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First synthesis of an olefin-coordinated platina(II)cyclobutane and its conversion into diphosphineplatina(II)cyclobutanes

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Abstract

The reaction of the 1,3-di-Grignard reagent 1,3-bis(bromomagnesio)-2,2-dimethylpropane (**1**) with dichloro(1,5-η^2-cyclooctadiene)platinum(II) (**2**) gave 1-(1,5-η^2-cyclooctadiene)-3,3-dimethylplatina(II)cyclobutane (**3**) in 90% yield. The diene ligand of **3** is easily replaced by monodentate phosphine ligands to give diphosphineplatina(II)cyclobutanes (**4**). Relationships between coupling constants $^1J(PtP)$ and the cone angles θ of the phosphine ligands and between $^1J(PtP)$ and the ring size of platinacycloalkanes are briefly discussed.

Introduction

Platinacyclobutanes have been prepared by oxidative addition of Zeise's dimer or zerovalent platinum complexes to cyclopropanes [1–3], by thermolysis of bis(trialkylphosphine)dineopentylplatinum(II) complexes [4], or by reaction of either platinum(II) or platinum(0) complexes with derivatives of 3-oxopentanedioic acid [5] or 3-chloro-2-(trimethylsiloxy)-1-propene [6]. The synthesis of platina(II)cyclobutanes by electrochemical reduction of platina(IV)cyclobutanes has also been reported [7].

Most of these methods have several drawbacks. For platina(IV)cyclobutanes, the choice of ligands at platinum is limited [1–3] (thermolysis of dineopentylplatinum(II) complexes gave the corresponding platina(II)cyclobutanes only in low yield [4]), and although several metallacyclobutanes have been prepared by one or more of these methods, none of the methods can be considered as a general procedure [8–13]. In contrast, the 1,3-di-Grignard approach has shown its advantages in the synthesis of four-membered metallacycles of many main group as well as transition metals [14–22]. In order to test the value of 1,3-di-Grignard reagent 1,3-bis(bromomagnesio)-2,2-dimethylpropane (**1**) in the synthesis of metallacyclobutanes of Group 10, we have investigated the reactions of **1** with dichloroplatinum(II) complexes.

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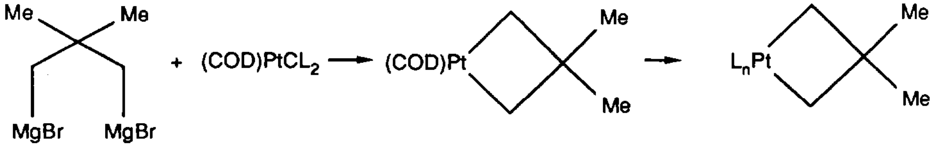
Results

When *cis*-bis(triphenylphosphine)dichloroplatinum(II) (the *cis* configuration had been established by IR and ^{31}P NMR spectroscopy [23,24]) was treated with a solution of **1** in diethyl ether or tetrahydrofuran at low temperature, bis(triphenylphosphine)-3,3-dimethylplatina(II)cyclobutane (**4d**) was isolated, but the yields were moderate (18–27%). Because in the synthesis of platina(II)cyclopentanes [25–28], (1,5-η^2-cyclooctadiene)dichloroplatinum(II) (**2**) appeared to be a better starting material than diphosphinedichloroplatinum(II) complexes, we expected that the analogous reaction of **1** with **2** would give more satisfactory results. After addition of an ethereal solution of **1** to a suspension of **2** in diethyl ether at −60 °C, the reaction mixture was stirred for 2 h at −20 °C. A yellow solution and a white precipitate (magnesium dihalide) were obtained. The diethyl ether was distilled off and n-pentane added, to produce an almost colourless solution and a light yellow precipitate. After filtration the solution was slowly evaporated and 1-(1,5-η^2-cyclooctadiene)-3,3-dimethylplatina(II)cyclobutane (**3**) isolated as colourless crystals in 90% yield. (Scheme 1). Whereas 1-(1,5-η^2-cyclooctadiene)platina(II)cyclopentane has been reported as decomposing in solution [25,26], **3** was found to be stable when kept in benzene at room temperature. The cyclooctadiene ligand in **3** is readily replaced by monodentate phosphine ligands. For this purpose, a solution of **3** in n-pentane was treated with two equivalents of a phosphine at −20 °C and the mixture was stirred for 15 h at room temperature. A colourless solution was obtained, and after evaporation of the solvent the platina(II)cyclobutanes **4a–4d** were isolated as colourless solids in high yield (90–95%). Only in the case of 1,2-bis(diphenylphosphino)ethane as a ligand could no definite product be obtained.

These results reveal the synthetic utility of the 1,3-di-Grignard approach to platina(II)cyclobutanes. In comparison with existing methods it has two advantages: the yields are high, and by use of one intermediate, **3**, various phosphine ligands can be introduced. The latter strategy has previously been exploited in the preparation of diphosphine complexes of platina(II)cyclopentanes [25–28].

The availability of NMR data for a number of platina(II)cyclobutanes from this work and that by others [4,33] provides an opportunity to make some observations. In phosphinemetal complexes, the metal phosphorus coupling constant is linearly related to the cone angle θ of the phosphine ligand [29,30]. This phenomenon is also



1 **2** **3** **4**

a : $L_n = (PMe_3)_2$
b : $L_n = (PEt_3)_2$
c : $L_n = (PBu_3)_2$
d : $L_n = (PPh_3)_2$

Scheme 1

Table 1

^{31}P NMR data for diphosphineplatina(II) metallacycles and diphosphinedimethylplatinum(II) complexes

Complex	δ [a]	$\Delta\delta$ [b]	^1J(PtP) (Hz)	Ref.
$(Me_3P)_2PtMe_2$	−23.8	38.2	1790	32
$(Me_3P)_2PtCH_2CMe_2CH_2$ (**4a**)	−24.8	37.2	1890	[d]
$(Et_3P)_2PtCH_2CH_2CH_2$	8.1	28.1	[c]	7
$(Et_3P)_2PtCH_2CMe_2CH_2$ (**4b**)	9.0	29.0	1870	33 [d]
$(Et_3P)_2PtCH_2CH_2CH_2CH_2$ (**5b**)	11.0	31.0	1782	26
$(Et_3P)_2PtCH_2CMe_2CMe_2CH_2$ (**6**)	11.5	31.5	1798	27
$(Et_3P)_2PtCH_2CMe_2CH_2CMe_2CH_2)$ (**7**)	9.7	29.7	1718	31
$(Bu_3P)_2PtCH_2CMe_2CH_2$ (**4c**)	3.0	35.7	1857	[d]
$(Bu_3P)_2PtCH_2CH_2CH_2CH_2$ (**5c**)	2.7	35.4	1775	26
$(Bu_3P)_2PtCH_2CH_2CH_2CH_2CH_2$ (**8**)	2.7	35.4	1723	26
$(Ph_3P)_2PtMe_2$	27.0	33.0	1902	32
$(Ph_3P)_2PtCH_2CH_2CH_2$	26.1	32.1	[c]	7
$(Ph_3P)_2PtCH_2CMe_2CH_2$ (**4d**)	27.4	33.4	1839	[d]
$(Ph_3P)_2PtCH_2CH_2CH_2CH_2$ (**5d**)	27.6	33.6	1842	26
$(iPr_3P)_2PtCH_2CMe_2CH_2$ (**4e**)	33.0	13.0	1831	4
$(Cy_3P)_2PtMe_2$	19.6	13.6	1852	28
$(Cy_3P)_2PtCH_2CMe_2CH_2$ (**4f**)	22.3	16.3	1797	4
$(Cy_3P)_2PtCH_2CH_2CH_2CH_2$ (**5f**)	19.6	13.6	1760	28

[a] δ (ppm) relative to external H_3PO_4. [b] $\Delta\delta = \delta(\text{complex}) - \delta(PR_3)$; $\delta(PR_3)$ from ref. [29,34]. [c] Not reported. [d] This work.

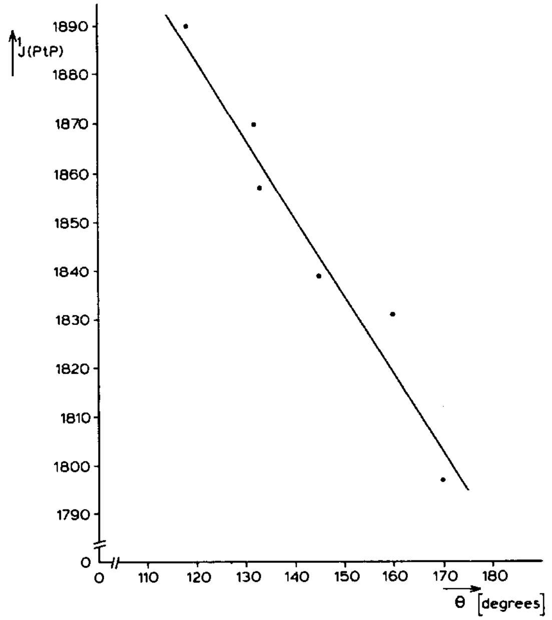


Fig. 1. ^1J(PtP) as a function of the cone angle θ.

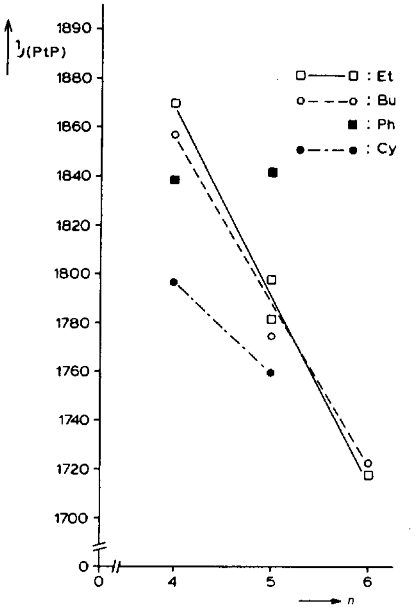


Fig. 2. Variation of ^1J(PtP) with the ring size of diphosphineplatina(II)metallacycles.

observed for **4** (Table 1 and Fig. 1). The relationship can be accounted for in terms of a change of *s*-character in the lone pair of phosphorus: an increase in θ results in an increase of *s*-character in the carbon phosphorus bond. As a consequence, the lone pair of phosphorus has more *p*-character, which leads to a smaller ^1J(PtP). It should be noted that the linear relationship between ^1J(PtP) and the cone angle θ observed for **4** does not hold for the platina(II)cyclopentane series (Table 1).

It is also of interest that the ^1J(PtP) coupling constants of the platina(II)cyclobutanes are diagnostically higher than those of their five-membered ring analogues containing the same phosphine ligands; although the data are too scarce for a reliable generalization, this observation seems to apply also to the six-membered analogues (Table 1 and Fig. 2). Only in the case of the triphenylphosphine ligand are the couplings for the four- and the five-membered rings practically the same (**4d**: 1839 Hz; **5d**: 1842 Hz).

Finally, it should be pointed out that, in contrast to the coupling constants ^1J(PtP), coordination chemical shifts $\Delta\delta$ of diorganylplatinum(II) compounds hardly vary with the carbon substituent on platinum, irrespective of ring size or methyl substitution (an exception should be made for very bulky dialkylplatinum(II) complexes [31,32]), and are practically constant and typical for a given phosphorus ligand (Table 1). The small $\Delta\delta$ values for triisopropylphosphine and tricyclohexylphosphine ligands are noteworthy.

Experimental

^{1}H NMR and ^{31}P{^{1}H} NMR spectra were recorded on a Bruker WM 250 spectrometer at 250 MHz or 101 MHz, respectively. For the ^{1}H NMR spectra, Lorentz Gauss transformation was carried out before Fourier transformation, yielding Gaussian enhanced spectra; chemical shifts are relative to C_6D_5H as internal standard. For the determination of J(PtP) and J(PH) coupling constants, $^1H\{^{31}P\}$ NMR spectra were also recorded. The yields of **3** and **4** were established by ^1H NMR analysis with hexamethylbenzene as internal standard.

Dichloro(1,5-η^2-cyclooctadiene)platinum(II) [35] was prepared as described by Whitesides and his coworkers [25]. All solvents were distilled from sodium potassium alloy. All experiments were performed in a completely sealed and evacuated glass apparatus [36].

1-(1,5-η^2-cyclooctadiene)-3,3-dimethylplatina(II)cyclobutane (3)

To a suspension of 0.071 mmol dichloro(1,5-η^2-cyclooctadiene)platinum(II) (26.6 mg) in 10 ml of diethyl ether was added a solution of 0.071 mmol of **1** in 10 mol of diethyl ether at $-60\,°C$. The mixture was stirred at $-60\,°C$ for 0.5 h then allowed to warm to $-20\,°C$ during 2 h and stirred at $-20\,°C$ for 2 h. The diethyl ether was distilled off at $-20\,°C$ and 10 ml of n-pentane was added. After filtration, the solution was slowly evaporated to dryness at $-20\,°C$. Yield: 90%. ^1H NMR (C_6D_5H): δ 1.19 (s, 4H, ^2J(PtH) 108.8 Hz, CH_2), 1.40 (s, 6H, ^4J(PtH) 2.7 Hz, CMe), 1.70 (d, 4H, ^2J(HH) 1.3 Hz, ^3J(PtH) 23.5 Hz), 1.82 (d, 4H, ^2J(HH) 1.3 Hz, ^3J(PtH) 25.4 Hz), 4.18 ppm (d, 4H, ^3J(HH) 2.0 Hz, ^2J(PtH) 36.8 Hz), 4.18 ppm (d, 4H, ^3J(HH) 2.0 Hz, ^2J(PtH) 36.8 Hz).

1,1-Diphosphine-3,3-dimethylplatina(II)cyclobutanes (4)

To 0.140 mmol of phosphine was added a solution of 0.070 mmol **3** (26.1 mg) in 10 ml of n-pentane at $-20\,°C$. The mixture was allowed to warm to room temperature during 0.5 h then stirred for 15 h. After evaporation of the solvent, **4** was isolated as a white solid. **4a**: Yield: 95%. ^1H NMR (C_6D_6): δ 0.88 (s, 4H, ^2J(PtH) 77.4 Hz, ^3J(PH) 6.5 Hz, CH_2), 1.02 (s, 18H, ^3J(PtH) 21.4 Hz, ^2J(PH) 7.6 Hz, PMe), 1.57 ppm (s, 6H, ^4J(PtH) 5.0 Hz, CMe). **4b**: Yield: 92%. ^1H NMR (C_6D_6): δ 0.73 (s, 4H, ^2J(PtP) 75.1 Hz, ^3J(PH) 5.4 Hz, CH_2), 1.01 (t, 18H, ^3J(HH) 7.8 Hz, ^4J(PtH) 7.6 Hz, ^3J(PH) 7.4 Hz, PCH_2CH_3), 1.57 (s, 6H, ^4J(PtH) 4.4 Hz, CMe), 1.95 ppm (q, 12H, ^3J(HH) 7.8 Hz, ^3J(PtH) 21.8 Hz, ^2J(PH) 7.6 Hz, PCH_2). **4c**: Yield: 93%. ^1H NMR (C_6D_6): δ 0.85 (s, 4H, ^2J(PtH) 76.3 Hz, ^3J(PH) 6.0 Hz, CH_2), 0.93 (t, 18H, ^3J(HH) 7.1 Hz, ^5J(PtH) 7.3 Hz, $PCH_2CH_2CH_2CH_3$), 1.39 (qt, 12H, ^3J(HH) 7.4 Hz, ^4J(PtH) 11.9 Hz, $PCH_2CH_2CH_2$), 1.56 (s, 6H, ^4J(PtH) 4.1 Hz, CMe), 1.52–1.73 ppm (m, 24H, PCH_2CH_2). **4d**: Yield: 90%. ^1H NMR (C_6D_6): δ 0.87 (s, 4H, ^2J(PtH) 84.5 Hz, ^3J(PH) 5.4 Hz, CH_2), 1.40 (s, 6H, ^4J(PtH) 4.6 Hz, CMe), 6.93 (m, 18H), 7.59 ppm (m, 12H).

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