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# Cyclooctadienemethylplatinum complexes: synthesis, reactivity, molecular structure and spectroscopic properties of the organometallic hydroxoplatinum(II) complex [(COD)PtMe(OH)]

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## Abstract

Organometallic complexes of the type [(COD)PtMeL] (COD = 1,5-cyclooctadiene, L = Cl, I, OH, Me,  $-\text{CH}_2\text{C}(\text{O})\text{CH}_3$ ,  $-\text{C}\equiv\text{C}-\text{Ph}$ , pyridine, *N*-methyl-pyrazinium) and the dinuclear complex  $\{[(\text{COD})\text{PtMe}]_2(\mu-\text{C}\equiv\text{C}-\text{C}\equiv\text{C})\}$  were prepared and characterised by  $^1\text{H-NMR}$  spectroscopy. The crystal structures for the complexes with L = Cl, OH and Me are reported. The complex [(COD)PtMe(OH)] is a unique example of a platinum complex containing an olefin and a hydroxy ligand on the same metal centre. It reacts with C–H acidic substrates to form Pt–C bonds. Representative reactions with acetone, phenylacetylene and 1,3-butadiyne and the corresponding products are reported. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Crystal structure; Cyclooctadiene platinum complexes; Hydroxoplatinum(II)

## 1. Introduction

Organoplatinum(II) complexes [(COD)PtRL] (R = alkyl or aryl) with COD (1,5-cyclooctadiene) as an easily exchangeable ligand have been known for decades and are used as precursors for mono- and polynuclear organometallic platinum(II) compounds [1–3]. They are also of interest for the generation of organoplatinum reaction centres on catalyst surfaces for heterogeneous catalysis [4] or as potential precursors for chemical vapour deposition (CVD) of platinum [5] and also as anti-tumour agents [6]. In view of the recent developments on the use of Group 10 organometallics in catalysis [7], it is of interest to investigate the chemical and spectroscopic properties of some basic molecules. Therefore a series of compounds of the type [(COD)PtMeL] was prepared and examined, with L representing a broad range of ligands including weak  $\sigma$ -donors (and  $\pi$ -donors) such as chlorine and iodine, coordinating solvents like acetone, THF or pyridine (with increasing donor capabilities in this se-

ries) and also the strong  $\pi$ -acceptor ligand *N*-methyl-pyrazinium. The introduction of the hydroxy group to form [(COD)PtMe(OH)] was also investigated. This species is of special interest since hydroxo-alkyl- or hydroxoarylplatinum complexes of the type  $[(\text{R}_3\text{P})_2\text{PtR}(\text{OH})]$  (R = alkyl or aryl) are known to deprotonate C–H acidic substrates to form Pt–C bonds [8,9] or to undergo insertion reactions with CO, SO<sub>2</sub> and COS [10]. Organometallic hydroxoplatinum complexes are also of relevance in catalysis, e.g. in the transformation of olefins during the Wacker process [11]. In this paper we report the synthesis and characterisation of several compounds [(COD)PtMeL] as well as the X-ray structures of some members of this series.

## 2. Experimental

### 2.1. Instrumentation

$^1\text{H-NMR}$  spectra were recorded on a Bruker AC 250 spectrometer. IR vibrational spectra were taken on a Perkin–Elmer FT-IR spectrometer Paragon 1000 PC.

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## 2.2. Materials and procedures

The platinum complexes [(COD)PtCl<sub>2</sub>], [(COD)PtI<sub>2</sub>], [(COD)PtMe<sub>2</sub>] and [(COD)PtMeCl] were prepared according to the procedures by Clark and Manzer [1a]. [(COD)PtMeI] was obtained from [(COD)PtMeCl] using NaI. Other reagents were commercially available and used without further purification. All preparations and physical measurements were carried out in dried solvents under an argon atmosphere, using Schlenk techniques. All reactions involving silver salts were performed under light protection.

## 2.3. Preparation of complexes

### 2.3.1. [(COD)PtMe(acetone)](PF<sub>6</sub>) (1), [(COD)PtMe(py)](PF<sub>6</sub>) (2) and [(COD)PtMe(Me-pz)]-(PF<sub>6</sub>)<sub>2</sub> (3)

A solution of 100 mg of [(COD)PtMeCl] (0.283 mmol) in 30 ml of acetone was mixed with 72 mg of AgPF<sub>6</sub> (0.285 mmol). AgCl immediately precipitated yielding an opaque solution. Stirring was continued for 30 min at ambient temperature and AgCl was filtered off yielding a colourless solution. [(COD)PtMe(py)](PF<sub>6</sub>) (2) was prepared by adding 25 mg of pyridine (0.30 mmol) to this solution. The mixture was stirred for 2 h. Evaporation of the solvents gave a fine colourless powder. Recrystallisation from acetone gave colourless microcrystals. Yield: 96 mg (0.18 mmol, 63%). Anal. Calc. for C<sub>14</sub>H<sub>20</sub>F<sub>6</sub>NP<sub>2</sub>Pt: C, 31.00; H, 3.72; N, 2.58. Found: C, 31.09; H, 3.81; N, 2.63%. <sup>1</sup>H-NMR (acetone-*d*<sub>6</sub>) δ: 8.91 (d, 2H, <sup>3</sup>J(H2-H3) = 5.77 Hz, H2,6-py), 8.17 (tt, 1H, <sup>3</sup>J(H4-H3) = 7.97 Hz, <sup>4</sup>J(H4-H2) = 1.37 Hz, H4-py), 7.80 (m, 2H, H3,5-py), 5.48 (s, 2H, <sup>2</sup>J(Pt-<sup>a</sup>CH=) = 34.1 Hz), 5.30 (s, 2H, <sup>2</sup>J(Pt-<sup>b</sup>CH=) = 72.1 Hz), 1.80–2.58 (m, 8H), 0.84 (s, 3H, <sup>2</sup>J(Pt-CH<sub>3</sub>) = 70.8).

2.3.1.1. [(COD)PtMe(Me-pz)](PF<sub>6</sub>)<sub>2</sub> (3). A 70 mg (0.293 mmol) sample of *N*-methyl-pyrazinium hexafluorophosphate (Me-pz)(PF<sub>6</sub>) was added to the filtered solution obtained as above. A faint yellow colour appeared. After stirring for 3 h the solvents were distilled off. The yellowish grey residue was dissolved in acetone and filtered. Slow evaporation of the solvent gave pale yellow microcrystals. Yield: 105 mg (0.15 mmol, 53%). Anal. Calc. for C<sub>14</sub>H<sub>22</sub>F<sub>12</sub>N<sub>2</sub>P<sub>2</sub>Pt: C, 23.91; H, 3.15; N, 3.98. Found: C, 24.43; H, 3.15; N, 4.11%. <sup>1</sup>H-NMR (acetone-*d*<sub>6</sub>) δ: 9.73 (s, 2H, H2,6-Me-pz), 9.35 (d, 2H, H3,5-Me-pz), 5.60 (s, 2H, <sup>2</sup>J(Pt-<sup>a</sup>CH=) = 33.6 Hz), 5.09 (s, 2H, <sup>2</sup>J(Pt-<sup>b</sup>CH=) = 88.5 Hz), 4.78 (s, 3H, H<sub>3</sub>C-pz), 2.37–2.80 (m, 8H), 0.79 (s, 3H, <sup>2</sup>J(Pt-CH<sub>3</sub>) = 66.13).

2.3.1.2. [(COD)PtMe(acetone)](PF<sub>6</sub>) (1). The solvento complex 1 was prepared by evaporating the filtered

solution to dryness. The oily brown residue was dissolved in 5 ml of acetone and filtered. After addition of heptane (15 ml) an off-white oily solid was precipitated and characterised by <sup>1</sup>H-NMR spectroscopy; satisfactory elemental analyses could not be obtained. <sup>1</sup>H-NMR (CD<sub>3</sub>NO<sub>2</sub>) δ: 5.65 (s, 2H, <sup>2</sup>J(Pt-<sup>a</sup>CH=) = 30.8 Hz), 4.95 (s, 2H, <sup>2</sup>J(Pt-<sup>b</sup>CH=) = 90.4 Hz), 2.44–2.83 (m, 8H), 2.40 (s, 6H, acetone), 0.88 (s, 3H, <sup>2</sup>J(Pt-CH<sub>3</sub>) = 64.33).

### 2.3.2. [(COD)PtMe(OH)] (4)

To a suspension of 100 mg of [(COD)PtMeCl] (0.283 mmol) in 30 ml of THF 72 mg of AgPF<sub>6</sub> (0.285 mmol) were added. After stirring at ambient temperature for 40 min the AgCl was filtered off and the resulting colourless solution was treated with 20 mg KOH (0.356 mmol) in 2 ml of deaerated water. After stirring for 10 min the reaction mixture was evaporated to dryness. The residue was dissolved in 10 ml of CH<sub>2</sub>Cl<sub>2</sub> and filtered. Upon evaporation of the solvent a pale brown solid was isolated. Yield: 61 mg (0.18 mmol, 64%). Anal. Calc. for C<sub>9</sub>H<sub>16</sub>OPT: C, 32.24; H, 4.81. Found: C, 32.08; H, 4.79%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ: 5.45 (s, 2H, <sup>2</sup>J(Pt-<sup>a</sup>CH=) = 33.1 Hz), 4.11 (s, 2H, <sup>2</sup>J(Pt-<sup>b</sup>CH=) = 65 Hz), 2.08–2.59 (m, 8H), 0.63 (s, 3H, <sup>2</sup>J(Pt-CH<sub>3</sub>) = 76.1), a signal for Pt-OH was not detected [12]. IR (CDCl<sub>3</sub>) cm<sup>-1</sup>: 3690 (m, ν(Pt-OH)), 3056, 3001, 2969, 2924, 2874, 2839, 2997 (s, ν(H<sub>2</sub>-C), ν(H-C=)).

### 2.3.3. [(COD)PtMe(CH<sub>2</sub>C(O)CH<sub>3</sub>)] (5)

Freshly prepared [(COD)PtMe(OH)] (95 mg, 0.283 mmol) obtained as above was dissolved in 10 ml of acetone. Upon filtration and evaporation of the solvent an off-white solid resulted. Yield: 90 mg (0.24 mmol, 85%). Anal. Calc. for C<sub>12</sub>H<sub>20</sub>OPT: C, 38.40; H, 5.37. Found: C, 38.13; H, 5.35%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ: 5.11 (s, 2H, <sup>2</sup>J(Pt-<sup>a</sup>CH=) = 37.9 Hz), 4.77 (s, 2H, <sup>2</sup>J(Pt-<sup>b</sup>CH=) = 51 Hz), 2.80 (s, 2H, <sup>2</sup>J(Pt-CH<sub>2</sub>) = 122.8 Hz), 2.17–2.42 (m, 8H), 2.02 (s, 3H, <sup>4</sup>J(Pt-CCCH<sub>3</sub>) = 15.8 Hz), 0.86 (s, 3H, <sup>2</sup>J(Pt-CH<sub>3</sub>) = 77.1). IR (CDCl<sub>3</sub>) cm<sup>-1</sup>: 2972, 2926, 2889, 2839, 2804 (s, ν(H<sub>2</sub>-C), ν(H-C=)), 1626 (s, ν(C=O)).

### 2.3.4. [(COD)PtMe(C≡CPh)] (6)

A 20 mg (0.06 mmol) sample of [(COD)PtMe(OH)] was dissolved in 20 ml of THF and mixed with 20 mg of phenylacetylene (0.2 mmol). The mixture was stirred for 1 h. Small amounts of a black solid were removed by filtration and the clear solution evaporated to dryness. The resulting brown solid was washed with heptane and dried in vacuo. Yield: 18 mg (0.043 mmol, 71%). Anal. Calc. for C<sub>17</sub>H<sub>20</sub>Pt: C, 48.68; H, 4.81. Found: C, 48.03; H, 4.73%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ: 7.37 (d, 2H, <sup>3</sup>J(H-H), *o*-Ph), 7.11–7.23 (m, 3H, *m*-Ph, *p*-Ph), 5.51 (s, 2H, <sup>2</sup>J(Pt-<sup>a</sup>CH=) = 33 Hz), 4.92 (s, 2H, <sup>2</sup>J(Pt-<sup>b</sup>CH=) = 51.3 Hz), 2.28–2.53 (m, 8H), 1.03 (s, 3H, <sup>2</sup>J(Pt-CH<sub>3</sub>) = 76.64).

### 2.3.5. $[(COD)PtMe]_2(\mu-C\equiv C-C\equiv C)$ (7)

A 40 mg (0.12 mmol) sample of  $[(COD)PtMe(OH)]$  was dissolved in 50 ml of THF and mixed with ca. 0.2 ml of 1,3-butadiyne. The mixture immediately turned yellow, then reddish-brown after 5 min and was stirred for 1 h. The volume was reduced to 10 ml which lead to precipitation of a black-brown material. Filtration, extraction of the residue with two 5 ml portions of THF and evaporation of the combined filtrates to dryness gave a slightly brownish microcrystalline material. This was recrystallised twice from  $CH_2Cl_2$  and dried in vacuo yielding off-white microcrystals. Yield: 26 mg (0.038 mmol, 32%). Anal. Calc. for  $C_{22}H_{30}Pt_2$ : C, 38.59; H, 4.42. Found: C, 38.14; H, 4.25%.  $^1H$ -NMR ( $CDCl_3$ )  $\delta$ : 5.44 (s, 2H,  $^2J(Pt^a-CH^a) = 36.3$  Hz), 4.79 (s, 2H,  $^2J(Pt^b-CH^b) = 50.7$  Hz), 2.15–2.60 (m, 8H), 0.92 (s, 3H,  $^2J(Pt-CH_3) = 77.6$ ).

### 2.3.6. $[(bpy)PtMe(CH_2C(O)CH_3)]$ (8)

A total of 20 mg  $[(COD)PtMe(CH_2C(O)CH_3)]$  (5) (0.053 mmol) and 20 mg of 2,2'-bipyridine (0.128 mmol) were dissolved in 50 ml of toluene and stirred at 40°C for 2 days. The orange solution was evaporated to give a red solid that was washed with heptane and dried in vacuo. Yield: 21 mg (0.05 mmol, 93%). Anal. Calc. for  $C_{14}H_{16}N_2O_1Pt$ : C, 39.72; H, 3.81; N, 6.62. Found: C, 39.54; H, 3.91; N, 6.59%.  $^1H$ -NMR ( $CDCl_3$ )  $\delta$ : 9.87 (d, 1H,  $^3J(Pt-H6') = 16.5$  Hz,  $^3J(H6'-H5') = 5.5$  Hz), 9.15 (d, 1H,  $^3J(Pt-H6) = 28.8$  Hz,  $^3J(H6-H5) = 6.6$  Hz), 8.09 (ddd,  $^3J(H4'-H5') = 7.42$  Hz,  $^3J(H4'-H3') = 8.25$  Hz,  $^4J(H4'-H6') = 1.65$  Hz), 8.04 (ddd, 1H,  $^3J(H4-H5) = 7.43$  Hz,  $^3J(H4-H3) = 7.97$  Hz,  $^4J(H4-H6) = 1.65$  Hz), 7.99 (d,  $^4J(H3'-H5') = 1.37$  Hz), 7.96 (d,  $^4J(H3-H5) = 1.38$  Hz), 3.16 (s, 2H,  $^2J(Pt-CH_2) = 124.8$  Hz), 2.16 (s, 3H,  $^4J(Pt-CCCH_3) = 23.37$  Hz), 1.24 (s, 3H,  $^2J(Pt-CH_3) = 80.28$ ).

## 2.4. General procedures for crystal structure analyses

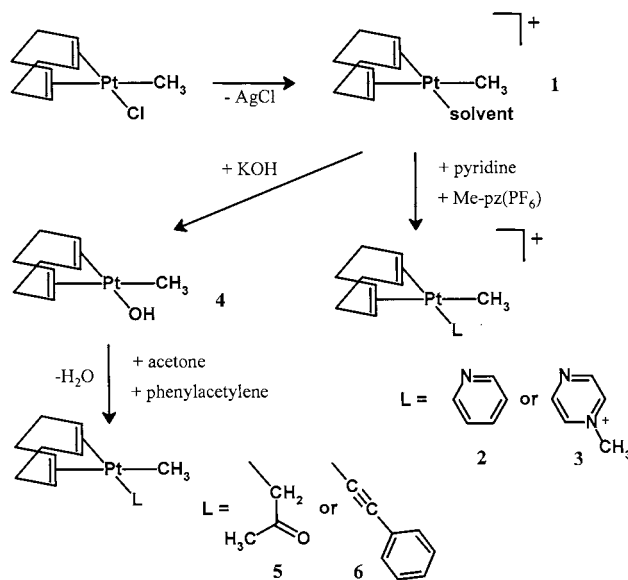
For all three compounds data collection was performed at  $T = 173(2)$  K on a Siemens P4 diffractometer with Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) using an empirical absorption correction ( $\psi$ -scan; min./max. transmission factors:  $[(COD)PtMe(OH)]$  0.22/0.43;  $[(COD)PtMe_2]$  0.53/0.64;  $[(COD)PtMeCl]$  0.33/0.41). The structures were solved by the Patterson method using the SHELXTL-PLUS package [13] and refinement was carried out with SHELXL-93 employing full-matrix least-squares methods on  $F^2$  [14] with  $F^2_o = -3\sigma(F^2_o)$ . All non-hydrogen atoms were treated anisotropically, hydrogen atoms were included by using appropriate riding models, and H(01) of the hydroxy group on  $[(COD)PtMe(OH)]$  was found from the Fourier map.

## 3. Results and discussion

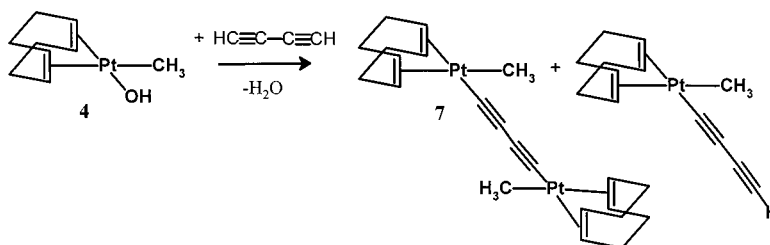
### 3.1. Synthesis and general properties

The cationic organoplatinum compounds  $[(COD)PtMeL]^+$  were prepared in high yields by reacting  $[(COD)PtMeCl]$  with silver hexafluorophosphate and addition of the desired nucleophile L to the intermediate solvento complex  $[(COD)PtMe(solvent)]^+$  (1) (see Scheme 1, solvent = THF or acetone). Their identity was checked by elemental analysis and  $^1H$ -NMR spectroscopy, the assignments being supported by coupling to platinum ( $^{195}Pt$  isotope with  $I = 0.5$  in 33.8% natural abundance, other isotopes  $I = 0$ ).

The organometallic hydroxoplatinum complex  $[(COD)PtMe(OH)]$  (4) was prepared by adding KOH to the solvento complex.  $^1H$ -NMR spectra did not give a signal for the OH proton. IR spectroscopy (in  $CDCl_3$  solution) however showed a band at  $3690$   $cm^{-1}$  for the O-H vibration. While the compounds with pyridine or *N*-methyl-pyrazinium are prepared in acetone solution the preparation of  $[(COD)PtMe(OH)]$  has to be performed in THF. If acetone is employed as solvent deprotonation occurs leading to the acetyl complex  $[(COD)PtMe(CH_2C(O)CH_3)]$  (5) exclusively. In order to confirm that the basic species is indeed the hydroxoplatinum complex 4 and not excess KOH, a sample of pure  $[(COD)PtMe(OH)]$  was dissolved in acetone- $d_6$  (99%). The  $^1H$ -NMR spectrum disclosed the formation of ca. 96% of  $[(COD)PtMe(CD_2C(O)CD_3)]$ ,  $[(COD)PtMe(CDHCO)CD_3]$  (triplet signal  $^2J(H-D) = 2.29$  Hz) and  $[(COD)PtMe(CD_2C(O)CD_2H)]$  (quintet signal  $^2J(H-D) = 2.30$  Hz), respectively (1.5% each). This demonstrates that the hydroxoplatinum moiety is able to deprotonate acetone ( $pK_a = 20$ ) and to form a Pt-C bond even in the presence of water.



Scheme 1. Synthetic procedures for novel complexes  $[(COD)PtMeL]$ .



Scheme 2. Reaction of  $[(\text{COD})\text{PtMe}(\text{OH})]$  (**4**) with 1,3-butadiyne. Formation of the dinuclear (**7**) and mononuclear complex.

This reaction was then applied to other C–H acidic compounds such as phenylacetylene ( $\text{HC}\equiv\text{CPh}$ ,  $\text{p}K_{\text{a}} = 18.5$ ) and 1,3-butadiyne ( $\text{p}K_{\text{a}} = 20.5$ , Scheme 2). The first reaction yielded the Pt–C bonded acetylide complex  $[(\text{COD})\text{PtMe}(\text{C}\equiv\text{C}-\text{Ph})]$  (**6**). From the second reaction the dinuclear complex  $\{[(\text{COD})\text{PtMe}]_2-(\mu-\text{C}\equiv\text{C}-\text{C}\equiv\text{C})\}$  (**7**) was obtained. In the crude material prior to recrystallisation we observed a second species with the following  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 5.43 (s, 2H,  $^2J(\text{Pt}-^a\text{CH}) = 35$  Hz), 4.93 (s, 2H,  $^2J(\text{Pt}-^b\text{CH}) = 51.0$  Hz), 2.20–2.53 (m, 8H), 1.97 (s, 1H,  $^5J(\text{Pt}-\text{C}_4\text{H}) = 11$  Hz), 0.95 (s, 3H,  $^2J(\text{Pt}-\text{CH}_3) = 76.18$ ). The species appeared in 1:3 ratio to the dinuclear complex (**8**) and we assign this species to the mononuclear complex  $[(\text{COD})\text{PtMe}(\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{H})]$ . After recrystallisation from  $\text{CH}_2\text{Cl}_2$ , only traces of this compound were left in the resulting solids but equivalent amounts of the chloro complex  $[\text{CODPtMeCl}]$  were detected instead. We therefore assume that the mononuclear complex is much more labile in chlorinated solvents than the dinuclear complex **7**.

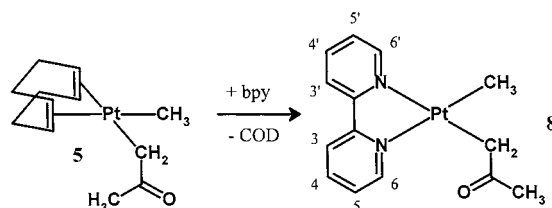
The same type of reaction was described for phosphine-stabilised organometallic hydroxoplatinum complexes of the type  $[(\text{R}'_3\text{P})_2\text{PtR}(\text{OH})]$  ( $\text{R} = \text{alkyl or aryl}$ ). It was shown that the hydroxy group is sufficiently basic to deprotonate a variety of weak acids  $\text{HX}$  such as  $p\text{-MeC}_6\text{H}_4\text{OH}$ ,  $\text{CH}_3\text{C}(\text{O})\text{CH}_3$ ,  $\text{CH}_3\text{NO}_2$ ,  $\text{PhCCH}$ ,  $\text{CH}_3\text{C}(\text{O})\text{NH}_2$ ,  $\text{PhNHCH}_3$  [9]. The  $[\text{CODPtMe}(\text{OH})]$  complex may prove to be advantageous over its phosphine analogues since the COD ligand is easily replaced by other ligands  $\text{L}$ . As a first example we reacted the acetyl complex **5** with 2,2'-bipyridine (bpy) to obtain the novel complex  $[(\text{bpy})\text{PtMe}(\text{CH}_2\text{C}(\text{O})\text{CH}_3)]$  (**8**) (Scheme 3).

At present we are investigating this reaction as a general methodology of forming Pt–C bonds with H–C acidic substrates. Acetylide and diacetylide complexes of platinum have been of great interest during the past decade as candidates for non-linear optical or liquid-crystalline materials [15]. They may also be used to construct platinum-containing dendrimers and polymers with acetylides as rigid spacers [16]. The methodology described herein may prove to be a good alternative to the now well-established methods using platinum–chloro substrates, copper(I) halogenides as

catalyst and amine bases to abstract HCl (Hagihara or Stille coupling) [17] or deprotonation/metathesis sequences using organolithium compounds [18]. Comparable procedures starting from  $\text{Rh}-\text{OH}$  [19] or  $\text{Ru}-\text{OH}$  [20] precursors were recently reported to lead to novel acetylide complexes. It is worth noting that during the preparation of  $[(\text{COD})\text{PtMe}_2]$  according to the procedure described by Clark and Manzer [1a], we observed that the first crop of crystalline material, obtained from the ether solution, contains two minor products as inferred from  $^1\text{H-NMR}$  studies. One side product is the monoalkylated  $[(\text{COD})\text{PtMeI}]$ ; the other is  $[(\text{COD})\text{PtMe}(\text{OH})]$ . The latter is most likely generated during the aqueous work-up from  $[(\text{COD})\text{PtMe}_2]$  with the formation of methane and  $[(\text{COD})\text{PtMe}(\text{OH})]$ . Pure  $[(\text{COD})\text{PtMeI}]$  did not react under comparable conditions with added KOH, thus supporting this assumption.

### 3.2. $^1\text{H-NMR}$ spectroscopy

$^1\text{H-NMR}$  spectra of  $[(\text{COD})\text{PtMeL}]$  in solution exhibit broad singlets for the olefinic COD protons with platinum satellites due to coupling to  $^{195}\text{Pt}$ . For unsymmetrically substituted complexes ( $\text{L} \neq \text{Me}$ ) two sets of signals appear.  $^{195}\text{Pt}$  coupling constants to the high-field signal ( $\text{H}^b\text{C}=\text{C}$ ) vary from 51 to 90 Hz, whereas the  $^{195}\text{Pt}$  coupling of the low field signal ( $\text{H}^a\text{C}=\text{C}$ ) varies only slightly from 31 to 38 Hz (Tables 1 and 2). The latter signal can thus be attributed to the olefinic protons *trans* to the methyl substituent in accord with the assignment by Clark and Manzer [1a]. The variation of the  $^{195}\text{Pt}$  coupling constants on the low-field position reflects the influence of various *trans* located donors  $\text{L}$ .



Scheme 3. Reaction of complex **5** to the bipyridine complex **8** with numbering for the bpy ligand.

Table 1  
Selected  $^1\text{H-NMR}$  data of neutral organoplatinum complexes in  $\text{CDCl}_3$  \*

Compound	$^2J(\text{Pt-CH}_3)$	$^2J(\text{Pt-}^a\text{CH})$	$^2J(\text{Pt-}^b\text{CH})$	$\delta \text{H}_3\text{C-Pt}$	$\delta \text{H}^a\text{C}$	$\delta \text{H}^b\text{C}$
$[\text{CODPtCl}_2]$	–	68.50	68.50	–	5.58	5.58
$[(\text{COD})\text{PtMeCl}]$	71.32	32.47	76.38	0.89	5.51	4.48
$[(\text{COD})\text{PtMeI}]$	72.18	37.86	74.87	1.10	5.52	4.63
$[(\text{COD})\text{PtMe}(\text{OH})]$ ( <b>4</b> )	76.07	33.14	65.05	0.63	5.45	4.11
$[(\text{COD})\text{PtMe}(\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{H})]$	76.18	35.33	52.78	0.95	5.43	4.93
$[(\text{COD})\text{PtMe}(\text{C}\equiv\text{C}-\text{Ph})]$ ( <b>6</b> )	76.64	32.96	51.27	1.03	5.51	4.92
$[(\text{COD})\text{PtMe}(\text{CH}_2\text{C}(\text{O})\text{CH}_3)]$ ( <b>5</b> )	77.13	37.95	51.02	0.86	5.11	4.77
$[\{(\text{COD})\text{PtMe}\}_2(\mu-\text{C}\equiv\text{C}-\text{C}\equiv\text{C})]$ ( <b>7</b> )	77.56	36.26	50.91	0.92	5.44	4.80
$[(\text{COD})\text{PtMe}_2]$	82.33	40.80	40.80	0.72	4.78	4.78

\* Coupling constants in Hz, chemical shifts  $\delta$  in ppm versus TMS as standard. <sup>a,b</sup> For an assignment of the olefinic protons see text.

Table 2  
Selected  $^1\text{H-NMR}$  data of cationic and neutral organoplatinum complexes in acetone- $d_6$  \*

Compound	$^2J(\text{Pt-CH}_3)$	$^2J(\text{Pt-}^a\text{CH})$	$^2J(\text{Pt-}^b\text{CH})$	$\delta \text{H}_3\text{C-Pt}$	$\delta \text{H}^a\text{C}$	$\delta \text{H}^b\text{C}$
$[(\text{COD})\text{PtMe}(\text{acetone})](\text{PF}_6)$ ( <b>1</b> ) <sup>c</sup>	64.33	30.80	90.45	0.88	5.65	4.95
$[(\text{COD})\text{PtMe}(\text{Me-pz})](\text{PF}_6)_2$ ( <b>3</b> )	66.13	33.55	88.52	0.79	5.60	5.09
$[(\text{COD})\text{PtMe}(\text{py})](\text{PF}_6)$ ( <b>2</b> )	70.82	34.10	72.07	0.84	5.48	5.30
$[(\text{COD})\text{PtMeI}]$	73.13	38.14	74.66	0.99	5.44	4.71
$[(\text{COD})\text{PtMeCl}]$	72.90	32.52	74.33	0.76	5.39	4.51
$[(\text{COD})\text{PtMe}(\text{OH})]$ ( <b>4</b> )	68.74	31.90	73.68	0.75	5.55	4.39
$[(\text{COD})\text{PtMe}(\text{CD}_2\text{C}(\text{O})\text{CD}_3)]$ ( <b>5</b> )	78.35	37.67	51.02	0.80	5.09	4.79
$[(\text{COD})\text{PtMe}_2]$	83.33	41.47	41.47	0.61	4.74	4.74

\* Coupling constants in Hz, chemical shifts  $\delta$  in ppm versus TMS as standard. <sup>a,b</sup> For an assignment of the olefinic protons see text.

<sup>c</sup> Measured in  $\text{CD}_3\text{NO}_2$ .

The  $^2J(\text{Pt-}^b\text{CH=})$  coupling constants as listed in Table 1 increase along the series  $\text{CH}_3 < \mu-\text{C}\equiv\text{C}-\text{C}\equiv\text{C} < \text{CH}_2-\text{C}(\text{O})\text{CH}_3 < \text{C}\equiv\text{C}-\text{Ph} < \text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{H} < \text{OH} < \text{I} < \text{Cl}$  with decreasing donor strength of the ligand L. This phenomenon can be attributed to the *trans* influence and was also reported for coupling constants ( $^{195}\text{Pt}$ ,  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{15}\text{N}$  or  $^{31}\text{P}$ ) in other square planar complexes [8e,10e,21]. The  $^2J(\text{Pt-}^b\text{CH=})$  coupling constants for cationic complexes are listed in Table 2. They also increase along the series  $\text{py} < \text{Me-pz} < \text{acetone}$  with decreasing donor strength of the ligand L. The  $^2J(\text{Pt-}^a\text{CH=})$  coupling constants increase slightly with increasing donating power of the ligand L but show no systematic correlation. The chemical shifts of the olefinic protons do also not correlate in a systematic way.

The methylene protons of the COD ligand are located at around 2 ppm as broad multiplets. The resonance for the methyl substituent is found at ca. 1 ppm as a singlet with platinum satellites. The  $^2J(\text{Pt-CH}_3)$  coupling constants decrease with decreasing basicity of the ligand L. The effect of the variation of L has a different sign and is much less pronounced than for the  $^2J(\text{Pt-}^b\text{CH=})$  coupling constants. Going from L = Me to L = acetone the  $^2J(\text{Pt-CH}_3)$  coupling constants decrease from 41.5 to 30.8 (–23%), whereas the  $^2J(\text{Pt-}^b\text{CH=})$  coupling constants increase from 41.5 to

90.5 (+118%, Table 2). This is in perfect agreement with the *cis* influence of the ligand L derived from the classical explanation using the hybridisation concept [21].

It is worth focusing on the positioning of the  $^{195}\text{Pt}$  coupling constants for the hydroxy complex **4** and the pyridine complex **2**. Although pyridine ( $\text{p}K_a = 5.25$ ) is a much weaker base than  $\text{OH}^-$ , the  $^2J(\text{Pt-}^b\text{CH=})$  is smaller for  $[\text{CODPtMe}(\text{py})]^+$  than for  $[\text{CODPtMe}(\text{OH})]$ . Also for the  $^2J(\text{Pt-CH}_3)$  the sequence is  $\text{py} > \text{OH}$ . This means that OH reveals only weak *trans*- and *cis*-influence in  $[\text{CODPtMe}(\text{OH})]$  very much closer to I or Cl than to the strong alkyl ligands. There is good agreement with NMR spectroscopic results on a series of compounds of the type  $[(\text{dppe})\text{PtMe}(\text{X})]$ . Alkoxide and hydroxide ligands reveal here also only moderate to weak *trans* influence and the binding properties are best described as covalent linkages in the organic solutions studied [8e,11a].

We did not succeed in locating the OH proton in  $[(\text{COD})\text{PtMe}(\text{OH})]$  in solvents like  $\text{CDCl}_3$ , acetone- $d_6$  or benzene- $d_6$  [12]. Protons of the ligand L maintain their typical signal patterns but are generally shifted downfield upon coordination to the  $(\text{COD})\text{PtMe}$  fragment as pyridine or *N*-methyl-pyrazinium or free forms for acetone or phenylacetylene, respectively.

Table 3  
Crystallographic data and structure refinement <sup>a</sup>

Compound	[(COD)PtMe(OH)] (4)	[(COD)PtMe <sub>2</sub> ]	[(COD)PtMeCl]
Empirical formula ( <i>F<sub>w</sub></i> )	C <sub>9</sub> H <sub>16</sub> OPt (335.31)	C <sub>10</sub> H <sub>18</sub> Pt (333.33)	C <sub>9</sub> H <sub>15</sub> ClPt (353.75)
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>C</i> 2/ <i>c</i>
Crystal system	Monoclinic	Monoclinic	Monoclinic
<i>a</i> (Å)	8.1872(17)	8.1705(11)	14.998(3)
<i>b</i> (Å)	18.264(5)	18.222(2)	6.9660(10)
<i>c</i> (Å)	7.3588(18)	7.3452(8)	19.114(4)
β (°)	115.940(17)	115.890(9)	102.03(3)
<i>V</i> (Å <sup>3</sup> )	989.5(4)	983.8(2)	1953.1(6)
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	2.2511	2.2511	2.406
<i>Z</i>	4	4	8
Absorption coefficient μ (mm <sup>-1</sup> )	14.127	14.201	14.578
<i>F</i> (000)	624	624	1312
θ Range (°)	2.23–30.00	2.24–30.00	2.18–29.91
Limiting indices	−11 ≤ <i>h</i> ≤ 4, −25 ≤ <i>k</i> ≤ 25, −9 ≤ <i>l</i> ≤ 10	−11 ≤ <i>h</i> ≤ 10, −25 ≤ <i>k</i> ≤ 3, −1 ≤ <i>l</i> ≤ 10	−20 ≤ <i>h</i> ≤ 20, −9 ≤ <i>k</i> ≤ 6, −26 ≤ <i>l</i> ≤ 26
No. of reflections collected	5741	3660	6464
No. of independent reflections	2893	2869	2814
<i>R</i> <sub>int</sub>	0.0396	0.0396	0.0846
Data/restraints/parameters	2892/0/103	2868/0/99	2812/0/98
Goodness-of-fit on <i>F</i> <sup>2</sup> <sup>b</sup>	1.090	1.047	1.085
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )] <sup>c</sup>	<i>R</i> <sub>1</sub> = 0.0330, <i>wR</i> <sub>2</sub> = 0.0697	<i>R</i> <sub>1</sub> = 0.0430, <i>wR</i> <sub>2</sub> = 0.1124	<i>R</i> <sub>1</sub> = 0.0489, <i>wR</i> <sub>2</sub> = 0.1257
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0492, <i>wR</i> <sub>2</sub> = 0.0753	<i>R</i> <sub>1</sub> = 0.0525, <i>wR</i> <sub>2</sub> = 0.1194	<i>R</i> <sub>1</sub> = 0.0543, <i>wR</i> <sub>2</sub> = 0.1356
Largest difference peak and hole (e Å <sup>-3</sup> )	1.671 and −1.651 <sup>d</sup>	4.597 and −3.327 <sup>d</sup>	3.002 and −3.517 <sup>d</sup>

<sup>a</sup> Measurement conditions: temperature 173(2) K, wavelength λ = 0.71073 Å.

<sup>b</sup> GOF = {Σw(|*F*<sub>o</sub>|<sup>2</sup> − |*F*<sub>c</sub>|<sup>2</sup>)<sup>2</sup>/(*n* − *m*)}<sup>0.5</sup>; *n* = no. of reflections; *m* = no. of parameters.

<sup>c</sup> *R* = (Σ||*F*<sub>o</sub>| − |*F*<sub>c</sub>||)/Σ|*F*<sub>o</sub>|, *wR* = {Σ[w(|*F*<sub>o</sub>|<sup>2</sup> − |*F*<sub>c</sub>|<sup>2</sup>)<sup>2</sup>]/Σ[w(*F*<sub>o</sub><sup>2</sup>)]}<sup>0.5</sup>.

<sup>d</sup> Located 0.7–1.8 Å beneath the Pt atom.

### 3.3. Crystal structure determination of [(COD)PtMe(OH)], [(COD)PtMeCl] and [(COD)PtMe<sub>2</sub>]

Colourless crystals (in each case cubes approx. 0.3 × 0.2 × 0.2 mm in size) were obtained from a saturated solution of [(COD)PtMe(OH)] or [(COD)PtMe<sub>2</sub>] in diethyl ether at −30°C or upon slow evaporation of a solution of [(COD)PtMeCl] in CHCl<sub>3</sub>. They were subjected to X-ray diffraction and the structures were solved according to procedures given in Section 2. Results are provided in Tables 3–5. The purity of the crystalline material was checked by <sup>1</sup>H-NMR and was generally ≤ 99%. Plots of the structures are provided in Figs. 1 and 2.

The complexes [(COD)PtMe<sub>2</sub>] and [(COD)PtMe(OH)] both crystallise in the space group *P*2<sub>1</sub>/*c*, whereas [(COD)PtMeCl] crystallises in *C*2/*c*. This might be due to the different crystallisation procedure. The cell constants of the former two are very similar. Replacement of CH<sub>3</sub> with OH in the refinement procedures gave in all cases significantly higher residuals, therefore the assignment is unambiguous. There are no relevant intermolecular interactions other than van der Waals interactions and most importantly, there are no hydrogen bridges present in [(COD)PtMe(OH)]. In all three complexes the platinum atom has a square planar

environment. The mean deviation from a best plane including platinum, the methyl carbon, Cl, O or C of the ligand L and the intermediate positions between the olefinic carbons is 0.0051 Å for L = Cl, 0.0225 Å for L = Me and 0.0260 Å for L = OH.

The distances from platinum to the binding atom in the ligands L increase in the series Me < OH < Cl with a rather long Pt–O distance in [(COD)PtMe(OH)] of

Table 4  
Bond lengths (Å) of [(COD)PtMe(OH)], [(COD)PtMe<sub>2</sub>] and [(COD)PtMeCl]

	[(COD)PtMe(OH)]	[(COD)PtMe <sub>2</sub> ]	[(COD)PtMeCl]
Pt(1)–C(1)	2.126(7)	2.134(6)	2.164(8)
Pt(1)–L	2.194(5) (O)	2.100(6) (C)	2.330(2) (Cl)
Pt(1)–C(14)	2.216(6)	2.216(7)	2.151(6)
Pt(1)–C(18)	2.229(6)	2.226(8)	2.278(8)
Pt(1)–C(13)	2.247(7)	2.233(7)	2.186(8)
Pt(1)–C(17)	2.240(6)	2.253(8)	2.286(8)
C(12)–C(13)	1.523(11)	1.504(10)	1.513(15)
C(12)–C(19)	1.541(12)	1.541(11)	1.509(13)
C(13)–C(14)	1.368(10)	1.388(12)	1.401(11)
C(14)–C(15)	1.506(10)	1.508(12)	1.502(10)
C(15)–C(16)	1.536(11)	1.531(13)	1.516(12)
C(16)–C(17)	1.516(10)	1.531(12)	1.501(11)
C(17)–C(18)	1.389(10)	1.374(11)	1.376(11)
C(18)–C(19)	1.513(10)	1.499(11)	1.502(13)

Table 5  
Selected bond angles (°) of [(COD)PtMe(OH)], [(COD)PtMe<sub>2</sub>] and [(COD)PtMeCl]

	[(COD)PtMe(OH)]	[(COD)PtMe <sub>2</sub> ]	[(COD)PtMeCl]
C(1)–Pt(1)–L(1)	83.7(2)	85.1(3)	85.6(3)
C(1)–Pt(1)–C(13)	95.9(3)	96.0(3)	95.8(4)
C(1)–Pt(1)–C(14)	93.0(3)	92.8(3)	92.2(3)
L(1)–Pt(1)–C(13)	164.3(2)	163.3(3)	161.5(2)
L(1)–Pt(1)–C(14)	159.9(2)	160.3(3)	160.8(2)
L(1)–Pt(1)–C(17)	97.0(2)	95.4(3)	95.8(2)
L(1)–Pt(1)–C(18)	94.1(2)	92.6(3)	91.8(2)
C(1)–Pt(1)–C(17)	163.6(3)	163.9(3)	162.9(3)
C(1)–Pt(1)–C(18)	160.2(3)	160.4(3)	162.0(3)
C(13)–Pt(1)–C(18)	81.0(3)	80.8(3)	81.1(3)
C(14)–Pt(1)–C(17)	80.7(3)	81.3(3)	80.8(3)
C(13)–Pt(1)–C(17)	87.9(2)	88.1(3)	88.2(3)
C(14)–Pt(1)–C(18)	95.5(3)	95.7(3)	95.9(3)
Bite angle <sup>a</sup>	85.9	86.1	86.1

<sup>a</sup> Bite angle for the COD ligand taken from averaged position for C13–C14 and C17–C18, respectively.

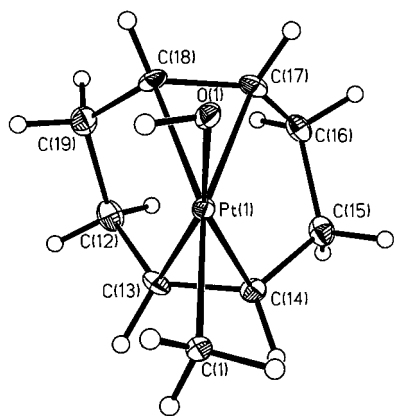


Fig. 1. View of [(COD)PtMe(OH)].

2.194(4) Å. Comparable compounds like [(dppe)PtMe(OH)] [11a] or [(<sup>t</sup>Bu<sub>2</sub>bpy)PtMe(O(H)-{B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>})] [22] show significantly shorter distances of 2.025(8) or 2.062(2) Å, respectively and also shorter Pt–C1 distances of 2.087(10) or 2.037(3) Å, respectively. Unfortunately, comparison with the latter compound is not straightforward, since the triarylborane acceptor on the oxygen atom will surely influence the Pt–O distance. A database survey gave mean values for Pt(II)–OH distances of 2.006 Å and average values of 2.107 Å for Pt(II)–CH<sub>3</sub> distances [23]. Isomorphous replacement of OH by Cl can be excluded since the purity of the crystals (checked by <sup>1</sup>H-NMR) was at least 99%. Generally it can be stated that all the Pt–L and Pt–CH<sub>3</sub> distances are rather long in the present complexes, which can be explained with a high donor strength of the COD ligand, but the Pt–OH is exceptionally long. At present we cannot find a reasonable explanation for

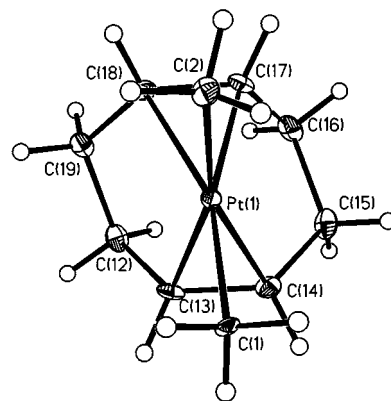


Fig. 2. View of [(COD)PtMe<sub>2</sub>].

this and more detailed investigations of properties of the Pt–OH bond like exchange kinetics are necessary. The platinum methyl distance increases across the series Me < OH ≪ Cl taking for the two different methyl–Pt distances an averaged value of 2.117 Å. This correlates with a decrease in donating power of the ligand L and an increase in the <sup>2</sup>J(Pt–CH<sub>3</sub>) coupling constants in the <sup>1</sup>H-NMR spectra. The distances between Pt and the olefinic carbons in *trans* position to the methyl substituent (H<sup>a</sup>C=) decrease in the same series whereas the distances to the *cis*-oriented olefinic carbons (H<sup>b</sup>C=) increase. For the COD ligand no significant alternation in the bond lengths is detected. For the complex [(COD)PtMe<sub>2</sub>] two different Pt–C distances and consequently unequal distances from platinum to the two sets of olefinic carbons are observed. Therefore the molecule does not retain its C<sub>2</sub> symmetry in the crystal. This is in full agreement with a recent work reporting solid state <sup>13</sup>C-NMR data for [(COD)PtMe<sub>2</sub>] [24]. Four different resonances were observed for the olefinic carbons which clearly indicates the asymmetry of this molecule in the solid state.

The bond angles of the three complexes do not change significantly upon variation of the ligand L and the bite angles of the COD chelate ligand, being taken from the averaged positions of C13–C14 and C17–C18, respectively, are also very similar (Table 5).

#### 4. Summary

With [(COD)PtMe(OH)] the first example of an organotransition metal complex is presented that contains a hydroxy and an olefin function bound to the same metal centre. This addresses the still unresolved question of how the attack of OH towards olefin complex species proceeds in transition metal-catalysed oxidations of olefins (e.g. in the Wacker process). The complex [(COD)PtMe(OH)] reacts with C–H acidic

compounds to form new Pt–C bonds. This method could be applied to the synthesis of novel platinum acetylide complexes as was shown for some examples, providing an alternative to established pathways. The structural and spectroscopic characterisation of a series of organoplatinum complexes of the type [(COD)PtMeL] reveals interesting aspects of the electronic structure and reactivity of these compounds. <sup>1</sup>H-NMR spectroscopy reveals that the <sup>195</sup>Pt coupling constants to the protons of the methyl substituent and the olefinic groups vary with the donor strength (basicity) of the ligand L as anticipated from the *trans* and *cis* influence. The OH<sup>−</sup> ligand in [(COD)PtMe(OH)] reveals only weak influence in this respect. The bond distances and bond angles taken from X-ray crystallographic studies of three of the complexes show the same trends. The crystal structure determination of [(COD)PtMe(OH)] reveals for the first time the molecular structure of a square planar organometallic hydroxomethylplatinum(II) complex with an exceptionally long Pt–O distance.

## 5. Supplementary material

Ten Tables and four Figures describing further X-ray structural details for [(COD)PtMe(OH)], [(COD)PtMe<sub>2</sub>] and [(COD)PtMeCl] are available from the author upon request.

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