in deg.): Pt–C1 2.069(8), Pt–Cl 2.436(2), Pt–P1 2.296(2), Pt–P2 2.276(2); P1–Pt–C1 89.3(2), P1–Pt–Cl 91.31(6), P1–Pt–P2 176.94(6), P2–Pt–C1 91.1(2), P2–Pt–Cl 88.72(7), C1–Pt–Cl 173.7(2).

To conclude, the reaction of the dinuclear platina-β-diketone [Pt$_2${(COMe)$_2$H}$_2$(μ-Cl)$_2$] (**1**) with phosphines to yield the *trans*-[Pt(COMe)Cl(PR_3)$_2$] complexes (**2**) is a useful alternative to classical procedures to synthesize type **2** complexes with a wide variety of phosphine ligands. The advantage over classical methods of preparation for type **2** complexes is that all these complexes can be prepared from the same starting complex **1**. This complex is easily accessible by the reaction of hexachloroplatinic acid in *n*-butanol with bis(trimethylsilyl)acetylene in yields of up to 80%.[4]

EXPERIMENTAL

General comments

Syntheses were performed under an argon atmosphere by using standard Schlenk techniques. Solvents were dried prior to use: $CHCl_3$ and CH_2Cl_2 over CaH_2; diethyl ether and pentane over Na. The ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectra were recorded at 27 °C on Varian Inova 500 and Gemini 2000 spectrometers. Chemical shifts (^{1}H, ^{13}C) are relative to solvent signals as internal references; δ(^{31}P) and δ(^{19}F) are relative to external H_3PO_4 (85%) and trifluorotoluene, respectively. Infrared (IR) spectra were recorded on a Galaxy FTIR spectrometer (Mattson 5000) using KBr pellets. Preparative centrifugal thin-layer chromatography was carried out using a Chromatotron (Harrison Research). Hexachloroplatinic acid (Degussa) and phosphines (Aldrich, Fluka, Merck) were commercially available. The complexes [Pt$_2${(COMe)$_2$H}$_2$(μ-Cl)$_2$] (**1**)[4] and [Pt(COMe)Cl(L)$_2$] (L = PPh_3, **2a**; P(4-FC_6H_4)$_3$, **2b**; P(*n*-Bu)$_3$, **2e**; $AsPh_3$, **2i**) were prepared as described previously.[5]

Preparation of *trans*-[Pt(COMe)Cl(L)$_2$] complexes (2)

To a suspension of **1** (200 mg, 0.31 mmol) in methylene chloride (5 ml), the phosphine (1.24 mmol) in chloroform (3 ml) was added with stirring at −20 °C. After 2 h the solvent was removed *in vacuo*. The residue was purified by preparative centrifugal thin-layer chromatography, first using *n*-pentane–diethyl ether (5:1) and then chloroform–acetone (1:1), to elute the excess phosphine and the complex **2**, respectively. Finally the complexes were dissolved in chloroform (≈2 ml) and reprecipitated with *n*-pentane (≈4 ml). After 2 days the white air-stable crystals of **2** were filtered, washed with pentane (10 ml) and dried *in vacuo*.

trans-[Pt(COMe)Cl($PMePh_2$)$_2$] ***(2c)***. Yield: 245 mg (59%); f.p.: 123–125 °C (dec.). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.17 (s + d, ^3J(Pt,H) = 13.23 Hz, 3H, COCH_3), 2.19 ('t' + 'dt', N = 7.54 Hz, ^3J(Pt,H) = 34.03 Hz, 6H, PCH_3), 7.40 (m, 12H, *o*-, *p*-C*H*), 7.72 (m, 8H, *m*-C*H*). Here and in the following, higher order multiplets are given in inverted commas. ^{13}C NMR (125 MHz, $CDCl_3$): δ 12.3 ('t', N = 38.1 Hz, PCH_3), 44.1 (t, ^3J(P,C) = 5.6 Hz, $COCH_3$), 128.5 ('t', N = 10.4 Hz, *m*-CH), 130.6 (s(br), *p*-CH), 132.2 ('t', N = 51.2 Hz, *i*-C), 133.0 ('t', N = 12.3 Hz, *o*-CH), 217.1 (t, ^2J(P,C) = 5.9 Hz, *C*O). ^{31}P NMR (202 MHz, $CDCl_3$): δ 6.9 (s + d, ^1J(Pt,P) = 3322 Hz). IR: ν 3051(m), 1631(s), 1483(m), 1435(s), 1003(s), 888(s), 740(s), 693(s), 508(s) cm^{-1}.

trans-[Pt(COMe)Cl(PMe_2Ph)$_2$] ***(2d)***. Yield: 200 mg (59%); f.p.: 128–131 °C (dec.). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.64 (s + d, ^3J(Pt,H) = 14.06 Hz, 3H, COCH_3), 1.78 ('t' + 'dt', N = 7.56 Hz, ^3J(Pt,H) = 35.69 Hz, 12H, PCH_3), 7.40 (m, 6H, *o*-, *p*-C*H*), 7.72 (m, 4H, *m*-C*H*). ^{13}C NMR (125 MHz, $CDCl_3$): δ 12.3 ('t', N = 38.1 Hz, PCH_3), 44.0 (t, ^3J(P,C) = 5.9 Hz, $COCH_3$), 128.4 ('t', N = 10.4 Hz, *m*-C*H*), 130.6 (s(br), *p*-CH), 132.2 ('t', N = 55.2 Hz, *i*-C), 133.0 ('t', N = 12.1 Hz, *o*-CH), 217.1 (t, ^2J(P,C) = 6.1 Hz, *C*O). ^{31}P NMR (81 MHz, $CDCl_3$): δ − 5.7 (s + d, ^1J(Pt,P) = 3148 Hz). IR: ν 3060(m), 2987(m), 2907(m), 1631(s), 1482(m), 1438(s), 1096(s), 958(s), 909(s), 746(s), 718(m), 696(s), 489(s) cm^{-1}.

trans-[Pt(COMe)Cl{P(o-tol)$_3$}$_2$] ***(2f)***. Yield: 410 mg (75%); f.p.: 214–216 °C (dec.). ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.2–3.0 (m(br), 21H, CH_3, COCH_3), 7.18–7.30 (m, 24H, C*H*). ^{13}C NMR (125 MHz, $CDCl_3$): δ 23.3 (s(br), CH_3), 39.0 (s(br), $COCH_3$), 125.5 (m(br), *C*5), 130.4 (m(br), *C*3), 131.6 (m(br), *C*6), 133.3 (m(br), *C*4), 134.7 (m(br), *C*2), 143.3 (m(br), *C*1), 212 (s(br), *C*O). ^{31}P NMR (202 MHz, $CDCl_3$): δ 16.9 (s + d(br), ^1J(Pt,P) = 3428 Hz). IR: ν 3052(m), 3006(w), 2975(m), 2919 (m), 1642(s), 1590 (w), 1471(m), 1447 (s), 1281(w), 1132(w), 1068(w), 754(s), 717(m), 533(m), 467(s) cm^{-1}.

trans-[Pt(COMe)Cl{P(m-tol)$_3$}$_2$] (**2g**). Yield: 230 mg (42%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.19 (s + d, ^3J(Pt,H) = 14.33 Hz, 3H, COCH_3), 2.37 (s(br), 18H, CH_3), 7.31–7.68 (m, 24H, C*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.5 (s(br), CH_3), 43.9 (t, ^3J(P,C) = 6.2 Hz, $COCH_3$), 128.1 ('t', N = 11.2 Hz, *C*5), 130.7 ('t', N = 55.4 Hz, *C*1), 131.6 (s(br), *C*4), 132.1 ('t', N = 12.1 Hz, *C*3), 135.8 ('t', N = 13.1 Hz, *C*6), 138.1 ('t', N = 10.8 Hz, *C*2), 215.9 (t, ^2J(P,C) = 5.6 Hz, *C*O). ^{31}P NMR (81 MHz, $CDCl_3$): δ 22.1 (s + d, ^1J(Pt,P) = 3478 Hz). IR: ν 3033(m), 2917 (m), 1593(m), 1478(s), 1449 (m), 1405(m), 1107(s), 780(s), 693(s), 557(s) cm^{-1}.

trans-[Pt(COMe)Cl{P(p-tol)$_3$}$_2$] (**2h**). Yield: 230 mg (42%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.17 (s + d, ^3J(Pt,H) = 14.11 Hz, 3H, COCH_3), 2.40 (s(br), 18H, CH_3), 7.24 (m, 12H, *m*-C*H*), 7.65 (m, 12H, *o*-C*H*). ^{13}C NMR (50 MHz, $CDCl_3$): δ 21.4 (s(br), CH_3), 44.0 (t, ^3J(P,C) = 6.1 Hz, $COCH_3$), 127.7 ('t', N = 57.6 Hz, *C*1), 129.1 ('t', N = 11.2 Hz, *C*5, *C*3), 135.0 ('t', N = 12.9 Hz, *C*2, *C*6), 141.3 (s, *C*4), 216.2 (t, ^2J(P,C) = 5.6 Hz, *C*O). ^{31}P NMR (81 MHz, $CDCl_3$): δ 19.9 (s + d, ^1J(Pt,P) = 3345 Hz). IR: ν 3017(m), 2921 (m), 1630(m), 1599(s), 1498(s), 1446 (m), 1397(m), 1190(w), 1097(s), 804(s), 632(m), 525(s) cm^{-1}.

Preparation of [Pt(Me)Cl(CO){P(*o*-tol)$_3$}] (3a)

To a suspension of **1** (200 mg, 0.31 mmol) in methylene chloride (2 ml), a solution of P(*o*-tol)$_3$ (190 mg, 0.62 mmol) in methylene chloride (3 ml) was added with stirring at −20 °C. After 5 min the solvent was removed *in vacuo*. The residue was dissolved in diethyl ether (2 ml), filtered and reprecipitated with *n*-pentane (≈10 ml). Yield: 150 mg (41%); f.p.: 158–160 °C (dec.). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.22 (d + dd, ^2J(Pt,H) = 58.37 Hz, ^3J(P,H) = 7.50 Hz, 3H, CH_3), 2.22 (s(br), 9H, CH_3, *o*-tol), 7.30 (m, 9H, C*H*), 7.74 (m, 3H, C*H*). ^{13}C NMR (125 MHz, $CDCl_3$): δ 0.8 (d + dd, ^1J(Pt,C) = 399.6 Hz, ^2J(P,C) = 86.4 Hz, *C*H_3), 23.3 (d(br), ^3J(P,C) = 5.8 Hz, CH_3, *o*-tol), 126.1 (d, ^2J(P,C) = 10.7 Hz, *C*6), 126.6 (d, ^1J(P,C) = 45.4 Hz, *C*1), 131.2 (d, ^3J(P,C) = 2.3 Hz, *C*3), 132.1 (d, ^3J(P,C) = 8.0 Hz, *C*5), 135.5 (s, *C*4), 142.5 (d, ^2J(P,C) = 8.1 Hz, *C*2), 164.7 (d + dd, ^1J(Pt,C) = 1965.6 Hz, ^2J(P,C) = 6.7 Hz, *C*O). ^{31}P NMR (81 MHz, $CDCl_3$): δ 25.1 (s + d(br), ^1J(Pt,P) = 1395 Hz).

Preparation of [Pt(Me)Cl(CO){P(C_6F_5)$_3$}] (3b)

To a suspension of **1** (200 mg, 0.31 mmol) in chloroform (5 ml), a solution of P(C_6F_5)$_3$ (700 mg, 1.32 mmol) in chloroform (3 ml) was added with stirring at 40 °C. After 2 h the solvent was removed *in vacuo*. The residue was washed with chloroform–diethyl ether (1:3, 10 ml), dissolved in methylene chloride (≈15 ml) and reprecipitated with *n*-pentane (≈5 ml). After 2 days the white air-stable crystals were filtered off, washed with pentane (10 ml) and dried *in vacuo*. Yield: 460 mg (92%); f.p.: 164–166 °C (dec.). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.43 (d + dd, ^2J(Pt,H) = 64.70 Hz, ^3J(P,H) = 8.85 Hz, 3H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 1.3 (d + dd, ^1J(Pt,C) = 430.8 Hz, ^2J(P,C) = 98.5 Hz, CH_3), 101.8 (m, *i*-*C*), 138.0 (m, *o*-CF), 143.3 (m, *p*-CF), 147.5 (m, *m*-CF), 163.3 (s + d, ^1J(Pt,C) = 1971.1 Hz, *C*O). ^{19}F NMR (470 MHz, $CDCl_3$): −157.6 ('t', N = 38.5 Hz, *m*-C*F*), −143.5 ('t', N = 41.3 Hz, *p*-C*F*), −126.7 (m, *o*-C*F*). ^{31}P NMR (202 MHz, $CDCl_3$): δ − 20.7 (s + d, ^1J(Pt,P) = 1073 Hz). IR: ν 2095(s), 1645(m), 1520(s), 1483(s), 1393(m), 1297(m), 1097(s), 985(s), 523(w) cm^{-1}.

Preparation of *trans*-[Pt(COMe)Cl($AsPh_3$)(PPh_3)] (4a)

At room temperature a solution of triphenylphosphine (59 mg, 0.23 mmol) in CH_2Cl_2 (2 ml) was added dropwise to a solution of [Pt(COMe)Cl($AsPh_3$)$_2$] (**2i**) (200 mg, 0.23 mmol) in CH_2Cl_2 (5 ml). After 1 h the solvent was removed *in vacuo* and the residue was purified by preparative centrifugal thin-layer chromatography using *n*-pentane–diethyl ether (5:1), diethyl ether–chloroform (2:1) and finally diethyl ether–chloroform (1:2) for elution of $AsPh_3$, **2a** and **4a**, respectively. After removal of the solvents, the last fraction was redissolved in chloroform (≈2 ml) and reprecipitated with *n*-pentane (≈4 ml). After 2 days the white air-stable crystals were filtered, washed with pentane (10 ml) and dried *in vacuo*. Yield: 125 mg (65%); f.p.: 214–217 °C (dec.). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.25 (s(br), 3H, COCH_3), 7.37 (m, 18H, C*H*) 7.77 (m, 12H, C*H*). ^{13}C NMR (50 MHz, CD_2Cl_2): δ 44.7 (d, ^3J(P,C) = 6.6 Hz, CH_3), 128.4 (d, ^3J(P,C) = 10.9 Hz, *m*-CH of PPh_3), 129.0 (s, *m*-CH of $AsPh_3$), 129.7 (d, ^1J(P,C) = 30.7 Hz, *i*-*C* of PPh_3), 130.6 (s, *p*-CH of $AsPh_3$), 131.1 (d, ^4J(P,C) = 0.7 Hz, *p*-CH of PPh_3), 132.7 (d, ^3J(P,C) = 4.7 Hz, *i*-*C* of $AsPh_3$), 134.3 (s, *o*-CH of $AsPh_3$), 135.1 (d, ^2J(P,C) = 11.2 Hz, *o*-CH of PPh_3), 214.3 (d, ^2J(P,C) = 4.8 Hz, *C*O). ^{31}P NMR (202 MHz, $CDCl_3$): δ 17.7 (s + d, ^1J(Pt,P) = 4237 Hz).

Reaction of 2a with P(*n*-Bu)$_3$ to yield 4b

To a solution of [Pt(COMe)Cl(PPh_3)$_2$] (**2a**) (50 mg, 0.063 mmol) in $CDCl_3$ (0.7 ml) a solution of tributylphosphine (12 mg, 0.06 mmol) in $CDCl_3$ (0.5 ml) was added dropwise with stirring at −20 °C. After warming to room temperature the solution was investigated by ^{31}P NMR spectroscopy. ^{31}P NMR (81 MHz, $CDCl_3$): δ − 4.3 (s, *P*Ph_3), −1.4 (d + dd, ^1J(Pt,P) = 3346 Hz, ^2J(P,P) = 15.6 Hz, *P*Bu_3 **4b**), 8.6 (s + d, ^1J(Pt,P) = 3053 Hz, *P*Bu_3, **2e**), 14.2 (d + dd, ^1J(Pt,P) = 3833 Hz, ^2J(P,P) = 15.6 Hz, *P*Ph_3 **4b**), 21.3 (s + d, ^1J(Pt,P) = 3470 Hz, *P*Ph_3 **2a**).

Preparation of [Pt(COMe)Cl(dppe)] (4c)

At room temperature a solution of dppe (88 mg, 0.22 mmol) in CH_2Cl_2 (2 ml) was added to a solution of **2b** (200 mg, 0.22 mmol) in CH_2Cl_2 (5 ml). After 1 h the solvent was removed *in vacuo* and the residue was purified by preparative centrifugal thin-layer chromatography using *n*-pentane–diethyl ether (5:1) to elute PPh_3 and using diethyl ether–chloroform (1:2) to elute **4c**. After removal of the solvent *in vacuo*, **4c** was obtained as a white air-stable powder. Yield: 100 mg (68%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.89

(d + dd, ^3J(Pt,H) = 7.28 Hz, ^4J(P,H) = 1.54 Hz, 3H, COCH_3), 2.15 (m, 2H, CH_2), 2.36 (m, 2H, CH_2), 7.43 (m, 12H, C*H*), 7.71 (m, 4H, C*H*), 7.85 (m, 4H, C*H*). ^{31}P NMR (81 MHz, $CDCl_3$): δ 31.0 (d + dd, ^1J(Pt,P) = 4438 Hz, $^{2/3}J$(P,P) = 4.4 Hz), 32.5 (d + dd, ^1J(Pt,P) = 1405 Hz, $^{2/3}J$(P,P) = 4.4 Hz). Comparison with the data given in Ref. 5 confirms the identity of the complex; erroneously, there a wrong value is given for the coupling constant ^3J(Pt,H).

Preparation of methylplatinum(II) complexes *trans*-[Pt(Me)Cl(L)$_2$] (5)

A solution of **2** (0.3 mmol) in benzene (7 ml) was refluxed for 2 h and the solvent was removed *in vacuo*. The crude product was washed with pentane–diethyl ether (1 : 5, 10 ml) and reprecipitated from chloroform–*n*-pentane (1 : 2, 6 ml). After 2 days white air-stable crystals of **5** were filtered off and dried *in vacuo*.

*trans-[Pt(Me)Cl(PPh$_3$)$_2$] (**5a**).* Yield: 220 mg (95%); f.p.: 283 °C (dec.). ^{1}H NMR (200 MHz, $CDCl_3$): δ − 0.10 (t + dt, ^2J(Pt,H) = 78.85 Hz, ^3J(P,H) = 6.64 Hz, 3H, CH_3), 7.38 (m, 18H, *p*-, *m*-C*H*), 7.70 (m, 12H, *o*-C*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ − 9.5 (t + dt, ^1J(Pt,C) = 678.0 Hz, ^2J(P,C) = 5.2 Hz, *C*H$_3$), 127.9 (m, *m*-CH), 130.1 (s, *p*-CH), 130.6 (m, *i*-C), 135.1 (m, *o*-CH). ^{31}P NMR (81 MHz, $CDCl_3$): δ 30.4 (s + d, ^1J(Pt,P) = 3146 Hz). IR: ν 3072(w), 3050(w), 2944(w), 2922(w), 1636(w), 1480(m), 1434(s), 1100(s), 744(m), 692(s), 524(s), 512(s) cm^{-1}.

*trans-[Pt(Me)Cl{P(4-FC$_6$H$_4$)$_3$}$_2$] (**5b**).* Yield: 242 mg (92%); f.p.: 231–233 °C (dec.). ^{1}H NMR (200 MHz, $CDCl_3$): δ − 0.15 (t + dt, ^2J(Pt,P) = 78.75 Hz, ^3J(P,H) = 6.64 Hz, 3H, CH_3), 7.10 (m, 12H, *o*-C*H*), 7.66 (m, 12H, *m*-C*H*). ^{13}C NMR (125 MHz, $CDCl_3$): δ − 8.9 (t + dt, ^1J(Pt,C) = 666.2 Hz, ^2J(P,C) = 5.1 Hz, CH_3), 115.5 ('dt', *N* = 21.3 Hz, *m*-CH), 125.6 ('t', *N* = 56.3 Hz, *i*-C), 137.0 ('dt', *N* = 8.3 Hz, *o*-CH), 165.5 (d(br), ^1J(C,F) = 254.1 Hz, *C*F). ^{31}P NMR (202 MHz, $CDCl_3$): δ 28.3 (s + d, ^1J(Pt,P) = 3158 Hz). IR: ν 3051(m), 1590 (s), 1497(s), 1394(m), 1233(s), 1163(s), 1095(s), 828(s), 528(s) cm^{-1}.

*trans-[Pt(Me)Cl(PMePh$_2$)$_2$] (**5c**).* Yield: 188 mg (97%). ^{1}H NMR (200 MHz, $CDCl_3$): δ − 0.07 (t + dt, ^2J(Pt,H) = 81.34 Hz, ^3J(P,H) = 6.64 Hz, 3H, CH_3), 2.20 ('t' + 'dt', *N* = 6.64 Hz, ^3J(Pt,H) = 28.22 Hz, 3H, PCH_3), 7.38 (m, 12H, *p*-, *m*-C*H*), 7.70 (m, 8H, *o*-C*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ − 13.7 (t + dt, ^1J(Pt,C) = 668.8 Hz, ^2J(P,C) = 5.8 Hz, *C*H$_3$),

Table 4. Crystallographic and data collection parameters for complexes **2a**·2$CHCl_3$, **2f, 3** and **5b**

	2a·2$CHCl_3$	**2f**	**3b**	**5b**
Empirical formula	$C_{40}H_{35}Cl_7OP_2Pt$	$C_{44}H_{45}ClOP_2Pt$	$C_{20}H_3ClF_{15}OPPt$	$C_{37}H_{27}ClF_6P_2Pt$
M_r	1036.86	882.28	805.73	878.07
Temperature (K)	220(2)	100(2)	220(2)	220(2)
Crystal size (mm)	0.27 × 0.27 × 0.09	0.23 × 0.07 × 0.07	0.27 × 0.13 × 0.09	0.33 × 0.24 × 0.06
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	*P*−1	$P2_1/n$	*P*−1	*P*−1
a (Å)	11.614(3)	10.529(2)	9.937(2)	10.022(2)
b (Å)	12.063(3)	24.535(5)	14.276(3)	12.075(3)
c (Å)	17.338(4)	14.537(3)	16.355(4)	15.170(4)
α (°)	78.04(3)		97.12(3)	75.89(3)
β (°)	73.07(2)	91.23(3)	96.44(3)	87.16(3)
γ (°)	66.50(2)		93.94(3)	72.72(3)
V(Å^3)	2119.4(8)	3755(1)	2279.8(9)	1699.4(7)
Z	2	4	4	2
D_{calc}(g cm^{-1})	1.625	1.561	2.347	1.716
μ(Mo K_α)(mm^{-1})	3.858	3.928	6.479	4.360
F(000)	1020	1768	1504	856
θ range (°)	2.12–25.98	2.86–30.00	2.04–26.02	2.00–25.00
Reflections collected	16 610	49 033	24 637	12 214
Reflections observed [$I > 2\sigma(I)$]	6881	7777	6531	4580
Reflections independent	7638 (R_{int} = 0.0403)	10 864 (R_{int} = 0.0842)	8335 (R_{int} = 0.0520)	5627 (R_{int} = 0.0670)
Data/restraints/parameters	7638/0/583	10 864/0/449	8335/0/705	5627/0/425
Goodness-of-fit on F^2	1.100	0.988	0.930	1.038
*R*1, *wR*2 [$I > 2\sigma(I)$]	0.0317, 0.0822	0.0377, 0.0412	0.0249, 0.0500	0.0336, 0.0797
*R*1, *wR*2 (all data)	0.0369, 0.0893	0.0458, 0.0754	0.0383, 0.0531	0.0488, 0.0950
Largest differential peak and hole (e Å^{-3})	1.51, −1.05	0.89, −0.82	0.97, −0.81	1.64, −1.96

12.4 ('t', $N = 37.6$ Hz, PCH_3), 128.1 ('t', $N = 10.2$ Hz, *m*-CH), 130.0 ('t', $N = 2.0$ Hz, *p*-CH), 132.3 ('t', $N = 53.3$ Hz, *i*-C), 133.1 ('t', $N = 12.3$ Hz, *o*-CH). ^{31}P NMR (81 MHz, $CDCl_3$): δ 14.8 (s + d, ^1J(Pt,P) = 3027 Hz). IR: ν 3052(m), 2918(m), 1483(m), 1435(s), 1003(s), 888(s), 735(s), 693(s), 508(s) cm^{-1}.

*trans-[Pt(Me)Cl(AsPh$_3$)$_2$] (**5d**).* Yield: 230 mg (89%); f.p.: 208–210 °C (dec.). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.08 (s + d, ^2J(Pt,H) = 76.64, 3H, CH_3), 7.40 (m, 18H, *o*-, *p*-CH), 7.72 (m, 12H, *m*-CH). ^{13}C NMR (50 MHz, $CDCl_3$): δ − 17.1 (s + d, ^1J(Pt,C) = 664.3 Hz, CH_3), 128.8 (s, *m*-CH), 130.8 (s, *p*-CH), 132.7 (s, *i*-C), 133.8 (s, *o*-CH).

X-ray crystal structure determination

Crystals of **2a**·2CHCl$_3$, **2f, 3b** and **5b** suitable for X-ray diffraction measurements were obtained from chloroform–*n*-pentane (**2a**·2CHCl$_3$, **2f, 5b**) and methylene chloride–*n*-pentane (**3**) solutions, respectively. Intensity data were collected on a Stoe-IPDS (**2a**·2CHCl$_3$, **3b, 5b**) or a KUMA KM4 CCD (**2f**) diffractometer, respectively, using graphite monochromatized Mo K_α radiation ($\lambda = 0.71073$ Å). A summary of the crystallographic data, the data collection parameters and the refinement parameters is given in Table 4. Absorption corrections were applied numerically ($T_{min}/T_{max} = 0.350/0.711$ for **2a**·2CHCl$_3$; 0.512/0.781 for **2f**; 0.383/0.588 for **3b**; 0.296/0.686 for **5b**). The structures were solved by direct methods with SHELXS-97 and refined using full-matrix least-squares routines against F^2 with SHELXL-97.[16] Non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms were refined isotropically. Hydrogen atoms in **2a**·2CHCl$_3$ were found in the difference Fourier map except for the hydrogen atoms at C2. These H atoms and the H atoms in **2f, 3b** and **5b** were included in the models in the calculated positions using the riding model. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Center (CCDC) as Supplementary Publication No. CCDC-272671 (**2a**·2CHCl$_3$), CCDC-272672 (**2f**), CCDC-272673 (**3b**) and CCDC-272674 (**5b**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk).

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