Polyhedron 32 (2012) 24–29

Contents lists available at SciVerse ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Carboxylation of pincer PCP platinum methoxide complexes under formation of metalla carbonates

Athimoolam Arunachalampillai, Nagarajan Loganathan, Ola F. Wendt *

Centre for Analysis and Synthesis, Department of Chemistry, Lund University, P.O. Box 124, S-221 00 Lund, Sweden

ARTICLE INFO

Article history:
Available online 3 September 2011

Keywords:
Platinum
Carbon dioxide
Pincer ligands
Alkoxide complexes
Carbonate complexes

ABSTRACT

The ligand 2,6-bis[(diphenylphosphino)methyl]benzene ((PCP)H) was prepared and characterised in an improved manner. With platinum it forms the complex (PCP)PtOTf which reacts with sodium methoxide to give (PCP)PtOMe as the major product together with a small amount of $[(PCP)Pt]_2$-μ-H. The platinum methoxide reacts with carbon dioxide to give (PCP)PtO(CO)OMe. Also the dinuclear $[(PCP)Pt]_2$(μ-O(CO)OMe) is formed in this reaction if (PCP)PtOTf is present. The crystal structures for $[(PCP)PtOH_2]$OTf, PCP)PtOMe, $[(PCP)Pt]_2$-μ-H and $[(PCP)Pt]_2$(μ-O(CO)OMe) are reported.

1. Introduction

The use of carbon dioxide as a raw material is attractive because it is abundant, cheap and non-toxic and transition metal mediated activation has received considerable attention lately. Among the reactions involving CO_2 that have the highest success probability in the short run are those where the (OCO)-fragment is intact in the product, such as carbonates, since these require the least energy input [1]. There has also been significant progress in making polymeric carbonates from epoxides and CO_2 [2], whereas the carboxylation of alcohols is still a challenge with the best homogeneous catalysts being tin or early transition metal alkoxides [3].

We have investigated the reactivity of transition metal-carbon bonds towards carbon dioxide using palladium ligated with tridentate PCP pincer ligands [4], and we decided to expand these investigations to include alkoxides, since, compared with the many studies of the reactivity of metal-carbon bonds, there is much less information on the reactivity of late metal alkoxides and several studies also suggest a difference in fundamental mechanisms, e.g. for β-elimination [5]. Late metal alkoxides are potentially interesting for catalytic transformations of carbon dioxide because of the high reactivity towards carbon dioxide reported for such species [6]. Lately there have been reports on the reactivity of nickel alkoxides and amides towards CO_2 and also on the insertion of CO_2 into a PCP platinum amides [7], but little has been reported on the reaction of platinum alkoxides towards carbon dioxide. Here we report on the synthesis, stability and CO_2 insertion reactivity of a (PCP) platinum methoxide complex.

2. Experimental

2.1. General procedures and materials

All experiments with air-sensitive compounds were carried out under an atmosphere of nitrogen in a glove box or using standard Schlenk or high vacuum-line techniques [8]. All non-deuterated solvents were vacuum-transferred from sodium/benzophenone ketyl directly to the reaction vessel, except chlorinated solvents which were distilled from calcium hydride. Commercial grade CO_2 was dried using P_2O_5 and a dry ice-acetone mixture prior to use. Benzene-d_6 was dried over sodium/benzophenone ketyl and vacuum transferred directly to the NMR tube. All the other commercially available reagents were purchased from Sigma–Aldrich and used as received. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Varian Unity INOVA 500 spectrometer working at 499.77 MHz (^{1}H). The NMR spectroscopic measurements were performed in benzene-d_6 unless otherwise stated. (COD)PtClN$(SiMe_3)_2$ was prepared according to a reported procedure [9]. Chemical shifts are given in ppm downfield from TMS using residual solvent peaks (^{1}H NMR, ^{13}C NMR) or H_3PO_4 as reference. Elemental analyses were performed by H. Kolbe, Mülheim an der Ruhr, Germany.

2.2. Synthesis of 2,6-bis[(diphenylphosphino)methyl]benzene, (PCP)H, (**1**)

This ligand was synthesised using a slightly modified literature procedure [10]. To a solution of α,α′-dichloro-*m*-xylene (0.78 g, 4.5 mmol) in THF (30 mL) a potassium diphenylphosphide solution (2.0 g, 8.9 mmol) in THF was added over a period of 10 min. The mixture was stirred vigorously for 6 h and the solvent was

---

* Corresponding author. Fax: +44 1223 336 033.
E-mail address: ola.wendt@organic.lu.se (O.F. Wendt).

0277-5387/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2011.08.028

evaporated *in vacuo*; the mixture was re-dissolved in ether (75 mL) and filtered through a glass frit with celite. Evaporation of the ether solution afforded the ligand as a low melting solid. Yield: 1.92 g (90.1%). *Anal.* Calc. for $C_{32}H_{28}P_2$: C, 81.00; H, 5.95; P, 13.05. Found: C, 80.76; H, 5.90; P, 13.00%. ^{1}H NMR: δ 3.22 (bs, 4H, PCH_2), 6.69 (d, 2H, ^3J = 7.5 Hz, p-H of centre phenyl), 6.79 (s, 1H, o-H of centre phenyl), 6.85 (t, 1H, ^3J = 7.5 Hz, m-H of centre phenyl), 7.19 (m, 12H, P-phenyl) and 7.26 (m, 8H, P-phenyl). $^{13}C\{^1H\}$ NMR: δ 35.87 (d, $^1J_{P\text{–}C}$ = 14.3 Hz, PCH_2), 127.10 (dd, $^5J_{P\text{–}C}$ = 2.9 and $^3J_{P\text{–}C}$ = 6.9 Hz, p-C of the centre phenyl), 128.21 (t, $^4J_{P\text{–}C}$ = 1.9 Hz, m-C of the centre phenyl), 128.5 (d, $^2J_{P\text{–}C}$ = 6.7 Hz, o-C of P-phenyls), 130.55 (t, $^3J_{P\text{–}C}$ = 7.2 Hz, o-C of the centre phenyl), 132.99 (s, p-C of P-phenyls), 133.14 (s, m-C of P-phenyls), 137.30 (dd, $^4J_{P\text{–}C}$ = 1.5 and $^2J_{P\text{–}C}$ = 7.9 Hz, i-C of the centre phenyl) and 138.10 (d, $^1J_{P\text{–}C}$ = 13.8 Hz, i-C of P-phenyls). $^{31}P\{^1H\}$ NMR: δ −9.3 (s).

2.3. Synthesis of (PCP)Pt–Cl (**3**), (PCP)Pt–I (**3a**), (PCP)Pt–OTf (**4**) and [(PCP)Pt–OH$_2$]CF$_3$SO$_3$ (**5**)

Complexes **3, 3a** and **4** were prepared according to reported procedures [9–11]. Recrystallisation of complex **4** from a wet dichloromethane and hexane mixture afforded colourless crystals of **5** quantitatively. *Anal.* Calc. for $C_{33}H_{29}F_3O_4P_2SPt$: C, 47.43; H, 3.50; P, 7.41. Found: C, 47.35; H, 3.58; P, 7.35%. ^{1}H NMR: δ 3.27 (t, 4H, $^2J_{P\text{–}H}$ = 4.5 Hz, PCH_2), 6.82 (d, 2H, $^3J_{H\text{–}H}$ = 7.5 Hz, p-H of centre phenyl), 6.95 (t, 1H, $^3J_{H\text{–}H}$ = 7.5 Hz, m-H of centre phenyl), 7.00 (t, 4H, $^3J_{H\text{–}H}$ = 7.5 Hz, P-phenyl), 7.05 (t, 8H, $^3J_{H\text{–}H}$ = 7.5 Hz, P-phenyl) and 7.80 (q, 8H, $^3J_{H\text{–}H}$ = 7.5 Hz, P-phenyl). $^{13}C\{^1H\}$ NMR: δ 41.82, 123.08, 126.09, 128.20, 128.88, 131.03, 131.68, 133.32 and 145.20. $^{31}P\{^1H\}$ NMR: δ 39.9 (s, with platinum satellites, $J_{Pt\text{–}P}$ = 3019 Hz). ^{19}F NMR: δ −77.58 (s).

2.4. Synthesis of [(PCP)Pt]$_2$-μ-H (**6**) and (PCP)Pt–OMe (**7**)

To a colourless solution of **4** (0.25 g, 0.3 mmol) in THF (10 mL), NaOMe (0.08 g, 1.5 mmol) was added and the mixture was stirred for 3 h. The solution was filtered and the THF was evaporated *in vacuo*. The slightly coloured solid was dissolved in benzene (25 mL), leaving behind colourless crystals of **6**, which were filtered and dried. Yield: 0.023 g (11%). *Anal.* Calc. for $C_{64}H_{55}P_4Pt_2$: C, 57.40; H, 4.21; P, 9.26. Found: C, 56.35; H, 4.10; P, 9.20%. ^{1}H NMR (dichloromethane-d$_2$): δ −6.59 (quintet with platinum satellites, 1H, $^2J_{P\text{–}H}$ = 9.0 Hz and $^1J_{Pt\text{–}H}$ = 504 Hz, hydride), 3.52 (t, 4H, $^2J_{P\text{–}H}$ = 4.0 Hz, PCH_2), 6.93 (t, 8H, $^3J_{H\text{–}H}$ = 8.0 Hz, phenyl), 7.07 (m, 4H, phenyl), 7.14–7.27 (m, 11H, phenyl). $^{13}C\{^1H\}$ NMR (dichloromethane-d$_2$): δ 44.45 (t, $^1J_{P\text{–}C}$ = 18.7 Hz, PCH_2), 123.26 (t, $^3J_{P\text{–}C}$ = 9.7 Hz, m-C of the centre phenyl), 126.70 (s, p-C of the centre phenyl), 128.5 (s, o-C of the centre phenyl), 128.8 (t, ^3J = 5.3 Hz, m-C of P-phenyls), 131.35 (s, p-C of P-phenyls), 131.51 (t, $J_{Pt\text{–}C}$ = 55.3 Hz, Pt–C), 132.82 (t, $^2J_{P\text{–}C}$ = 6.2 Hz, o-C of P-phenyls) and 145.30 (t, $^1J_{P\text{–}C}$ = 7.7 Hz, i-C of P-phenyls). ^{31}P NMR (dichloromethane-d$_2$): δ 38.1 (d, with platinum satellites, $^2J_{P\text{–}H}$ = 6 Hz, $^1J_{Pt\text{–}P}$ = 2892 Hz, $^3J_{Pt\text{–}P}$ = 32 Hz). Evaporation of the benzene solution afforded slightly coloured solid **7** which was recrystallised from a benzene/ether mixture. Yield: 0.15 g (71%). *Anal.* Calc. for $C_{33}H_{30}OP_2Pt$: C, 56.65; H, 4.32. Found: C, 56.55; H, 4.30%. ^{1}H NMR: δ 3.55 (t, 4H, $^2J_{P\text{–}H}$ = 4.5 Hz, PCH_2), 4.41 (s, with platinum satellites, 3H, $^3J_{Pt\text{–}H}$ = 23.5 Hz, Pt–OMe), 6.96 (d, 2H, $^3J_{H\text{–}H}$ = 6.0 Hz, m-H of the centre phenyl), 7.00 (t, 4H, $^3J_{H\text{–}H}$ = 8.0 Hz, p-H of the P-phenyls), 7.05 (t, 8H, $^3J_{H\text{–}H}$ = 7.0 Hz, o-H of the P-phenyls), 7.13 (t, 1H, $^3J_{H\text{–}H}$ = 7.5 Hz, p-H of the centre phenyl), 8.01 (q, 8H, $^3J_{H\text{–}H}$ = 6.0 Hz, m-H of the P-phenyls). $^{13}C\{^1H\}$ NMR: δ 43.47 (t, $^1J_{P\text{–}C}$ = 18.9 Hz, PCH_2), 63.60 (t, $^4J_{P\text{–}C}$ = 5.8 Hz, Pt–OMe), 122.47 (t, $^3J_{P\text{–}C}$ = 9.5 Hz, m-C of the centre phenyl), 124.40 (s, p-C of the centre phenyl), 128.18 (s, o-C of the centre phenyl), 128.68 (t, $^3J_{P\text{–}C}$ = 5.2 Hz, m-C of P-phenyls), 130.35 (s, p-C of P-phenyls), 133.25 (t, $^2J_{P\text{–}c}$ = 6.5 Hz, o-C of P-phenyls), 133.43 (t, $^1J_{Pt\text{–}C}$ = 47.7 Hz, Pt–C) and 148.20 (t, $^1J_{P\text{–}C}$ = 9.1 Hz, i-C of P-phenyls). $^{31}P\{^1H\}$ NMR: δ 31.8 (s, with platinum satellites, $J_{Pt\text{–}P}$ = 3142 Hz).

2.5. Synthesis of (PCP)Pt–O(CO)OMe (**9**)

To a pale yellow coloured solution of **7** (0.10 g, 0.14 mmol) in benzene (5 mL) 3 atm of dry carbon dioxide was added and the mixture was stirred for 10 min. The solution was concentrated to 2 mL and left standing at room temperature. Colourless crystalline plates of **9** were formed and these were filtered and dried. Yield: 0.10 g (96%). *Anal.* Calc. for $C_{34}H_{30}O_3P_2Pt$: C, 54.92; H, 4.07; P, 8.33. Found: C, 55.06; H, 4.20; P, 8.26%. ^{1}H NMR: 3.33 (t, 4H, $^2J_{P\text{–}H}$ = 4.5 Hz, PCH_2), 3.49 (s, –COOMe), 6.90 (t, 1H, $^3J_{H\text{–}H}$ = 7.5 Hz, p-H of the centre phenyl), 6.93 (d, 2H, $^3J_{H\text{–}H}$ = 7.5 Hz, m-H of the centre phenyl), 6.98 (tt, 12H, $^3J_{H\text{–}H}$ = 1.5 and 7.0 Hz, phenyls), 7.88 (tq, 8H, $^3J_{H\text{–}H}$ = 1.0 and 6.0 Hz, phenyls). $^{13}C\{^1H\}$ NMR: δ 42.34 (t, $^1J_{P\text{–}C}$ = 18.2 Hz, PCH_2), 53.34 (s, –OMe), 122.72 (t, $^3J_{P\text{–}C}$ = 9.1 Hz, m-C of the centre phenyl), 125.20 (s, p-C of the centre phenyl), 128.65 (t, $^3J_{P\text{–}C}$ = 5.3 Hz, m-C of P-phenyls), 130.47 (s, p-C of P-phenyls), 132.52 (s, $^1J_{Pt\text{–}C}$ = 52.8 Hz, Pt–C), 133.27 (t, $^2J_{P\text{–}c}$ = 6.8 Hz, o-C of P-phenyls), 140.0 (s, o-C of the centre phenyl), 148.20 (t, $^1J_{P\text{–}C}$ = 9.1 Hz, i-C of P-phenyls) and 160.2 (s, Pt–O–C). $^{31}P\{^1H\}$ NMR: δ 36.9 (s, with platinum satellites, $J_{Pt\text{–}P}$ = 3091 Hz). IR: $\nu(C{=}O)$ 1661 cm^{-1}.

2.6. Crystallography

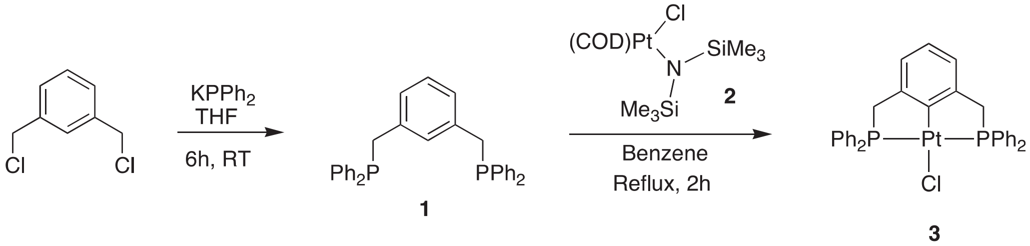
Intensity data were collected at 293 K with an Oxford Diffraction Xcalibur 3 system using ω-scans and Mo Kα (λ = 0.71073 Å) [12]. CCD data were extracted and integrated using Crysalis RED [13]. The structures were solved using direct methods and refined by full-matrix least-squares calculations on F^2 using SHELXTL 5.1 [14]. Non-H atoms were refined with anisotropic displacement parameters, unless otherwise indicated. Hydrogen atoms were constrained to parent sites, using a riding model. In the structure of complex **5** there are two remaining large difference Fourier peaks but they are located <1 Å from the platinum atom. In the crystal structure of complex **6** we tried to resolve the disorder in the benzene and triflic acid molecules using restraints but this was unsuccessful. The crystal quality of compound **8** was low giving poor data. Thus, only a few non-H atoms were refined with anisotropic displacement parameters and most were refined isotropically. All atoms could be located but the solvent molecules were disordered and these were instead treated using a SQUEEZE procedure [15]. Overall this gives a model with many remaining alert A's in the CIF-check and the structure is only reliable insofar as connectivity is concerned. All crystallographic data is available in CIF format. CCDC reference numbers 778661–778664.

3. Results and discussion

3.1. Synthesis and characterisation of the platinum alkoxide

The diphenyl phosphine ligand **1** was first synthesised in 1983, but no thorough characterisation data have been reported [10,11b]. To improve the synthetic procedure we employed the commercially available potassium diphenyl phosphide, reacting this with α,α'-dichloro xylene in THF. This afforded the ligand analytically pure in 90% yield. It was characterised by multinuclear NMR spectroscopy and elemental analysis. Cyclometallation was then achieved using a procedure recently reported by us giving the chloro complex **3**, cf. Scheme 1 [9].

Platinum alkoxides have sometimes been synthesised through salt metathesis of the halides and initially we attempted this



Scheme 1.

reaction for the synthesis of the tert-butoxide derivatives of **3**. We chose the tert-butoxide to avoid any elimination reactions thinking that the bulky tert-butoxide should be sterically compatible with the diphenyl phosphine moiety. However, **3**, and its iodo analogue **3a**, failed to react with sodium tert-butoxide in THF also at elevated temperatures. This has been observed earlier and the usual solution has been to use triflate or, as reported recently for nickel derivatives, fluoride as the leaving group [16]. Thus, we synthesised the triflate complex **4** using the standard silver triflate reaction as reported in the literature [11c]. Upon recrystallisation from dichloromethane/hexane under ambient conditions we obtained a material that is probably the corresponding aqua complex **5**, cf. Scheme 2. It was characterised by multinuclear NMR spectroscopy, elemental analysis and X-ray crystallography. Although no obvious coordinated water peak could be observed in the ^{1}H NMR there is a peak at δ 0.40 ppm corresponding to free water although dry benzene was used. This indicates that in solution there is some ion pairing at least partly displacing the water molecule. The molecular structure is given in Fig 1 and crystal data and details about data collection are given in Table 1.

The structure is the expected mononuclear pseudo square planar platinum exhibiting the typical bent-back P–Pt–P angle (165.5°) because of the limitations from the rigid ligand backbone, as is almost always seen for PCP complexes. The complexes form hydrogen bonded dimers together with two triflate anions with O–O distance of 2.668(11) Å (O1–O3) and 2.715(4) Å (O1*–O4) indicating fairly strong hydrogen bonds. Thus, an 8-membered ring is formed from the two sulfur and six oxygen atoms. We formulate complex **5** as an aqua complex, but of course it cannot be ruled out that it is a hydroxide complex with a molecule of triflic acid in the crystal lattice. However, the hydroxide would be highly basic and probably react with the triflic acid [17]. Furthermore, looking at bond distances seems to support our formulation; the Pt–O distance is 2.156(7) Å which is in line with similar aqua complexes, whereas corresponding hydroxides usually display shorter distances [18]. Similar triflate displacements are well known [19].

However, also **4** was unreactive towards sodium tert-butoxide and we conclude that the steric demand of the PCP ligand is not compatible with the bulky tert-butoxide. It has been reported previously that tert-butoxides are too bulky to react with pincer ligated palladium [5b] and we then reacted **4** with sodium methoxide at room temperature in THF. This gave a mixture of two products, which were fairly easily separated with the minor one being sparingly soluble in benzene. By filtering, it could be isolated analytically pure in 11% yield and it was identified as the dinuclear hydride, **6**, cf. Scheme 3.

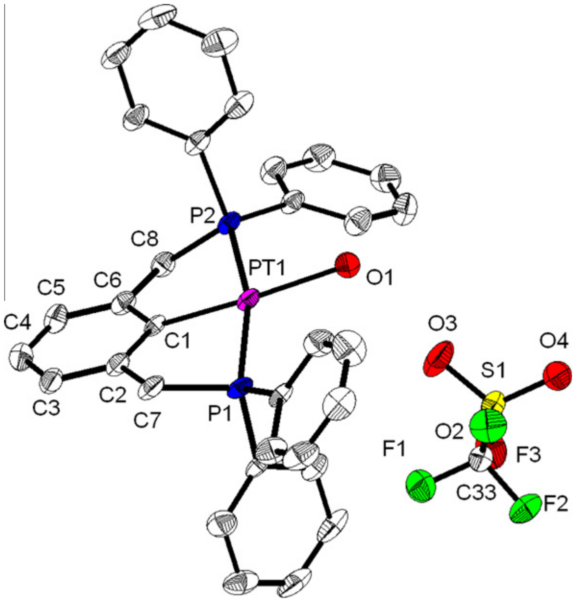
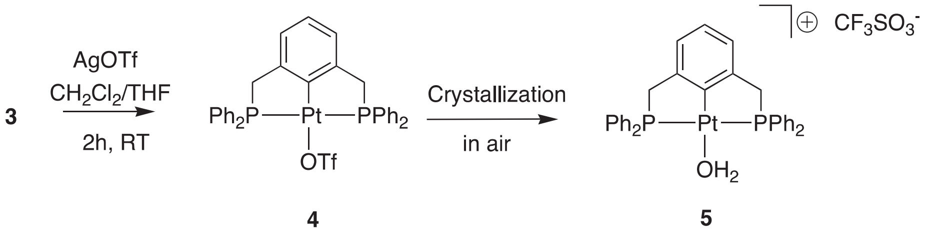


Fig. 1. DIAMOND drawing of **5**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å): Pt1–C1 1.995(9), Pt1–O1 2.156(7), Pt1–P2 2.294(3), Pt1–P1 2.298(3).

The hydride is observed as a quintet ($\delta = -6.59$ ppm) in ^{1}H NMR spectroscopy with $^2J_{HP} = 9$ Hz. The structure of complex **6** was unambiguously (apart from the number and positions of the hydrogens) confirmed using X-ray crystallography. A perspective view of the molecular structure (excluding the phosphine phenyl groups) is shown in Fig. 2, including selected bond distances and angles. The two coordination planes are situated at a 67° angle towards each other. In addition to **6** the unit cell contains highly disordered molecules of benzene, THF and triflate. The position of the hydrogens in complex **6** is clearly a case of “proton ambiguity”, where a reasonable structure would be a cationic, dinuclear

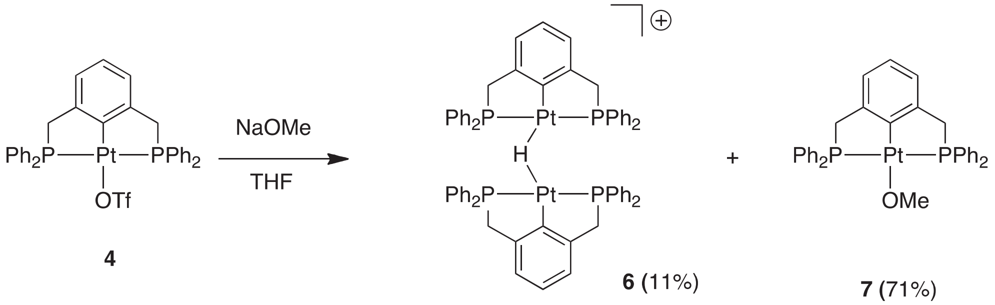


Scheme 2.

Table 1
Crystal data for **5**, **6**, **7** and **8**.

	5	**6**	**7**	**8**
Formula	$C_{33}H_{29}F_3O_4P_2PtS$	$C_{75}H_{68}F_3O_4P_4Pt_2S$	$C_{36}H_{33}OP_2Pt$	$C_{74}H_{62}F_6O_9P_4Pt_2S_2$
Formula weight	835.65	1636.41	738.65	1787.42
Space group	$P\bar{1}$	P2(1)/n	$P\bar{1}$	$P\bar{1}$
a (Å)	9.6441(14)	15.4226(3)	8.824(2)	9.9203(2)
b (Å)	13.8854(19)	17.5298(3)	12.5170(19)	16.1494(4)
c (Å)	14.012(3)	25.4852(4)	14.712(2)	23.4661(7)
α (deg)	119.084(13)	90	91.936(12)	72.573(2)
β (deg)	93.431(17)	97.309(2)	104.959(16)	83.991(2)
γ (deg)	104.595(12)	90	104.199(17)	74.829(2)
V (Å^3)	1549.6(4)	6834.1(2)	1513.6(5)	3460.45(15)
Z	2	4	2	2
D_{calc} (g cm^{-3})	1.791	1.590	1.621	1.715
μ (mm^{-1})	4.754	4.270	4.768	4.265
θ (range/deg)	2.23–32.30	2.27–32.76	2.10–32.65	2.13–19.59
No. of reflections collected	8361	49860	13124	8237
No. of unique reflections	6926	22441	9323	5589
$R(F)$ ($I > 2\sigma(I)$)[a]	0.0729	0.0400	0.0609	0.0965
$wR2(F^2)$ (all data)[b]	0.1795	0.0929	0.1485	0.2933
S[c]	0.979	0.841	0.809	4.843
R_{int}	0.0308	0.0453	0.0692	0.0182
CCDC	778661	778662	778663	778664

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$.
[b] $wR2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{0.5}$.
[c] $S = [\Sigma w(|F_o| - |F_c|)^2/(m - n)]1/2$.



Scheme 3.

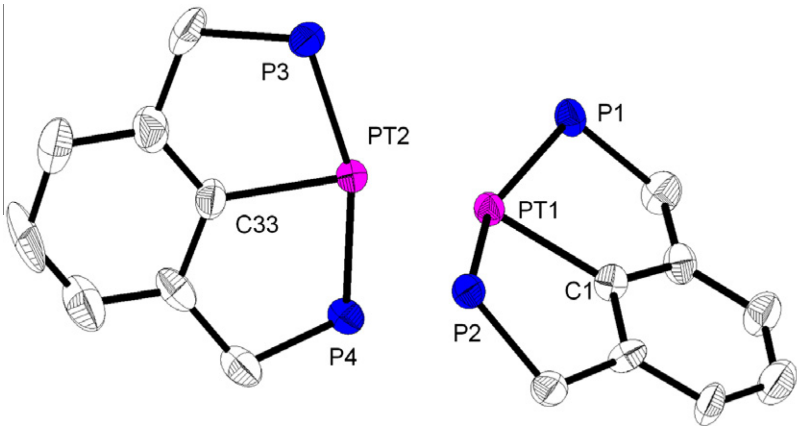


Fig. 2. DIAMOND drawing of **6**. Hydrogen atoms phenyl rings on the phosphines are omitted for clarity. Selected bond distances (Å) and angles (deg): Pt1–C1 2.062(5), Pt1–P1 2.2662(12), Pt1–P2 2.2836(13), Pt1–Pt2 2.9131(3), Pt2–C33 2.073(5), Pt2–P3 2.2759(14), Pt2–P4 2.2976(14), P1–Pt1–P2 153.91(5), P3–Pt2–P4 160.94(5).

platinum monohydride with a triflate counteranion. The platinum methoxide complex could undergo a β-hydride elimination as is often observed for such ligands [20] and the so formed hydride could displace the triflate of unreacted **4** to give complex **6**. This is also compatible with the coupling pattern of the hydrides. They appear as a quintet with coupling to the 4 equivalent phosphorus atoms and applying ^{31}P broadband decoupling the quintet collapses to a singlet. More importantly, applying off-resonance (from the hydride peak) ^{1}H decoupling the ^{31}P spectrum of **6** displays an ill-resolved doublet with a $^{2}J_{PH}$ coupling constant of approximately 6 Hz, a value which is in the same region as in the proton spectrum; this clearly indicates the presence of one hydride.

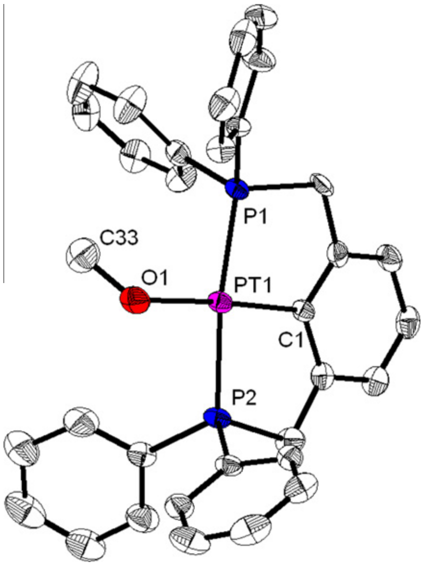
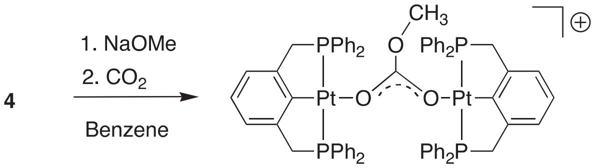


Fig. 3. DIAMOND drawing of **7**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Pt1–C1 2.054(7), Pt1–O1 2.086(6), Pt1–P2 2.263(2), Pt1–P1 2.270(2), P2–Pt1–P1 166.61(7).



Scheme 4.

Interestingly, the ^{31}P spectrum also shows the presence of long-range platinum satellites with a ^{3}J coupling constant of ca 32 Hz; with poor decoupling all peaks broaden and the satellites can easily be mistaken for a triplet, which would indicate the presence of two equivalent hydrides. Integration also supports the formulation of a monohydride. The Pt–Pt distance is 2.913(1) Å, which is in the lower range compared to similar complexes indicating the presence of some metal–metal interaction [21]. The dimerisation could be triggered by the lower solubility of the dimer [22].

After removal of **6** by filtration, the remaining solution contained a single product which was isolated in 71% yield and characterised as the methoxide complex **7**. The ^{31}P{^{1}H} NMR resonance is seen at 31.8 ppm and the ^{1}H NMR spectrum displays a methoxide resonance at 4.41 ppm with typical platinum satellites. Compound **7** is fairly thermally stable but we were unable to synthesise it without some accompanying formation of **6**, as mentioned earlier [23]. Still, due to their different solubilities, **7** was easily obtained in an analytically pure form. Compound **7** is also sensitive to moisture forming what is probably the hydroxide. No systematic study of its thermal stability was performed. The compound was also characterized by X-ray crystallography and the molecular structure is shown in Fig 3. It displays a mononuclear distorted square-planar coordination geometry with only weak intermolecular forces. The lattice contains one molecule of benzene solvent/platinum and the methoxy oxygens form interactions to the solvent, typical for a weak O···C–H hydrogen bond (D = 3.47 Å; d = 2.61 Å; θ = 155°) [24].

Having obtained the methoxide complex **7** we were very interested in its reactivity towards carbon dioxide. Initially we therefore reacted **4** with NaOMe in THF and then stripped the solvent, added benzene and reacted the resulting solution with carbon dioxide in situ. From this reaction we harvested a small amount of a crystalline material that was subjected to an X-ray analysis and turned out to be the dinuclear carbonate complex, **8**, cf. Scheme 4. The molecular structure is shown in Fig. 4. In addition to the dinuclear cationic species shown in Fig. 4 the unit cell contains one triflate moiety and disordered solvent. We did not optimise the reaction conditions to obtain **8** and it was never isolated in a large amount enough to allow micro analysis. It cannot be excluded that the isolation of the di-nuclear species was in part due to its lower solubility and that it was formed concomitantly with **9**. However, to avoid this dimerization we instead reacted the isolated platinum methoxide with carbon dioxide in benzene (Scheme 5). This immediately gave the monomeric hemicarbonate **9**, which was isolated and fully characterised by micro analysis and multinuclear NMR spectroscopy. Unfortunately, it failed to give X-ray quality crystals and we were only able to generate very poor data sets. The methoxy group of the terminal carbonate is seen as a peak at 3.49 and 53.34 ppm in the ^{1}H and ^{13}C NMR spectra [25]. The ^{13}C carbonyl carbon resonance is found at 160.2 ppm similar to what has been observed in terminal alkyl carbonate complexes of manganese and tin [26]. It displays an HMBC correlation with the ^{1}H NMR peak of the methoxy group.

In conclusion we have been able to show that with a (PCP) platinum framework the tert-butoxide complex is unattainable probably for steric reason but the corresponding methoxide complex can

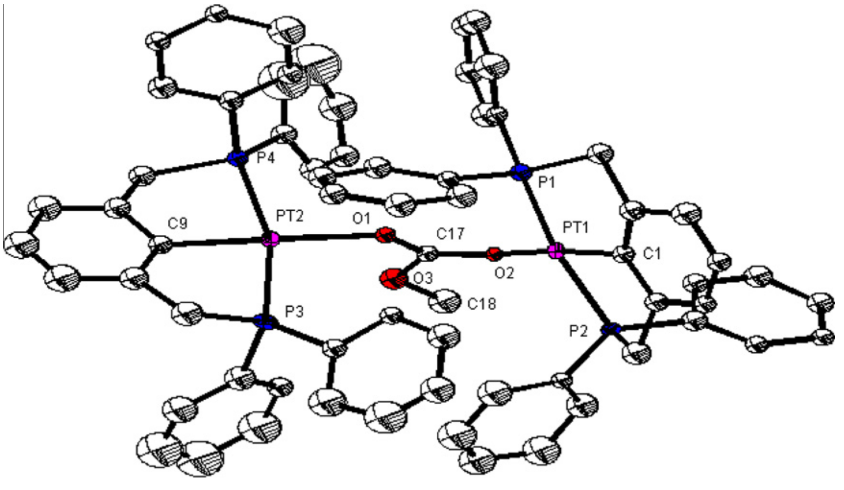
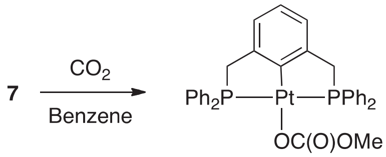


Fig. 4. DIAMOND drawing of **8**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å).



9

Scheme 5.

be synthesised together with a small amount of metal hydride complex. The methoxide readily undergoes insertion to form a methyl carbonate complex. The functionalisation of the platina carbonate is the subject of on-going investigations.

Acknowledgement

Financial support from the Swedish Research Council, the Crafoord Foundation, the Knut and Alice Wallenberg Foundation and the Royal Physiographic Society in Lund is gratefully acknowledged.

Appendix A. Supplementary data

CCDC 778661–778664 contains the supplementary crystallographic data for compounds **5**, **6**, **7** and **8**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

References

[1] (a) S.N. Riduan, Y. Zhang, Dalton Trans. 39 (2010) 3347;
(b) T. Sakakura, K. Kohno, Chem. Comm. (2009) 1312;
(c) T. Sakakura, J.-C. Choi, H. Yasuda, Chem. Rev. 107 (2007) 2365.
[2] (a) D.J. Darensbourg, Chem. Rev. 107 (2007) 2388;
(b) G.W. Coates, D.R. Moore, Angew. Chem. Int. Ed. 43 (2004) 6018.
[3] (a) T. Sakakura, Y. Saito, M. Okano, J.-C. Choi, T. Sako, J. Org. Chem. 63 (1998) 7095;
(b) A. Dibenedetto, C. Pastore, M. Aresta, Catal. Today 115 (2006) 88;
(c) M. Aresta, A. Dibenedetto, C. Pastore, Inorg. Chem. 42 (2003) 3256 (For a review see ref 1(b) or (c)).
[4] (a) R. Johansson, M. Jarenmark, O.F. Wendt, Organometallics 24 (2005) 4500;
(b) R. Johansson, O.F. Wendt, Dalton Trans. (2007) 488;
(c) R. Johansson, O.F. Wendt, Organometallics 26 (2007) 2426;
(d) M.T. Johnson, R. Johansson, M.V. Kondrashov, G. Steyl, M.S.G. Ahlquist, A. Roodt, O.F. Wendt, Organometallics 29 (2010) 3521.
[5] (a) J.R. Fulton, A.W. Holland, D.J. Fox, R.G. Bergman, Acc. Chem. Res. 35 (2002) 44;
(b) C.M. Fafard, O.V. Ozerov, Inorg. Chim. Acta 360 (2007) 286;
(c) N.A. Smythe, K.A. Grice, B.S. Williams, K.I. Goldberg, Organometallics 28 (2009) 277;
(d) I. Matas, J. Cámpora, P. Palma, E. Álvarez, Organometallics 28 (2009) 6515.
[6] (a) D.J. Darensbourg, K.M. Sanchez, A.L. Rheingold, J. Am. Chem. Soc. 109 (1987) 290;
(b) D.J. Darensbourg, W.-Z. Lee, A.L. Phelps, E. Guidry, Organometallics 22 (2003) 5585;
(c) H. Yasuda, J.C. Choi, S.-C. Lee, T. Sakakura, Organometallics 21 (2002) 1216;
(d) D.S. Glueck, L.J.N. Winslow, R.G. Bergman, Organometallics 10 (1991) 1462.
[7] (a) S. Park, Bull. Korean Chem. Soc. 22 (2001) 1410;
(b) J. Cámpora, I. Matas, P. Palma, E. Álvarez, C. Graiff, A. Tiripicchio, Organometallics 26 (2007) 3840.
[8] B.J. Burger, J.E. Bercaw, in: A. Wayda, M.Y. Darensbourg (Eds.), New Developments in the Synthesis, Manipulation and Characterization of Organometallic Compounds, vol. 357, American Chemical Society, Washington, DC, 1987.
[9] A. Athimoolam, M.T. Johnson, O.F. Wendt, Organometallics 27 (2008) 4541.
[10] (a) M.A. Bennett, H. Jin, A.C. Willis, J. Organomet. Chem. 451 (1993) 249;
(b) S. Fischer, O.F. Wendt, Acta Cryst. E60 (2004) m69.
[11] (a) F. Gorla, L.M. Venanzi, A. Albinati, Organometallics 13 (1994) 43;
(b) H. Rimml, L.M. Venanzi, J. Organomet. Chem. 259 (1983) C6;
(c) J.M. Seul, S. Park, J. Chem. Soc., Dalton Trans. (2002) 1153.
[12] Crysalis CCD, Oxford Diffraction Ltd. Abingdon, Oxfordshire, UK, 2005.
[13] Crysalis RED, Oxford Diffraction Ltd. Abingdon, Oxfordshire, UK, 2005.
[14] G.M. Sheldrick, Acta Cryst. A64 (2008) 112.
[15] A.L. Spek, Acta Cryst. D65 (2009) 148.
[16] (a) R.D. Simpson, R.G. Bergman, Angew. Chem. Int. Ed. Engl. 31 (1992) 220;
(b) P.L. Holland, R.A. Andersen, R.G. Bergman, J. Huang, S.P. Nolan, J. Am. Chem. Soc. 119 (1997) 12800;
(c) J. Cámpora, I. Matas, P. Palma, C. Graiff, A. Tiripicchio, Organometallics 24 (2005) 2827.
[17] H.E. Bryndza, W. Tam, Chem. Rev. 88 (1988) 1163.
[18] (a) R.P. Hughes, A.J. Ward, J.A. Golen, C.D. Incarvito, A.L. Rheingold, L.N. Zakharov, Dalton Trans. (2004) 2720;
(b) C. Scriban, D.S. Glueck, J.A. Golen, A.L. Rheingold, Organometallics 26 (2007) 1788;
(c) J.J. Adams, N. Arulsamy, D.M. Roddick, Organometallics 28 (2009) 1148.
[19] G.A. Lawrance, Chem. Rev. 86 (1986) 17.
[20] J.F. Hartwig, Organotransition Metal Chemistry–From Bonding to Catalysis, University Science Books, Sausolito, CA, 2010. p. 402.
[21] A. Albinati, S. Chaloupka, J. Eckert, L.M. Venanzi, M.K. Wolfer, Inorg. Chim. Acta 259 (1997) 305 (See also ref 18c).
[22] This has been observed for (PCP) iridium nitrogen complexes: R. Ghosh, M. Kanzelberger, T.J. Emge, G.S. Hall, A.S. Goldman, Organometallics 25 (2006) 5668.
[23] Platinum methoxides have been shown to undergo β-elimination already at room temperature: see ref 17 and H.E. Bryndza, J.C. Calabrese, M. Marsi, D.C. Roe, W. Tam, J.E. Bercaw, J. Am. Chem. Soc. 108 (1986) 4805.
[24] G.R. Desiraju, T. Steiner, The Weak Hydrogen Bond In Structural Chemistry and Biology; IUCr Monographs on Crystallography 9, Oxford University Press, New York, 1999.
[25] For a platinum methyl carbonate structure, see: A. Immirzi, A. Musco, Inorg. Chim. Acta 22 (1977) L35.
[26] (a) S.M. Mandal, D.M. Ho, M. Orchin, Organometallics 12 (1993) 1714;
(b) L. Ferro, P.B. Hitchcock, M.P. Coles, H. Cox, R.J. Fulton, Inorg. Chem. 50 (2011) 1879.