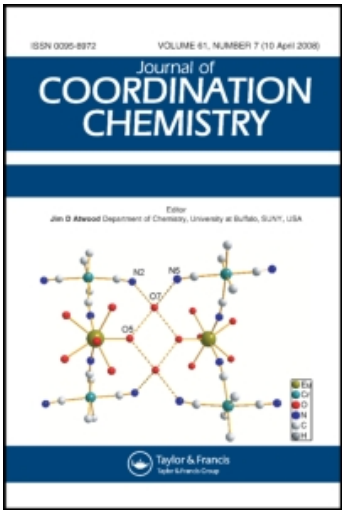

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Mono- and dinuclear metallacyclic complexes of Pt(II) synthesized from some eugenol derivatives

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Mono- and dinuclear metallacyclic complexes of Pt(II) synthesized from some eugenol derivatives

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The complexes $K[PtCl_3(Meug)]$ (**1**; Meug = methyleugenol), $K[PtCl_3(Meteug)]$ (**2**; Meteug = methyl eugenoxyacetate), and $K[PtCl_3(Eteug)]$ (**3**; Eteug = ethyl eugenoxyacetate) reacted with $AgNO_3$, $SnCl_2$, KOH, or ethanol–water solutions to lose one aryl proton and form dinuclear metallacyclic complexes $Pt_2Cl_2(Meug\text{-}1H)_2$ (**4**), $Pt_2Cl_2(Meteug\text{-}1H)_2$ (**5**), and $Pt_2Cl_2(Eteug\text{-}1H)_2$ (**6**), respectively. Complexes **4–6** reacted with aliphatic, aromatic, and heterocyclic amines to give various mononuclear metallacyclic platinum complexes **7–15**. ^1H NMR spectra showed that in **4–15** Meug, Meteug, and Eteug are bound with Pt(II) both at the benzene carbon and at the ethylenic double bond of the side chain. NOESY spectra and single-crystal X-ray diffraction indicated that in **7–15** the amines are in *cis*-position with respect to the ethylenic double bond.

Keywords: Platinum complexes; Metallacyclic complexes; Eugenol derivatives; Aryl C–H activation

1. Introduction

Eugenol (4-allyl-2-methoxyphenol), a main component of clove oil, and its derivatives find application in a number of areas because of varied biological properties. For example, eugenol and methyleugenol (4-allyl-1,2-dimethoxybenzene) are used in perfumery and flavoring, in formulating insect attractants, UV absorbers, analgesics, biocides, antiseptics [1–4], in manufacturing food additives and stabilizers, and as antioxidants for plastics and rubbers [5]. When mixed with zinc oxide, eugenol forms a material which has restorative and prosthodontic applications in dentistry as dental cement [6]. Interest in metal complexes containing biologically active ligands is increasing; for example, several complexes of transition metal with caffeine [7], omeprazole [8], fluoroquinolone antibiotics [9], oxicams [10] have been synthesized, characterized and screened for antibacterial activity. It is, therefore, worthwhile to search for pathways that introduce eugenol derivatives (natural arylolefins in wider

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classification) into metal coordination sphere and then chemically transform them to biologically active compounds. Various syntheses involving arylolefin in which transition metal–olefin complexes are key intermediates are well known [11], but complexes containing eugenol derivatives are rarely studied [12].

Recently, we reported that activation of aryl C–H bond in the platinum–safrole analog of Zeise's salt led to formation of metallacyclic complexes [13]. Hence, we expected that the activation of aryl C–H bond in eugenol derivatives would lead to formation of metallacyclic complexes containing eugenol derivatives as well, which may be utilized for their functionalization.

2. Experimental

2.1. *General consideration and instrumentation*

IR spectra were recorded on an IMPACK-410 NICOLET spectrometer in KBr discs from 400 to 4000 cm^{-1}. NMR spectra were recorded on a Bruker AVANCE 500 MHz at 298–300 K, in a suitable solvent, with TMS as the internal standard. ESI MS (+MS or −MS) are recorded on 1100 LC-MSD-Trap-SL. Pt was analyzed according to the weight method [14] and, C and H were analyzed on a LECO CHNS model 932 elemental analyzer. Single-crystal X-ray data are recorded at the Department of Chemistry and Nano Science, Ewha Womans University, Seoul, Korea, on a Bruker SMART APX diffractometer equipped with a monochromator in Mo-Kα ($\lambda = 0.71073$ Å) incident beam. Crystals were mounted on a glass fiber. The CCD data were integrated and scaled using the Bruker-SAINT software package, and the structures were solved and refined using SHEXTL V6.12. Hydrogens were located in calculated positions.

2.2. *Preparation*

2.2.1. K[$PtCl_3$(Meug)] (1). This complex was prepared starting from 10 mmol of Zeise's salt and 16 mmol methyleugenol (Meug), according to the procedure for the preparation of K[$PtCl_3$(Safrole)] [13]. The yield was 4.15 g (80%). IR (cm^{-1}): 3075, 3010, 2953, 2845 (ν_{CH}); 1588, 1513 ($\nu_{C=C}$), ^{1}H NMR (table 1). Calcd for $KPtCl_3C_{11}H_{14}O_2$ (%): Pt + 1/2(K_2SO_4), 54.4; C, 25.5; H, 2.7. Found: Pt + 1/2(K_2SO_4), 54.7; C, 25.7; H, 2.6.

2.2.2. K[$PtCl_3$(Meteug)] (2). This complex was prepared starting from 10 mmol of Zeise's salt and 16 mmol methyl eugenoxyacetate (Meteug), according to the procedure for the preparation of K[$PtCl_3$(Safrole)] [13]. The yield was 5.0 g (85%), yellow crystals. IR (cm^{-1}): 3089, 3038, 2952, 2845 (ν_{CH}); 1750 ($\nu_{C=O}$); 1592, 1515 ($\nu_{C=C}$), ^{1}H NMR (table 1). Calcd for $KPtCl_3C_{13}H_{16}O_4$: M, 574–582† au (%): Pt + 1/2(K_2SO_4), 48.9. Found: M + K^+, 614.9 au (from + MS); Pt + 1/2(K_2SO_4), 48.6.

2.2.3. K[$PtCl_3$(Eteug)] (3). This complex was prepared starting from 10 mmol of Zeise's salt and 16 mmol ethyl eugenoxyacetate (Eteug), according to the procedure for

Table 1. ^{1}H NMR signals of coordinated Meug, Meteug and Eteug in **1–6**, δ (ppm), J (Hz).

	1 CD_3OD	**2** CD_3COCD_3	**3** CD_3COCD_3	**4** $CDCl_3$	**5** $CDCl_3$	**6** $CDCl_3$
H3	7.36; d; ^4J 1.5	7.41; d; ^4J 2	7.49; d; ^4J 1.5	6.47; s	6.57; s	6.57; s
H5	6.93; dd; ^3J 8; ^4J 1.5	6.86; dd; ^3J 8; ^4J 2	6.88; dd; ^3J 8; ^4J 1.5	–	–	–
H6	6.91; d; ^3J 8	6.83; d; ^3J 8	6.86; d; ^3J 8	6.53; s	6.42; s	6.41; s
H7a	3.89; s	4.66; s	4.66; s	3.82; s	4.62; s	4.60; s
H7b	3.87; s	3.85; s	3.89; s	3.79; s	3.79; s	3.79; s
H8a	2.90; dd; ^2J 15; ^3J 6.5	2.85; dd; ^2J 15; ^3J 7	2.85; dd; ^2J 15; ^3J 8	2.58; d; ^2J 16.5	2.57; d; ^2J 16	2.58; d; ^2J 16.5
H8b	3.49; dd; ^2J 15; ^3J 7	3.43; dd; ^2J 15; ^3J 7	3.48; dd; ^2J 15; ^3J 7	3.81; ov	3.81; ov	3.75; ov
H9	5.21; m; $^2J_{PtH}$ 75	5.03; m; $^2J_{PtH}$ 75	5.03; m; $^2J_{PtH}$ 75	5.11; m; $^2J_{PtH}$ 75	5.09; m; $^2J_{PtH}$ 75	5.09; m; $^2J_{PtH}$ 75
cis-H10	4.30; d; ^3J 7.5; $^2J_{PtH}$ 70	4.13; dd; ^3J 8; ^2J 1.5; $^2J_{PtH}$ 70	4.11; dd; ^3J 8; ^2J 1.5; $^2J_{PtH}$ 70	4.30; d; ^3J 7; $^2J_{PtH}$ 75	4.28; d; ^3J 7; $^2J_{PtH}$ 70	4.29; ov
trans-H10	4.46; d;^3J 13.5; $^2J_{PtH}$ 70	4.29; dd; ^2J 1.5; ^3J 13.5; $^2J_{PtH}$ 70	4.28; dd; ^2J 1.5; ^3J 13.5; $^2J_{PtH}$ 70	4.03; d; ^3J 13; $^2J_{PtH}$ 70	4.00; d; ^3J 13.5; $^2J_{PtH}$ 70	4.01; d; ^3J 13; $^2J_{PtH}$ 70
Others	–	Hα: 3.71; s	Hα: 4.20; q; ^3J 7; Hβ: 1.25; t; ^3J 7	–	Hα: 3.79; s	Hα: 4.26; q; ^3J 7; Hβ: 1.30; t; ^3J 7

ov, overlapped.

the preparation of K[$PtCl_3$(Safrole)] [13]. The yield was 5.0 g (85%), yellow crystals. IR (cm^1): 3089, 3038, 2952, 2845 (ν_{CH}); 1750 ($\nu_{C=O}$); 1592, 1515 ($\nu_{C=C}$), ^{1}H NMR (table 1). Calcd for $KPtCl_3C_{14}H_{18}O_4$: M, 588–596 au (%): Pt + 1/2(K_2SO_4), 47.8. Found: $M - K^+$, 551.3 au (from −MS); Pt + 1/2(K_2SO_4), 48.0.

2.2.4. [Pt_2Cl_2(Meug-1H)$_2$] (4). This complex was prepared starting from 5 mmol of **1**, according to the procedure for the preparation of [Pt_2Cl_2(Safrole-1H)$_2$] [13]. Yellow crystals. IR (cm^{-1}): 3060, 3003, 2946, 2837 (ν_{CH}); 1584, 1490 ($\nu_{C=C}$), ^{1}H NMR (table 1). Calcd for $Pt_2Cl_2C_{22}H_{26}O_4$: M, 812–820 au (%): Pt, 47.9; C, 32.4; H, 3.2. Found: $M + H^+$, 816.2 au (from +MS); Pt, 47.6; C, 32.1; H, 3.4.

2.2.5. [Pt_2Cl_2(Meteug-1H)$_2$] (5). This complex was prepared starting from 5 mmol of **2**, according to the procedure for the preparation of [Pt_2Cl_2(Safrole-1H)$_2$] [13]. Light yellow crystals. IR (cm^{-1}): 3067, 2945, 2845 (ν_{CH}); 1749 ($\nu_{C=O}$), 1588, 1491 ($\nu_{C=C}$), ^{1}H NMR (table 1). Anal. Calcd for $Pt_2Cl_2C_{26}H_{30}O_8$: M, 928–936 au (%): Pt, 41.9; C, 33.5; H, 3.2. Found: $M + H^+$, 931 au (from +MS); Pt, 42.2; C, 33.8; H, 3.0.

2.2.6. [Pt_2Cl_2(Eteug-1H)$_2$] (6). This complex was prepared starting from 5 mmol of **3**, according to the procedure for the preparation of [Pt_2Cl_2(Safrole-1H)$_2$] [13]. Light yellow crystals. IR (cm^{-1}): 3080, 2974, 2845 (ν_{CH}); 1742 ($\nu_{C=O}$), 1587, 1490 ($\nu_{C=C}$),

^{1}H NMR (table 1). Calcd for $Pt_2Cl_2C_{28}H_{34}O_8$: M, 956–964 au (%): Pt, 40.6; C, 35.0; H, 3.6. Found: $M + Cl^-$, 995.5 au (from −MS); Pt, 40.3; C, 34.8; H, 3.5.

2.2.7. [PtCl(Meug-1H)(Me_2NH)] (7). To a mixture of 407.5 mg (0.5 mmol) of **4** and 6 mL of acetone was added a solution of 1 mmol of Me_2NH in 3 mL of acetone. The reaction mixture was stirred at room temperature for 30 min, then cooled to −18°C. Light yellow crystals were collected, washed with EtOH, Et_2O, and recrystallized from EtOH. The yield was 303 mg (67%). IR (cm^{-1}): 3268 (ν_{NH}); 3075, 3003, 2933, 2838 (ν_{CH}); 1574, 1474 ($\nu_{C=C}$), ^{1}H NMR (table 2 and Supplementary material). Calcd for $PtClC_{13}H_{20}NO_2$ (%): Pt, 43.0; C, 34.5; H, 4.4. Found: Pt, 43.4; C, 34.2; H, 4.6.

2.2.8. [PtCl(Meug-1H)(piperidine)] (8). This complex was prepared starting from 0.5 mmol of **4** and 1 mmol of piperidine, according to the procedure for the preparation of **7**. White crystals. The yield was 285 mg (58%). IR (cm^{-1}): 3247 (ν_{NH}); 3060, 2946, 2838 (ν_{CH}); 1581, 1557 ($\nu_{C=C}$), ^{1}H NMR (table 2 and Supplementary material). Calcd for $PtClC_{16}H_{24}NO_2$: M, 491–495 au (%): Pt, 39.6. Found: $M - H^+$: 490.1 au (from −MS); Pt, 39.9.

2.2.9. [PtCl(Meug-1H)(pyridine)] (9). To a mixture of 407.5 mg (0.5 mmol) of **4** and 6 mL of acetone was added a solution of 1 mmol of pyridine in 3 mL of acetone. The reaction mixture was stirred at room temperature for 90 min. Colorless crystals were filtered, washed with EtOH, Et_2O, and recrystallized from EtOH. The yield was 389 mg (80%). IR (cm^{-1}): 3070, 2998, 2839 (ν_{CH}); 1594, 1559 ($\nu_{C=C}$), ^{1}H NMR (table 2 and Supplementary material). Calcd for $PtClC_{16}H_{18}NO_2$ (%): Pt, 40.1; C, 39.5; H, 3.7. Found: Pt, 40.5; C, 39.1; H, 3.4.

2.2.10. [PtCl(Meug-1H)(*o*-toluidine)] (10). This complex was prepared starting from 0.5 mmol of **4** and 1 mmol of *o*-toluidine, according to the procedure for the preparation of **7**. Light yellow crystals. The yield was 262 mg (51%). IR (cm^{-1}): 3295, 3234, 3149 (ν_{NH}); 3078, 3025, 2998, 2841 (ν_{CH}); 1584, 1557 ($\nu_{C=C}$), ^{1}H NMR (table 2 and Supplementary material). Calcd for $PtClC_{18}H_{22}NO_2$ (%): Pt, 37.9; C, 42.0; H, 4.3. Found: Pt, 37.6; C, 42.3; H, 4.0.

2.2.11. [PtCl(Meteug-1H)(piperidine)] (11). This complex was prepared starting from 0.5 mmol of **5** and 1 mmol of piperidine, according to the procedure for the preparation of **7**. White crystals. The yield was 412 mg (75%). IR (cm^{-1}): 3261 (ν_{NH}); 3060, 2931, 2852 (ν_{CH}); 1746 ($\nu_{C=O}$); 1582, 1476 ($\nu_{C=C}$), ^{1}H NMR (table 2 and Supplementary material). Calcd for $PtClC_{18}H_{26}NO_4$: M, 548–552 au (%): Pt, 35.4. Found: $M + H^+$, 552.1 au (from +MS); Pt, 35.1.

2.2.12. [PtCl(Meteug-1H)(pyridine)] (12). This complex was prepared starting from 0.5 mmol of **5** and 1 mmol of pyridine, according to the procedure for the preparation of **7**. White crystals. The yield was 414 mg (76%). IR (cm^{-1}): 3060, 3012, 2919, 2848 (ν_{CH}); 1754 ($\nu_{C=O}$); 1604, 1477 ($\nu_{C=C}$), ^{1}H NMR (table 2 and Supplementary material). Calcd for $PtClC_{18}H_{20}NO_4$ (%): Pt, 35.8; C, 39.7; H, 3.7. Found: Pt, 35.5; C, 39.9; H, 3.4.

Table 2. ^{1}H NMR signals of coordinated Meug, Meteug, and Eteug in **7–15**, CD_3COCD_3, δ (ppm), J (Hz).

	H3	H6	H7a	H7b	H8a	H8b	H9	*cis*-H10	*trans*-H10	Others
7	6.58; s	7.00; s; $^{3}J_{PtH}$ 39	3.71; s	3.67; s	2.55; d; ^{2}J 17	3.63; dd; ^{2}J 17; ^{3}J 5	4.71; m; $^{2}J_{PtH}$ 76	3.86; d; ^{3}J 7; $^{2}J_{PtH}$ 76	3.60; d; ^{3}J 13	–
8	6.57; s	7.00; s; $^{3}J_{PtH}$ 38	3.71; s	3.66; s	2.53; d; ^{2}J 17	3.61; dd; ^{2}J 17; ^{3}J 6	4.70; m; $^{2}J_{PtH}$ 74	3.89; d; ^{3}J 7; $^{2}J_{PtH}$ 76	3.57; d; ^{3}J 13; $^{2}J_{PtH}$ 70	–
9	6.62; s	7.09; s; $^{3}J_{PtH}$ 40	3.74; s	3.70; s	2.65; d; ^{2}J 17	3.76; dd; ^{2}J 17; ^{3}J 6	4.83; m; $^{2}J_{PtH}$ 75	3.77; d; ^{3}J 7	3.83; d; ^{3}J 13; $^{2}J_{PtH}$ 70	–
10	6.54; s	7.00; s; $^{3}J_{PtH}$ 40	3.72; s	3.66; s	2.41; d; ^{2}J 17	3.45; dd; ^{2}J 17; ^{3}J 6	4.34; m; $^{2}J_{PtH}$ 75	3.38; d; ^{3}J 7; $^{2}J_{PtH}$ 75	3.47; d; ^{3}J 12	–
11	6.61; s	6.97; s; $^{3}J_{PtH}$ 38	4.59; s	3.70; s	2.55; d; ^{2}J 17	3.61; dd; ^{2}J 17; ^{3}J 6	4.70; m; $^{2}J_{PtH}$ 70	3.90; d; ^{3}J 7; $^{2}J_{PtH}$ 75	3.57; d; ^{3}J 13; $^{2}J_{PtH}$ 75	Hα: 3.73; s
12	6.66; s	7.04; s; $^{3}J_{PtH}$ 40	4.59; s	3.73; s	2.66; d; ^{2}J 17	3.74; d; ^{2}J 17	4.83; m; $^{2}J_{PtH}$ 75	3.77; d; ^{3}J 6.5	3.81; d; ^{3}J 13; $^{2}J_{PtH}$ 75	Hα: 3.74; s
13	6.62; s	6.95; s; $^{3}J_{PtH}$ 39	4.55; s	3.70; s	2.56; d; ^{2}J 17	3.62; dd; ^{2}J 17; ^{3}J 6	4.71; m; $^{2}J_{PtH}$ 70	3.86; d; ^{3}J 7	3.58; d; ^{3}J 13	Hα: 4.20; q; ^{3}J 7; Hβ:1.27; t; ^{3}J 7
14	6.60; s	6.96; s; $^{3}J_{PtH}$ 40	4.53; s	3.69; s	2.54; d; ^{2}J 17	3.59; dd; ^{2}J 17; ^{3}J 6	4.69; m; $^{2}J_{PtH}$ 75	3.89; d; ^{3}J 7 $^{2}J_{PtH}$ 75	3.55; d; ^{3}J 13; $^{2}J_{PtH}$ 75	Hα: 4.20; q; ^{3}J 7; Hβ: 1.27, t; ^{3}J 7
15	6.66; s	7.05; s; $^{3}J_{PtH}$ 40	4.57; s	3.73; s	2.65; d; ^{2}J 17	3.74; m	4.82; m; $^{2}J_{PtH}$ 75	3.77; d; ^{3}J 7	3.81; d; ^{3}J 13; $^{2}J_{PtH}$ 70	Hα: 4.21; q; ^{3}J 7; Hβ:1.28, t; ^{3}J 7

2.2.13. [PtCl(Eteug-1H)(Me_2NH)] (13). This complex was prepared starting from 0.5 mmol of **5** and 1 mmol of Me_2NH, according to the procedure for preparation of **7**. Light yellow crystals. The yield was 315 mg (60%). IR (cm^{-1}): 3266 (ν_{NH}); 2945, 2844 (ν_{CH}); 1736 ($\nu_{C=O}$); 1586, 1480 ($\nu_{C=C}$), ^{1}H NMR (table 2 and Supplementary material). Calcd for $PtClC_{16}H_{24}NO_4$ (%): Pt, 37.2; C, 36.6; H, 4.6. Found: Pt, 36.9; C, 36.9; H, 4.4.

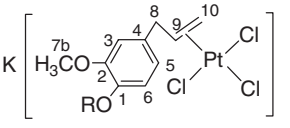
2.2.14. [PtCl(Eteug-1H)(piperidine)] (14). This complex was prepared starting from 0.5 mmol of **5** and 1 mmol of piperidine (Pip), according to the procedure for preparation of **7**. Light yellow crystals. The yield was 452 mg (80%). IR (cm^{-1}): 3250 (ν_{NH}); 3069, 2941, 2848 (ν_{CH}); 1739 ($\nu_{C=O}$); 1584, 1481 ($\nu_{C=C}$), ^{1}H NMR (table 2 and Supplementary material). Calcd for $PtClC_{19}H_{28}NO_4$: M, 563–567 au (%): Pt, 34.5. Found: M + $PipH^+$, 651 au (from +MS); Pt, 34.8.

2.2.15. [PtCl(Eteug-1H)(pyridine)] (15). This complex was prepared starting from 0.5 mmol of **5** and 1 mmol of pyridine, according to the procedure for the preparation of **7**. Colorless crystals. The yield was 458 mg (83%). Crystal data, formula sum: $C_{19}H_{22}ClNO_4Pt$, formula weight: 558.92, crystal system: monoclinic, space group: *P121/c1* (no. 14), $a = 13.240(3)$ Å, $b = 11.959(3)$ Å, $c = 12.609(3)$ Å, $\beta = 100.84(0)^\circ$, cell volume: 1960.83(80) $Å^3$, important distances (Å) and angles (°): Pt1–C1 = 2.103(7), Pt1–C2 = 2.122(6), Pt1–N1 = 2.132(6), Pt1–Cl1 = 2.308(4), Pt1–C5 = 1.987(7), C5–Pt1–C1 = 87.88(27), C5–Pt1–C2 = 82.40(25), C1–Pt1–C = 38.46(24), C5–Pt1–N1 = 176.98(24), C1–Pt1–N1 = 90.09(25), C2–Pt1–N1 = 94.62(22), C5–Pt1–Cl1 = 94.08(18), C1–Pt1–Cl1 = 158.80(18), C2–Pt1–Cl1 = 162.65(17), N1–Pt1–Cl1 = 88.63(14). IR (cm^{-1}): 3053, 2988, 2845 (ν_{CH}); 1754 ($\nu_{C=O}$); 1605, 1490 ($\nu_{C=C}$), ^{1}H NMR (table 2 and Supplementary material). Calcd for $PtClC_{19}H_{22}NO_4$ (%): Pt, 34.9; C, 40.8; H, 3.9. Found. Pt, 34.6; C, 41.1; H, 3.6.

3. Results and discussion

The eugenol derivatives used are 4-allyl-1,2-dimethoxybenzene (methyleugenol: Meug), methyl 4-allyl-2-methoxyphenoxyacetate (methyl eugenoxyacetate: Meteug), and ethyl 4-allyl-2-methoxyphenoxyacetate (ethyl eugenoxyacetate: Eteug). The ethylene from Zeise's salt is replaced by the eugenol derivatives under mild condition to form the following analogs of Zeise's salt: K[$PtCl_3$(Meug)] (**1**), K[$PtCl_3$(Meteug)] (**2**), and K[$PtCl_3$(Eteug)] (**3**) (figure 1).

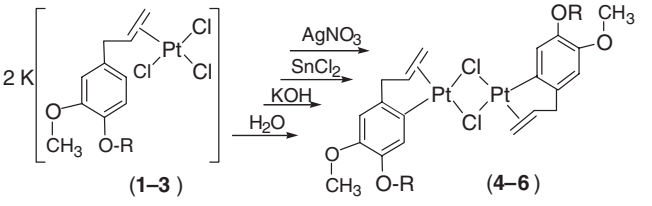
In the IR spectra of Meug, Meteug, and Eteug, there is a band at 1640 cm^{-1} from the C = C double bond of allyl which is absent in spectra of **1**–**3**. The resonances of Pt(II)-coordinated ethylenic protons (H9, *cis*-H10, and *trans*-H10; table 1) are upfield in comparison with those of noncoordinated Meug, Meteug, and Eteug. The frequency difference between two ^{195}Pt satellites in signals from H9, *cis*-H10, and *trans*-H10, $^2J_{PtH}$, is 70–75 Hz (table 1). In ^{1}H NMR spectra, for the noncoordinated Meug, Meteug, and Eteug, two protons of CH_2 of allyl group (H8) give rise to a doublet at 3.2–3.3 ppm with $^3J = 6.5$ Hz, but in the spectra of **1**–**3**, one doublet of doublets centered at 2.8–2.9 ppm and another centered at 3.4–3.5 ppm are observed for H8a and H8b,



7a(*) 7a α 7a α β
R: CH_3 (**1**); CH_2COOCH_3 (**2**); $CH_2COOCH_2CH_3$ (**3**)

(*) The numeration specially for analysis of NMR spectra

Figure 1. Structures of **1**, **2**, and **3**.



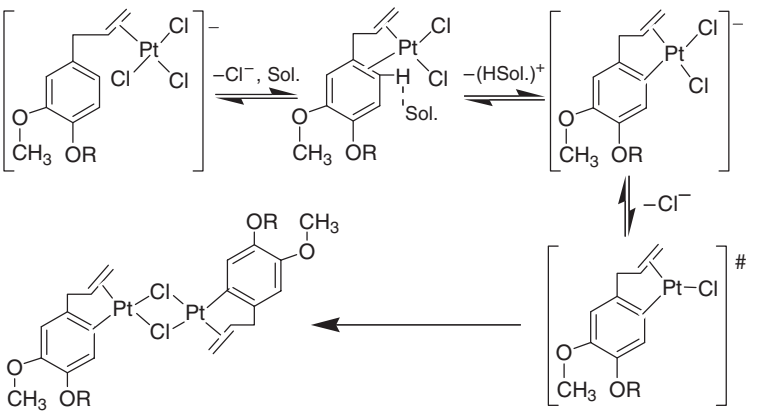
Scheme 1. Formation and structure of dinuclear metallacyclic complexes **4**–**6**.

respectively (table 1). These data show that in **1**–**3**, Meug, Meteug, and Eteug are η^2-allyl ligands, that is, they coordinate with Pt(II) at the ethylenic double bond of allyl group. Complexes **1**, **2**, and **3** react with silver nitrate, tin chloride, potassium hydroxide, and ethanol–water solutions to form dinuclear metallacyclic complexes **4**, **5**, and **6**, respectively (scheme 1).

In ^{1}H NMR spectra of **4**–**6**, there are only two singlets because of two aromatic protons of Meug, Meteug, and Eteug and the chemical shift of these two protons (H3, H6) is considerably reduced (table 1), indicating that one of their aromatic protons is lost and the coupling constant between the two remaining aromatic protons is zero. It is noteworthy that each coordinated eugenol derivative loses proton H5 to form σ-bound (C5)-Pt. The other resonances of coordinated Meug, Meteug, and Eteug in **4**–**6** resemble those in **1**–**3**, respectively (table 1). In contrast to **1**–**3**, **4**–**6** are almost insoluble in ethanol, but are soluble in chloroform because of their nonionic nature. The elemental analysis shows the absence of K in **4**–**6**. The molecular mass of **4**–**6** (see the "Experimental" section) indicates that they occur as dinuclear complexes Pt_2Cl_2(Meug-1H)$_2$ (**4**), Pt_2Cl_2(Meteug-1H)$_2$ (**5**), and Pt_2Cl_2(Eteug-1H)$_2$ (**6**). In these complexes, deprotonated eugenol derivatives are bound with Pt(II) both at the benzene carbon and at the ethylenic double bond of the side chain.

Complexes **1**–**3** lose an HCl molecule in the formation of **4**–**6**. The silver nitrate and tin chloride facilitate the elimination of Cl^- from **1**–**3** by generating AgCl precipitate and stable $[SnCl_3]^-$, respectively, while potassium hydroxide and ethanol or water facilitate the elimination of H^+ from **1**–**3** by generating H_2O and $(HSol.)^+$, respectively. Thus, a plausible pathway for formation of **4**–**6** is suggested in scheme 2.

Deprotonation of hydrocarbons in the coordination sphere of Pt(II) is of great interest in organometallic chemistry and catalytic chemistry. In the deprotonation of coordinated olefins, usually one allylic proton is lost to form η^1-allyl or η^3-allyl species [15, 16]. In the deprotonation of *p*-diethylbenzene and *p*-xylene, one benzylic proton is lost to form η^3-benzyl complexes [17, 18].



Scheme 2. Pathway for formation of dinuclear metallacyclic complexes **4**–**6**.

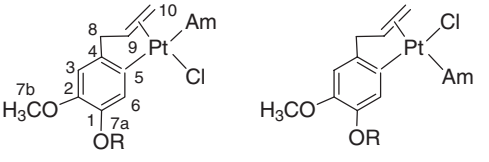


Figure 2. Two possible structures of **7**–**15**. R: CH_3, Am: Me_2NH (**7**), piperidine (**8**), pyridine (**9**), *o*-toluidine (**10**); R: CH_2COOCH_3, Am: piperidine (**11**), pyridine (**12**); R: $CH_2COOCH_2CH_3$, Am: Me_2NH (**13**), piperidine (**14**), pyridine (**15**).

The formation of stable metallacyclic from allylbenzene in Bercaw's work [18], safrole in our previous report [13] and eugenol derivatives in the present study demonstate that the allylbenzenes have a significant tendency to chelate.

To study the reactivity of dinuclear metallacyclic complexes **4**–**6**, we carried out their reaction with various amines (aliphatic, aromatic, and heterocyclic) and thus obtained mononuclear metallacyclic complexes **7**–**15**. The structures of **7**–**15** (figure 2) were determined by IR-, ^{1}H NMR-, NOESY-, and MS spectra (see section 2 and table 2 and Supplementary material).

The assignment of ^{1}H NMR signals (tables 1 and 2 and Supplementary material) is based on their chemical shift, spin–spin splitting patterns, and 2-D NMR spectra. For example, some ambiguous signals are assigned as follows: (1) For **7**–**15**, the H6-singlet is distinguished from the H3-singlet by ^{195}Pt satellites with a $^3J_{PtH}$ value of 38–40 Hz (table 2, figure 3). For **4**–**6**, the ^{195}Pt satellites in signal from H6 are unclear and therefore the H6-singlet and H3-singlet are assigned using HMBC spectra: H3-singlet has a cross peak with signal from C8 (38–40 ppm) while H6 does not. Two ^{195}Pt satellites in the signal from H6 (table 2, figure 3) are evidence to support the formation of σ-bound (C5)–Pt. (2) For **7**–**10**, the H7a-singlet and H7b-singlet of two CH_3O groups are assigned using NOESY spectra. For instance, in figure 1, the cross peak *a* indicates that the singlet at 3.71 ppm corresponds to protons adjacent to H6 (the singlet accompanied by the ^{195}Pt satellites), that is, the singlet at 3.71 ppm corresponds to H7a; the cross peak *b* indicates that the singlet at 3.67 ppm corresponds to protons adjacent to H3, that is, the singlet at 3.67 ppm corresponds to H7b.

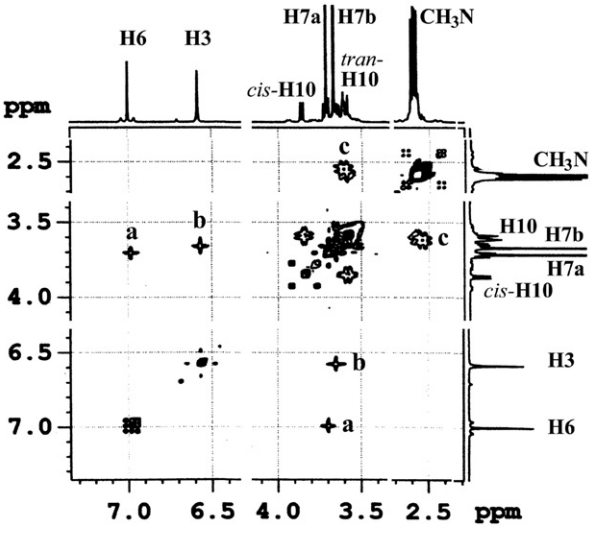


Figure 3. Part of the NOESY spectrum of **7** (in CD_3COCD_3).

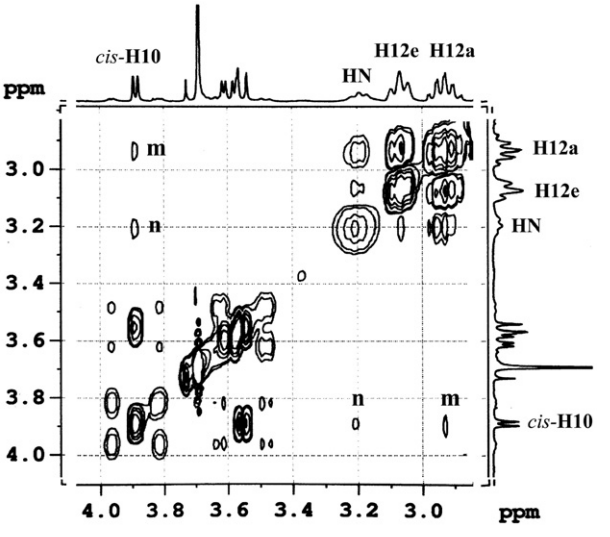


Figure 4. Part of the NOESY spectrum of **14** (in CD_3COCD_3).

To know which structure (**A** or **B**) **7**–**15** have when **4**–**6** are treated with amines, NOESY spectra of **7**–**15** are studied. The evidence for structure **A** is the presence of cross peaks between protons of the amines and H10 of the allyl group accompanied by the absence of cross peaks between protons of amines and H3 or H6 of phenyl. In figure 3, there is the cross peak *c* between CH_3N and *trans*-H10, but there is no cross peak between CH_3N and either H3 or H6; in figure 4, the cross peaks *m* and *n* indicate that H12a and

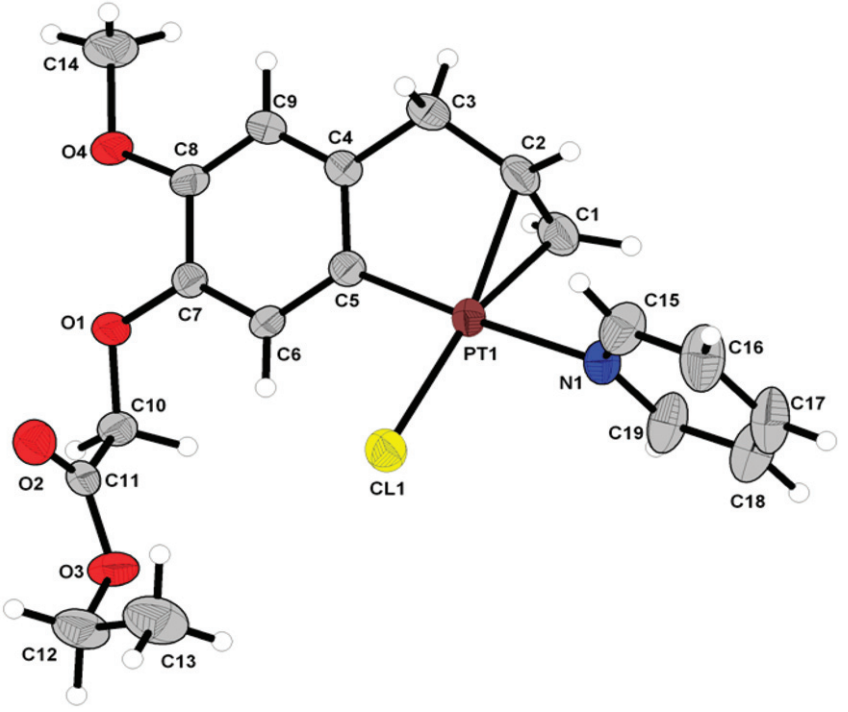


Figure 5. Structure of **15** on the basis of XRD.

HN of piperidine are adjacent to *cis*-H10 of allyl. Structure **A** has been confirmed by single-crystal X-ray diffraction of [PtCl(Eteug-1H)Py] (figure 5).

Surprisingly, in reaction of amines with $[Pt_2Cl_2(Meug\text{-}1H)_2]$, $[Pt_2Cl_2(Meteug\text{-}1H)_2]$, and $[Pt_2Cl_2(Eteug\text{-}1H)_2]$ the amines are not in *trans*-position (structure **B**), but are *cis* (structure **A**), with respect to ethylenic double bond as observed [9] for reaction of piperidine with $[Pt_2Cl_2(Safrole\text{-}1H)_2]$. This orientation is controlled by steric effects rather than the *trans* effect.

^{1}H NMR signals of piperidine in the coordination sphere of Pt(II) are analyzed in detail [19]. The multiplicity and magnitude of coupling constant of piperidine's protons for **8**, **11**, and **14** (Supplementary material) indicate that the piperidine ring has a chair conformation, with the nitrogen bound to the Pt equatorially.

In ^{1}H NMR spectra of **7** and **13**, two CH_3 groups of dimethylamine give two doublets (Supplementary material), that is, they are nonequivalent. Similarly, for **8**, **11**, and **14**, positions 12 and 16, are nonequivalent, and also positions 13 and 15 are nonequivalent. Most likely, the cause of this phenomenon is that in these metallacyclic complexes, rotation around the coordinated Pt–N bond does not occur on the NMR time scale at the recorded temperature.

4. Conclusion

Fifteen new mono- and dinuclear complexes of Pt(II) containing methyleugenol, methyl eugenoxyacetate, and ethyl eugenoxyacetate were synthesized and characterized by

elemental analyses, IR, ^{1}H NMR, NOESY, and ESI MS spectra. The deprotonation of aromatic H under mild condition to form chelate complexes and the replacement of Cl from *cis*-position with respect to ethylenic double bond by an amine (not obeying the *trans* effect) were reported.

Acknowledgement

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