On the Reactivity of Platina-β-diketones – Synthesis and Characterization of Acylplatinum(II) Complexes

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Dedicated to Professor Karl-Heinz Thiele on the Occasion of his 70th Birthday

Abstract. The platina-β-diketones $[Pt_2\{(COR)_2H\}_2(\mu\text{-}Cl)_2]$ (**1**, R = Me **a**, Et **b**) react with phosphines L in a molar ratio of 1 : 4 through cleavage of acetaldehyde to give acylplatinum(II) complexes *trans*-$[Pt(COR)Cl(L)_2]$ (**2**) (R/L = Me/P(*p*-$FC_6H_4)_3$ **a**, Me/P(*p*-$CH_2{=}CHC_6H_4)Ph_2$ **b**, Me/P(*n*-$Bu)_3$ **c**, Et/P(*p*-$MeOC_6H_4)_3$ **d**). **1a** reacts with $Ph_2As(CH_2)_2PPh_2$ (dadpe) in a molar ratio of 1 : 2 through cleavage of acetaldehyde yielding [Pt(COMe)Cl(dadpe)] (**3a**) (configuration index: *SP*-4-4) and [Pt(COMe)Cl(dadpe)] (configuration index: *SP*-4-2) (**3b**) in a ratio of about 9 : 1. All acyl complexes were characterized by ^1H, ^{13}C and ^{31}P NMR spectroscopy. The molecular structures of **2a** and **3a** were determined by single-crystal X-ray diffraction. The geometries at the platinum centers are close to square planar. In both complexes the plane of the acyl ligand is nearly perpendicular to the plane of the complex (88(2)° **2a**, 81.2(5)° **3a**).

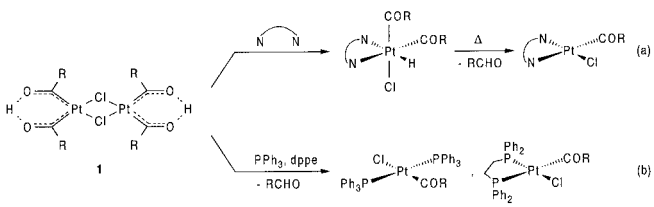
Keywords: Platina-β-diketones; Platinum(II) complexes; Crystal structure.

Zur Reaktivität von Platina-β-diketonen – Synthese und Reaktvität von Acylplatin(II)-Komplexen

Inhaltsübersicht. Die Platina-β-diketone $[Pt_2\{(COR)_2H\}_2 \cdot (\mu\text{-}Cl)_2]$ (**1**, R = Me **a**, Et **b**) reagieren mit Phosphinen L im molaren Verhältnis 1 : 4 unter Abspaltung von Acetaldehyd zu Acylplatin(II)-Komplexen *trans*-$[Pt(COR)Cl(L)_2]$ (**2**) (R/L = Me/P(*p*-$FC_6H_4)_3$ **a**, Me/P(*p*-$CH_2{=}CHC_6H_4)Ph_2$ **b**, Me/P(*n*-$Bu)_3$ **c**, Et/P(*p*-$MeOC_6H_4)_3$ **d**). **1a** setzt sich im Molverhältnis 1 : 2 mit $Ph_2As(CH_2)_2PPh_2$ (dadpe) unter Abspaltung von Acetaldehyd zu [Pt(COMe)Cl(dadpe)] (**3a**) (Konfigurationsindex: *SP*-4-4) und [Pt(COMe)Cl(dadpe)] (Konfigurationsindex: *SP*-4-2) (**3b**) im Verhältnis von ungefähr 9 : 1 um. Alle Acylkomplexe sind durch ^1H-, ^{13}C- und ^{31}P-NMR-Spektroskopie charakterisiert worden. Die Molekülstrukturen von **2a** und **3a** sind durch Röntgeneinkristallstruturanalyse ermittelt worden. Sie weisen eine ungefähr quadratisch-planare Anordnung der zentralen Platinatome auf. In beiden Komplexen steht die Ebene des Acylliganden nahezu senkrecht auf der Komplexebene (88(2)° **2a**, 81.2(5)° **3a**).

Introduction

Reactions of trimethylsilylacetylenes with hexachloroplatinic acid in butanol afford platina-β-diketones $[Pt_2\{(COR)_2H\}_2(\mu\text{-}Cl)_2]$ (**1**) in high yields [1, 2]. These 16-valence-electron complexes with kinetically labile ligands exhibit reactivity that is in marked contrast to that of Lukehart's metalla-β-diketones $[L_xM\{(COR)_2H\}]$ (M = Mo, W, Mn, Re, ...; L = CO, Cp, ...) which are both electronically saturated (18 valence electrons) and kinetically inert [3]. The reactivity of complexes **1** can be understood as that of intramolecular-hydrogen-bond-stabilized acyl(hydroxycarbene)platinum(II) complexes [4]. With bidentate nitrogen donor ligands (2,2′-bipyridine and 1,10-phenanthroline derivatives), an intramolecular oxidative addition takes place yielding acyl(hydrido)platinum(IV) complexes that undergo reductive elimination of aldehyde at higher temperatures (Scheme 1, a) [5, 6]. With triphenylphosphine and 1,2-bis(diphenylphosphino)ethane (dppe), aldehyde is cleaved with formation of acylplatinum(II) complexes (Scheme 1, b) [7].



Scheme 1

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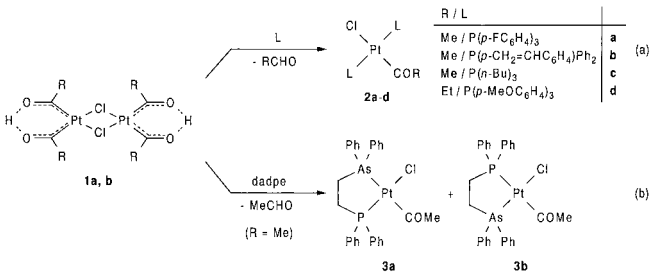
Here we report the reaction of platina-β-diketones **1** with substituted triarylphosphines, with tri(*n*-butyl)-phosphine as a representative alkylphosphine, as well as with the unsymmetrical bidentate ligand 1-(diphenylarsino)-2-(diphenylphosphino)ethane (dadpe).

Results and Discussion

Synthesis

In methylene chloride at room temperature, platina-β-diketones **1** react with phosphines in a molar ratio of 1 : 4 through cleavage of aldehyde to give acyl(chloro)-platinum(II) complexes **2** (Scheme 2, a). By addition of diethyl ether, complexes **2a** and **2d** are formed as colorless (**2a**) or pale-yellow crystals (**2d**) in high yields (**2a** 82%, **2d** 84%). **2a** and **2d** are air stable and freely soluble in methylene chloride and chloroform but insoluble in diethyl ether and hydrocarbons. Complexes **2b** and **2c** were identified in solution only.



Scheme 2

The platina-β-diketone **1a** reacts with 1-(diphenylarsino)-2-(diphenylphosphino)ethane (dadpe) in a molar ratio of 1 : 2 according to Scheme 2 (b) through cleavage of acetaldehyde yielding the stereoisomeric acyl(chloro)platinum(II) complexes **3a** and **3b** in a ratio of about 9 : 1 (^{31}P NMR). By standing 12 hours, the major isomer **3a** precipitates as pale-yellow crystals in 78% yield. **3a** is slightly air-sensitive (decomposition within 3–5 days in air) and freely soluble in acetone but insoluble in diethyl ether and hydrocarbons.

Spectroscopic characterization

The identities of the acyl(chloro)platinum(II) complexes were confirmed by NMR spectroscopy (Table 1). The trans configuration of the complexes **2** follows from the triplet pattern of the carbonyl carbon atom resonance and the singlet pattern of the phosphorus signal in the ^{13}C and ^{31}P NMR spectra, respectively. The coordination-induced shift of the phosphorus signal ($\delta(^{31}P)_{coord}$–$\delta(^{31}P)_{non\text{-}coord}$) is between 26 and 41 ppm to lower field. These values and the magnitudes of the ^1J(Pt, P) coupling constants (3075–3501 Hz) are as expected [8]. As for other acylplatinum complexes *trans*-[Pt(COR)Cl(L)$_2$] (L = phosphine) [9], the C–O stretching vibrations in the IR spectra are at 1636 (**2a**) and 1649 cm^{-1} (**2d**) and the Pt–Cl stretching vibrations are at 265 (**2a**) and 260 cm^{-1} (**2d**).

Table 1 Selected NMR data (chemical shifts in ppm, coupling constants in Hz) for *trans*-[Pt(COR)Cl(L)$_2$] complexes **2a**–**2d**.

R/L	δ(*CO*)	$\delta(^{31}P)$ [$\Delta\delta(^{31}P)$][a]	^1J(Pt, C)	^2J(P, C)	^1J(Pt, P)
Me/P(*p*-FC$_6$H$_4$)$_3$ (**2a**)	217.9	18.6 [27]	922	5.0	3499
Me/P(*p*-CH$_2$=CHC$_6$H$_4$)Ph$_2$ (**2b**)	216.1	20.8 [27]	[b]	5.8	3501
Me/P(*n*-Bu)$_3$ (**2c**)	215.8	8.2 [41]	[b]	6.8	3075
Et/P(*p*-MeOC$_6$H$_4$)$_3$ (**2d**)	219.8	17.9 [28]	ca 950	6.0	3449
Me/PPh$_3$ [c]	218.4	20.9 [26]		6	3480
Et/PPh$_3$ [c]	218.8	21.1 [26]	917	6	3505

[a] $\Delta\delta(^{31}P) = \delta(^{31}P)_{coord} - \delta(^{31}P)_{non\text{-}coord}$. Data $\delta(^{31}P)_{non\text{-}coord}$ are own measurements or are taken from lit. [17].
[b] Not observed due to poor S/N ratio.
[c] For comparison; values taken from lit. [7].

The diastereomeric structures of complexes **3a** and **3b** with their *trans*-P–Pt–Cl (**3a**, configuration index: *SP*-4-4) and *trans*-P–Pt–COMe (**3b**, configuration index: *SP*-4-2) arrangement, respectively, were established by the high and low value, respectively, of ^1J(Pt, P) (**3a**, 4454 Hz; **3b**, 1720 Hz), reflecting the large difference in trans influences (Cl < COMe) [10]. The phosphorus resonances were found at 32.2 ppm (**3a**) and 43.7 ppm (**3b**). In both cases the signals are shifted to low field in comparison with the phosphorus resonance of the free dadpe ligand (δ = –12.5), as expected when five-membered rings are formed [8]. The ^{1}H and ^{13}C NMR spectra of **3a** fully support the identity of the complex. The ^{13}C resonance of the acetyl carbon atom *C*OMe is slightly shifted to high field compared to that in the analogous dppe complex [7] [Pt(COMe)Cl(dppe)] (231.5 vs. 244.3 ppm).

Molecular structures

The molecular structures of **2a** and **3a** determined by single-crystal X-ray diffraction are shown in Figures 1 and 2. Selected bond lengths and angles are listed in Tables 2 and 3. The unit cells contain discrete molecules without any unusually short intermolecular contacts.

The molecular structure of complex **2a** reveals close to square-planar configuration with angles between 88.6(2) and 91.8(5)° at the platinum atom (sum of the angles: 360.6°; greatest deviation of the mean square plane for C(37) by 0.11(2) Å). The plane of the acyl ligand is nearly perpendicular (88(2)°) to the plane of the complex, to minimize steric interactions with the bulky phosphine ligands.

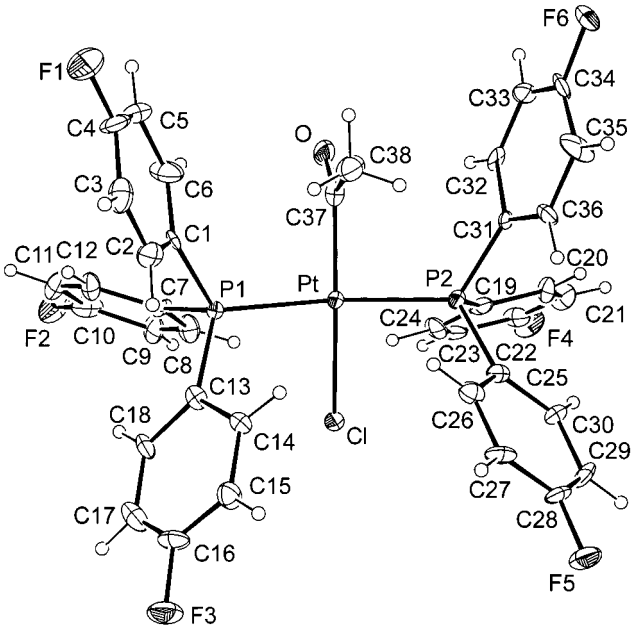


Fig. 1 ORTEP-III plot [18] of *trans*-[Pt(COMe)Cl{P(*p*-$FC_6H_4)_3$}$_2$] (**2a**), showing atom numbering (displacement ellipsoids at 30% probability); H atoms omitted for clarity.

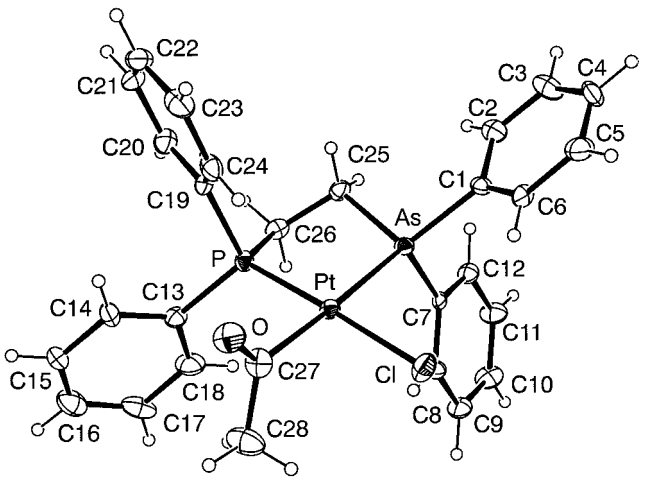


Fig. 2 ORTEP-III plot [18] of [Pt(COMe)Cl(dadpe)] (**3a**), showing atom numbering (displacement ellipsoids at 30% probability).

Table 2 Selected bond lengths (in Å) and bond angles (in °) for *trans*-[Pt(COMe)Cl{P(*p*-$FC_6H_4)_3$}$_2$] (**2a**).

Pt–C(37)	2.03(2)	P(1)–Pt–P(2)	173.1(2)
Pt–Cl	2.436(4)	P(1)–Pt–C(37)	91.8(5)
Pt–P(1)	2.305(4)	P(1)–Pt–Cl	88.7(1)
Pt–P(2)	2.304(4)	P(2)–Pt–C(37)	91.5(5)
C(37)–C(38)	1.48(3)	P(2)–Pt–Cl	88.6(2)
C(37)–O	1.22(2)	Cl–Pt–C(37)	175.0(5)
P–C	1.80(2)–1.87(2)	Pt–C(37)–C(38)	118(1)
C–F	1.34(2)–1.36(2)	Pt–C(37)–O	118(1)
		C(38)–C(37)–O	124(2)
		C–P–C	102.9(8)–107.9(8)

Table 3 Selected bond lengths (in Å) and bond angles (in °) for [Pt(COMe)Cl(dadpe)] **3a**.

Pt–C(27)	2.031(9)	As–Pt–P	85.7(1)
Pt–P	2.219(2)	As–Pt–Cl	96.5(1)
Pt–As	2.4628(8)	As–Pt–C(27)	176.6(3)
Pt–Cl	2.366(2)	P–Pt–C(27)	91.0(3)
C(27)–O	1.20(1)	P–Pt–Cl	177.7(1)
P–C(26)	1.834(8)	Cl–Pt–C(27)	86.8(3)
As–C(25)	1.965(9)	Pt–C(27)–C(28)	115.7(6)
		Pt–C(27)–O	123.8(8)
		C(28)–C(27)–O	120.2(9)

The coordination at the platinum center in complex **3a** is close to square planar (angles at Pt: 85.7(1)–96.5(1)°; sum of angles: 360.0°; greatest deviation of the mean square plane for the Pt atom by 0.0118(3) Å). The "bite" angle of the dadpe ligand (P–Pt–As 85.7(1)°) is in the range of those in other dadpe complexes (79.1(1)–88.09(6)°; mean value: 83.1°; $n = 9$, n – number of datapoints [11]). The chelate ring exhibits a slightly distorted half-chair conformation with C(25) and C(26) beneath (–0.29(1) Å) and above (+0.47(1) Å), respectively, the Pt–P–As plane. The plane of the acyl ligand is nearly perpendicular to the plane of the complex (81.2(5)°).

In both complexes, the magnitudes of the Pt–C bond lengths (2.03(2)/2.031(9) Å) as well as the C–O bond lengths (1.22(2)/1.20(1) Å) are in the range of those found in other acylplatinum(II) complexes [9b, 12]. The Pt–Cl bond in **2a** (2.436(4) Å) is longer than those in **3a** (2.366(2) Å) and in the corresponding dppe complex [Pt(COMe)Cl(dppe)] (2.368(3) Å) [7] reflecting the difference in trans influence of acetyl and phosphine donors. As expected from the trans influences (phosphine > Cl), the Pt–P bonds in **2a** are longer (2.304(4)/2.305(4) Å) than those in **3a** (2.219(2) Å) and in [Pt(COMe)Cl(dppe)] (2.223(3) Å, P *trans* to Cl) [7].

Quantum Chemical Calculations

To help decide whether the reactions shown in Scheme 2 (a) yielding the trans isomers **2** are thermodynamically or kinetically controlled, DFT calculations were carried out for model complexes *cis/trans*-[Pt(COMe)Cl$(PR_3)_2$] (R = H **4a/b**, Me **5a/b**, Ph **6a/b**). In all cases the *trans* isomers are more stable than the *cis* isomers by 1.9 (**4**), 8.3 (8.1) (**5**) and 15.8 (13.4) (**6**) kcal mol^{-1}.[1)] The dihedral angles P–Pt–C–O are for the PH_3 complexes 10.6/168.1° (**4a**) and 153.5°[2)] (**4b**) as well as for the PMe_3 complexes 50.3/117.4° (**5a**) and 105.1°[2)] (**5b**). This is showing that, in complexes with the more bulky PMe_3 ligands, the acetyl ligands

[1)] Values are given for B3LYP level and in parantheses for BP86 level.

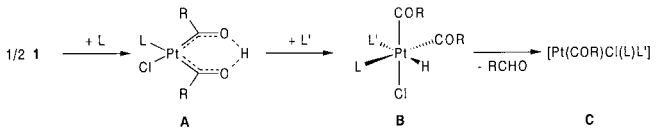
[2)] Only the value for the phosphorus cis to the acetyl ligand is given.

do not lie in the plane of the complex. This is in agreement with the solid-state structures of *trans*-[Pt(COMe)Cl{P(*p*-FC_6H_4)$_3$}$_2$] (**2a**) and [Pt(COMe) · Cl(dadpe)] (**3a**) where the dihedral angles are P(1/2)–Pt–C(37)–O 91(2)/95(2)° and P–Pt–C(27)–O 85.7(9)°, respectively.

Due to differences in the trans influences (Cl < PR_3 < COMe), the Pt–C bonds in trans complexes are shorter (**4b**: 2.024, **5b**: 2.010 Å) than those in cis complexes (**4a**: 2.035, **5a**: 2.040 Å) and the Pt–Cl bonds are longer in trans complexes (**4b**: 2.545, **5b**: 2.570 Å) than those in cis complexes (**4a**: 2.439, **5a**: 2.475 Å). There are no noticable differences in C–O bond lengths (1.253–1.255 Å).

Discussion

As the quantum chemical calculations (see above) and experimental observations [13] show, reactions according to Scheme 2 (a) result in the formation of the thermodynamically more stable trans isomers **2**. Taking into account the higher trans influence of the phosphorus donor site than the arsenic donor site in the unsymmetrical chelate ligand dadpe, the major isomer **3a** should be thermodynamically favoured over the minor isomer **3b** (Scheme 2, b).



Scheme 3

We showed [7] that the donor (L/L′) induced cleavage of aldehyde proceeds most probably via the reaction sequence i) formation of a mononuclear platina-*β*-diketone complex **A** by Pt–Cl–Pt bridge cleavage, ii) oxidative addition yielding an hydridoplatinum(IV) complex **B** followed by iii) reductive elimination of aldehyde and formation of an acyl(chloro)platinum(II) complex **C** (Scheme 3). Thus, reactions with monodentate phosphines L/L′ should proceed via the (unseen) intermediate **B**. The diastereomeric structure of **B** is quite analogous to that of the (isolated) platinum(IV) complex shown in Scheme 1. Due to the higher trans influence of the *P* donor over Cl, the acetyl group trans to phosphorus (L in intermediate **B**) should undergo reductive elimination yielding directly the thermodynamically favoured trans complexes **2**. The unsymmetrical dadpe ligand should attack the platinum-*β*-diketone **1** through the stronger donor (phosphorus) yielding the (unseen) intermediate **B** (L ⌒L′ = P ⌒As). Due to the higher trans influence of the *P* donor over the chloro ligand the acyl group trans to P should undergo reductive elimination in such a way that the thermodynamically more stable isomer **3a** is formed.

Experimental

All reactions were performed under an Ar atmosphere using standard Schlenk techniques. The solvents were dried and distilled prior to use. Infrared spectra were recorded on a Galaxy Mattson 5000 FT-IR spectrometer using CsBr pellets. NMR spectra were obtained on Varian Gemini 200, VXR 400, and Unity 500 spectrometers. Chemical shifts are relative to C*H*DCl_2 (δ 5.32), *C*D_2Cl_2 (δ 53.8), *CH*Cl_3 (δ 7.24) and *C*DCl_3 (δ 77.0) as internal references; δ(^{31}P) is relative to external H_3PO_4 (85%). Complexes [Pt_2{(COR)$_2$H}$_2$(μ-Cl)$_2$] (**1**) were prepared according to literature methods [1]. Other chemicals were commercial materials used without further purification or after distillation.

*Synthesis of trans-[Pt(COMe)Cl{P(p-FC_6H_4)$_3$}$_2$] (**2a**)*

To [Pt_2{(COMe)$_2$H}$_2$(μ-Cl)$_2$] (**1**) (75.8 mg, 0.12 mmol) in methylene chloride (3 ml) P(*p*-FC_6H_4)$_3$ (151 mg, 0.48 mmol) was added. After 15 min diethyl ether (10 ml) was added to the pale-yellow solution. After standing 12 hours crystals formed were filtered off and dried in vacuo.

Yield: 178 mg (82%). M. p. 250–252 °C (dec.). $C_{38}H_{27}ClF_6OP_2Pt$ (906.12). C 50.46 (calc. 50.37); H 3.00 (3.00)%.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.24 (s, 3 H, *CH*$_3$), 7.12 ('t', 12 H, Ph), 7.77 (m, 12 H, Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 44.4 (t+d(br), ^3J(P, C) = 6.2 Hz, ^2J(Pt, C) = 121 Hz, *C*H$_3$), 115.9 (d't', ^2J(F, C) = 21.5 Hz, *N* = ^{3+5}J(P, C) = 11.8 Hz, *C*$_m$), 125.4 (d't', ^4J(F, C) = 3.0 Hz, *N* = ^{1+3}J(P, C) = 59 Hz, *C*$_i$), 136.9 ('q', *N* = ^{2+4}J(P, C) = 22.6 Hz, *C*$_o$), 164.5 (d, ^1J(F, C) = 255 Hz, *C*$_p$), 217.9 (t+d, ^2J(P, C) = 5.0 Hz, ^1J(Pt, C) = 922 Hz, *C*O). ^{31}P NMR (81 MHz, $CDCl_3$): δ = 18.6 (s+d, ^1J(Pt, P) = 3499 Hz). IR: ν = 1636 (s, CO), 265 (w, PtCl) cm^{-1}.

*Synthesis of trans-[Pt(COEt)Cl{P(p-$MeOC_6H_4$)$_3$}$_2$] (**2d**)*

To [Pt_2{(COEt)$_2$H}$_2$(μ-Cl)$_2$] (**1**) (94.0 mg, 0.14 mmol) in methylene chloride (3 ml) P(*p*-$MeOC_6H_4$)$_3$ (196.8 mg, 0.56 mmol) was added. Work-up was as described above.

Yield: 133 mg (84%). M. p. 187–189 °C (dec.). $C_{45}H_{47}ClO_7P_2Pt$ (992.37). C 53.51 (calc. 54.47); H 4.65 (4.77), Cl 3.65 (3.65)%.

^{1}H NMR (400 MHz, CD_2Cl_2): δ = –0.09 (t, ^3J(H, H) = 6 Hz, 3 H, *C*H$_3$), 1.52 (q, ^3J(H, H) = 6 Hz, 2 H, CH_2), 3.84 (s, 18 H, O*CH*$_3$), 6.95 ('d', 12 H, *m*-*CH*), 7.65 (m, 12 H, *o*-*CH*). ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 8.2 (*C*H$_3$), 51.1 (t+d(br), ^3J(P, C) = 5.6 Hz, ^2J(Pt, C) ca 180 Hz, *C*H$_2$), 55.5 (O*C*H$_3$), 113.8 ('t', *N* = ^{3+5}J(P, C) = 11.6 Hz, *C*$_m$), 122.3 ('t', *N* = ^{1+3}J(P, C) = 60.5 Hz, *C*$_i$), 136.5 ('t', *N* = ^{2+4}J(P, C) = 13.6 Hz, *C*$_o$), 161.4 (*C*$_p$), 219.8 (t+d(br), ^2J(P, C) = 6.0 Hz, ^1J(Pt, C) ca 950 Hz, *C*O). ^{31}P NMR (81 MHz, CD_2Cl_2): δ = 17.9 (s+d, ^1J(Pt, P) = 3449 Hz). IR: ν = 1649 (s, CO), 260 (w, PtCl) cm^{-1}.

*Synthesis of trans-[Pt(COMe)Cl{P(p-CH_2=CHC_6H_4)Ph_2}$_2$] (**2b**) and trans-[Pt(COMe)Cl{P(n-Bu_3}$_2$] (**2c**)*

To [Pt_2{(COMe)$_2$H}$_2$(μ-Cl)$_2$] (**1**) (32.4 mg, 0.05 mmol) in CD_2Cl_2 (1 ml) the phophine (0.21 mmol) was added. After 10–20 min the pale-yellow solution was investigated by NMR spectroscopy.

2b: ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 1.20 (s, 3 H, C*H*$_3$), 5.40 (d, ^3J(H^a, H^c)[3] = 10.8 Hz, 2 H, *H*^{c}), 5.87 (d, ^3J(H^a, H^b) = 17.6 Hz, 2 H, *H*^{b}), 6.78 (dd, ^3J(H^a, H^c) = 11.0 Hz, ^3J(H^a, H^b) = 17.8 Hz, 2 H, *H*^{a},), 7.55 (m, 16 H, Ph), 7.78 (m, 12 H, Ph). ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 44.1 (t+d(br), ^3J(P, C) = 6.4 Hz, *C*H$_3$), 116.1 (CH=*C*H$_2$), 136.2 (*C*H=CH$_2$), 216.1 (t, ^2J(P, C) = 5.8 Hz, *C*O); *C*$_{arom}$[4]: 126.1 ('t', *N* = 10.7 Hz), 128.5 ('t', *N* = 10.8 Hz), 131, 135.1 ('t', *N* = 12.5 Hz), 135.4 ('t', *N* = 12.4 Hz), 140.2. ^{31}P NMR (81 MHz, CD_2Cl_2): δ = 20.8 (s+d, ^1J(Pt, P) = 3501 Hz).

[3] CH^{b}H^c=CH^a–: H^b/H^c – trans/cis to H^a.

[4] 6 of 8 aromatic carbon atoms were detected.

2c: ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 0.88 (t, 18 H, CH_2CH_3), 1.45 (m, 24 H, CH_2), 1.76 (m, 12 H, CH_2), 2.16 (s+d, ^3J(Pt, H) = 12.8 Hz, 3 H, $COCH_3$). ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 13.7 (CH_2CH_3), 21.9 ('t', $N = {}^{3+5}J$(P, C) = 32.4 Hz, CH_2CH_3), 24.4 ('t', $N = {}^{2+4}J$(P, C) = 17.5 Hz, PCH_2CH_2), 26.2 (s+d, ^2J(Pt, C) = 25.3 Hz, PCH_2), 47.1 (t+d, ^3J(P, C) = 4.4 Hz, ^2J(Pt, C) = 287 Hz, $COCH_3$), 215.8 (t, ^2J(P, C) = 6.8 Hz, *C*O). ^{31}P NMR (81 MHz, CD_2Cl_2): δ = 8.2 (s+d, ^1J(Pt, P) = 3075 Hz).

*Synthesis of [Pt(COMe)Cl(dadpe)] (**3a**)*

To $[Pt_2\{(COMe)_2H\}_2(\mu\text{-}Cl)_2]$ (**1**) (65.0 mg, 0.10 mmol) in acetone (2 ml) a solution of dadpe (88 mg, 0.20 mmol) in acetone (2 ml) was added dropwise at –30 °C. The reaction mixture was slowly warmed to room temperature and investigated by means of ^{31}P NMR spectroscopy exhibiting a ratio **3a**:**3b** of about 9:1 (^{31}P NMR (81 MHz, CD_2Cl_2): δ = 32.2 (s+d, ^1J(Pt, P) = 4454 Hz, *P*(**3a**)), 43.7 (s+d, ^1J(Pt, P) = 1720 Hz, *P*(**3b**))). After standing 12 hours, the crystals of 3a were filtered off and dried in vacuo. Yield: 56 mg (78%).

^{1}H NMR (400 MHz, CD_2Cl_2): δ = 1.89 (s(br), 3 H, CH_3), 2.05 (m, 2 H, CH_2), 2.51 (m, 2 H, CH_2), 7.46–7.78 (m, 20 H, Ph). ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 21.2 (d, ^2J(P, C) = 6.0 Hz, $AsCH_2$), 30.0 (d+d, ^1J(P, C) = 41 Hz, ^2J(Pt, C) = 195 Hz, PCH_2), 41.3 (d, ^3J(P, C) = 5 Hz, CH_3), 128.8 (d, ^1J(P, C) = 60 Hz, C_i(P)), 129.3 (d, ^3J(P, C) = 10 Hz, C_m(P)), 129.6 (C_m(As)), 130.8 (C_p(P)[5]), 131.9 Hz, (C_i(As)[5]), 133.1 (C_o(As)), 133.6 (d, ^2J(P, C) = 11 Hz, C_o(P)), 133.9 (C_p(As)[5]), 231.5 (*C*O).

Crystallographic studies

Intensity data for **2a** and **3a** were collected on a Siemens Smart diffractometer with MoKα radiation (0.71073 Å, graphite monochromator). A summary of crystallographic data, data collection parameters, and refinement parameters is given in Table 4. **2a** and **3a** were corrected for absorption empirically and numerically, respectively. The structures were solved by direct methods with SHELXS-86 [14] and refined using full-matrix least-squares routines against F^2 with SHELXL-93 [14]. Non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atom positions were calculated and allowed to ride on the corresponding carbon atoms. The isotropic displacement parameters were tied to those of the adjacent carbon atoms by a factor of 1.2.

Crystallographic data (excluding structure factors) for **2a** and **3a** have been deposited at the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-137940 (**2a**) and 137941 (**3a**), respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2, 1EZ, UK [Fax: (internat.) +44(0)1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Quantum Chemical Calculations

DFT (B3LYP/LANL2DZ and BP86/LANL2DZ) closed shell calculations were carried out for model complexes *cis*/*trans*-$[Pt(COMe)Cl(PR_3)_2]$ (R = H **4a/b**, Me **5a/b**, Ph **6a/b**), using effective core approximations for the core orbitals of platinum [15] and a double zeta split for the other orbitals applying the Gaussian 98 package [16]. Complexes **4** and **5** were fully optimized and characterized as equilibrium structures by the analysis of the vibrational frequencies. Due to the large number of atoms, for complexes **6** the optimized structures of complexes **5** were used in which the methyl substituents at phosphorus were formally replaced by phenyl rings which were optimized with the semiempirical method PM3.

[5] Assignment uncertain.

Table 4 Crystal data and structure refinement for *trans*-$[Pt(COMe)Cl\{P(p\text{-}FC_6H_4)_3\}_2]$ **2a** and [Pt(COMe)Cl(dadpe)] **3a**.

formula	$C_{38}H_{27}ClF_6OP_2Pt$	$C_{28}H_{27}AsClOPPt$
formula weight	906.08	715.93
T, K	150(2)	150(2)
crystal system, space group	monoclinic, $P2_1$ (no. 4)	monoclinic, $P2_1/n$ (no. 14)
a, b, c, Å	11.1640(6), 14.6189(8), 11.8404(6)	8.9883(1), 27.2048(4), 12.1843(2)
β, °	115.176(1)	105.13(1)
V, Å^3	1748.9(2)	2876.13(7)
Z	2	4
ρ_{calc}, g cm^{-3}	1.721	1.653
μ, mm^{-1}	4.242	6.186
θ range, °	2.36–26.00	2.29–29.59
limiting indices	$-8 \le h \le 13$; $-17 \le k \le 17$; $-14 \le l \le 12$	$-11 \le h \le 11$; $-37 \le k \le 27$; $-16 \le l \le 11$
refl. collected	10351	35992
refl. unique	6669 [R(int) = 0.0545]	6207 [R(int) = 0.0145]
refl. observed [$I > 2\sigma(I)$]	5622	5857
data/restraints/parameters	6669/1/442	6207/0/299
Goodness-of-fit on F^2	1.182	1.245
$R1$ (obs. data)	0.0707	0.0509
$wR2$ (all data)	0.1615	0.1422
absolute structure parameter	–0.02(2)	–
largest peak/hole, e Å^{-3}	3.212/–1.519	2.551/–2.196

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