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Preliminary communication

Arene ruthenium(II) complexes coordinated by phosphino and two phenoxide groups in tris(2,6-dimethoxyphenyl)phosphine: crystal structure of $(\eta^6\text{-}1,2,3,4\text{-}Me_4C_6H_2)Ru[P\{2,6\text{-}(MeO)_2C_6H_3\}\{2\text{-}O\text{-}6\text{-}MeOC_6H_3\}_2]$

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Abstract

The title compound has been prepared from bis[dichloro(η^6-arene)ruthenium] (η^6-arene = 1,2,3,4-$C_6Me_4H_2$ (**1a**), p-cymene (**1b**) and tris(2,6-dimethoxyphenyl)phospine (TDMPP). The crystal structure features a type of η^3-phosphino-two phenoxides coordination. Reactions with its related phosphines, bis(2,6-dimethoxyphenyl)phenylphosphine (BDMPP) and (2,6-dimethoxyphenyl)diphenylphosphine (MDMPP) gave complexes with η^2-phosphino-phenoxide and η^1-phosphino coordinations, and *trans*-$RuCl_2(MDMPP)_2$, depending on phosphines and arene groups.

Keywords: Ruthenium; Dealkylation; Tris(2,6-dimethoxyphenyl)phosphine

It is known that phosphine ligands with ortho-methoxy phenyl substituents undergo dealkylation reactions to give phosphino-phenoxide ligands [1]. The phosphine ligand with ortho-methoxy groups in the 2- and 6-positions, such as tris(2,4,6-trimethoxyphenyl) phosphine (TMPP) and tris(2,6-dimethoxyphenyl) phosphine (TDMPP), show interesting chemical behavior; high nucleophilicity and large cone angle (184°) [2]. The TMPP ligand displays a wide variety of geometries and hapticities. The arrangements are influenced by steric and electronic requirements of the metal center and three coordination modes are known: (a) the usual monohapto-ligand by phosphino coordination [3a–f]; (b) dihapto-ligand by phosphino-phenoxide or phosphine-O donor (O coordination of MeO group) [3c,d,g–j]; and (c) trihapto-ligand by phosphino-two O donor or phosphino-phenoxide-O donor [3k–n]. Formation of the trihapto-mode by a phosphino-two phenoxide coordination is unknown in the literature. Coordination chemistry of the TDMPP ligand is not as high as that of TMPP. Here we report the preparation of ruthenium(II) complexes with a variety of coordination modes by the reactions of bis[dichloro(η^6-arene)-ruthenium(II)] with TDMPP and its related phosphines.

When a solution of $[(\eta^6\text{-}1,2,3,4\text{-}C_6Me_4H_2)RuCl_2]_2$ **1a** in CH_2Cl_2 was treated with TDMPP at room temperature, a yellow compound, $[(\eta^6\text{-}1,2,3,4\text{-}C_6Me_4H_2)Ru[P\{2,6\text{-}(MeO)_2C_6H_3\}\{2\text{-}O\text{-}6\text{-}MeO_6H_3\}_2]$ **2a**, was obtained [4,5]. X-ray analysis showed that the complex consists of two independent molecules (**2a–A** and **2a–B**) and the TDMPP ligand acts as a trihapto-ligand; phosphino-two phenoxide coordination (Fig. 1) [6].

This coordination type is the first example of coordination of aromatic phosphine ligands containing the methoxy groups in the 2,6-positions. The average distances of Ru–O bonds for two molecules are 2.062(5) Å for **2a–A** and 2.050(6)Å for **2a–B**; these values are in good agreement with usual metal–σ–oxygen bond distance. This difference of bond distances is traced back to that of the Ru–P bond distances, where the bond length (2.272(3) Å) in **2a–A** is shorter than that in **2a–B** (2.282(3) Å). The ^{1}H NMR spectrum showed four kinds of methyl protons at δ 1.72 (s), 2.26 (d,

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J_{PH} = 1.6 Hz), 3.46(s) and 3.49(s) consisting of a 6 : 6 : 6 : 6 intensity ratio; the first two peaks correspond to the methyl protons on the benzene ring and others to the O-methyl protons. An analogous complex, $[(\eta^6$-p-cymene)Ru[P{2,6-$(MeO)_2$-C_6H_3}{2-O-6-$MeOC_6H_3$}$_2$] **2b**, was isolated from the reaction of $[(\eta^6$-p-cymene)$RuCl_2]_2$ **1b** with TDMPP [4,5]. The fate of Me and Cl groups was detected as a phosphonium salt of chloride in the ^{1}H NMR spectroscopic studies in situ.

Complex $[(\eta^6$-p-cymene)$RuCl_2]_2$ **1b** reacted with bis(2,6-dimethoxyphenyl)phenylphosphine (BDMPP) to give an orange compound, $(\eta^6$-*p*-cymene)RuCl[PPh {2,6-$(MeO)_2C_6H_3$}{2-O-6-$MeOC_6H_3$}] **3b** [4,7]. The structure was confirmed by an X-ray analysis [8]. The phosphine ligand acts as a bidentate ligand by a phosphino-phenoxide coordination (Fig. 2).

The Ru–O bond length is 2.069(6) Å, the same as that of **2a**. The Ru–P bond length is 2.342(3) Å, longer than that of **2a**, probably minimizing the repulsive interaction between Cl and P ligand. The molecule has two chiral centers (Ru and P atoms). A priority order of the ligands is *p*-cymene > Cl > P > O for a metal configuration and Ru > 2-O-(6-MeO)C_6H_3 > 2,6-$(MeO)_2C_6H_3$ > Ph for a P configuration. The PLUTO diagram shows that the molecule is a pair of $R_{Ru}R_P/S_{Ru}S_P$. The ^{31}P{H} NMR spectrum of the crystallized material in $CDCl_3$ showed two peaks at δ 31.56 and 39.00 consisting of ca. 1 : 1.2 intensity ratio, suggesting the existence of two kinds of complexes ($R_{Ru}R_P/S_{Ru}S_P$ and $R_{Ru}S_P/S_{Ru}R_P$) in solution [9]. The ^{1}H NMR spectrum also supported the existence of a diastereometer. It results in the chiral centers in the molecule that the methyl protons of *iso*-propyl group showed the existence of two kinds of isomers (A* and A**) and each of them is in a different environment, appearing at δ 1.05 (J_{HH} = 7.0 Hz)* and 1.06 (J_{HH} = 7.0 Hz)*, and at δ 1.12 (J_{HH} = 7.2 Hz)** and 1.15 (J_{HH} = 7.2 Hz)**. The 1,2,3,4-$Me_4C_6H_2$ complex **3a** was also obtained from the reaction of **1a** with BDMPP [4,7]. Reaction of complex **1a** with (2,6-dimethoxyphenyl)diphenylphosphine (MDMPP) underwent a formation of two compounds, yellow crystals $(\eta^6$-1,2,3,4-$Me_4C_6H_2)RuCl_2[PPh_2${2,6-$(MeO)_2C_6H_3$}] and **4a** and $(\eta^6$-1,2,3,4-$Me_4C_6H_2)RuCl[PPh_2${2-O-6-$MeOC_6H_3$}] **5a** [4,10], and the transformation of **4a** to **5a** occurred easily, whereas the reaction with **1b** led to elimination of an arene ring to give $RuCl_2[PPh_2${2,6-$(MeO)_2C_6H_3$}]$_2$ **6** [4,11]. The ^{31}P{H} NMR spectrum showed a single band at δ 61.1. The ^{1}H NMR spectrum showed an existence of two methyl groups at δ 3.17 and 4.53 consisting of a 1 : 1 ratio, probably being assignable to a free OMe and a coordinated OMe group, respectively. Complex **5** is tentatively assumed to be an octahedral structure with a *trans*-configuration as depicted in Scheme 1.

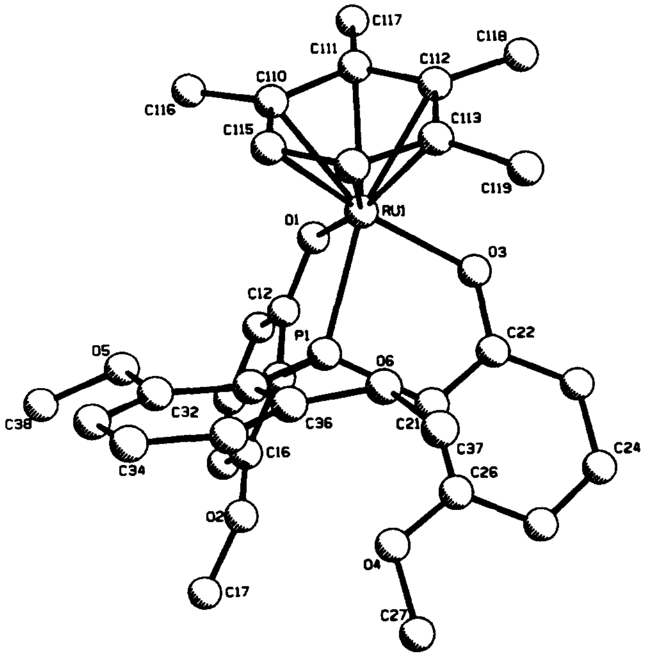


Fig. 1. Molecular structure of $[(\eta^6$-1,2,3,4-$Me_4C_6H_2$)Ru[P{2,6-$(MeO)_2C_6H_3$}{2-O-6-$MeOC_6H_3$}$_2$] **2a**.

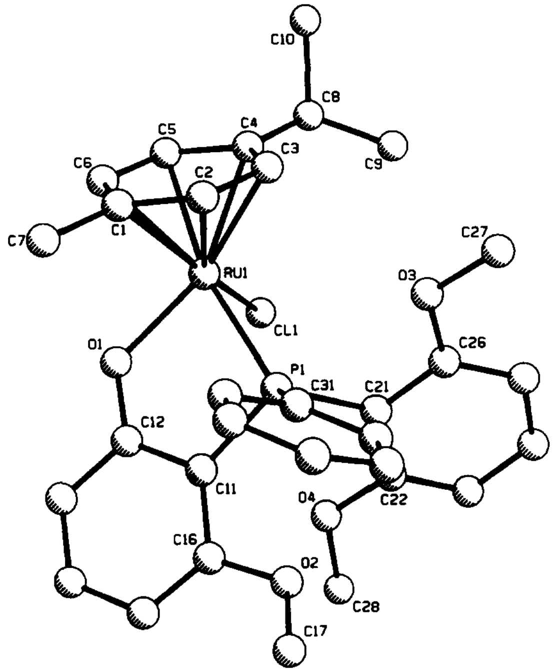
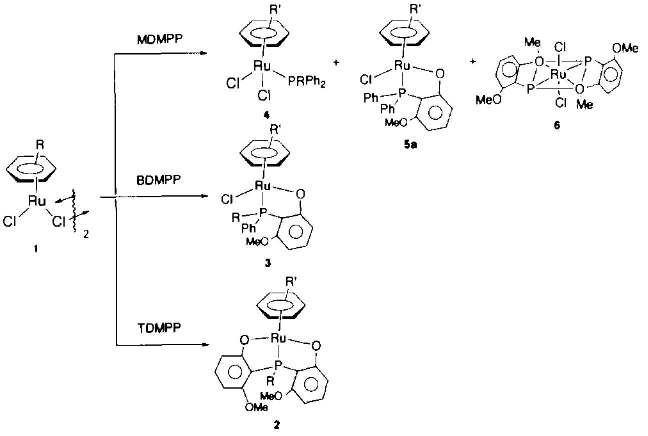


Fig. 2. Molecular structure of $(\eta^6$-*p*-cymene)RuCl[PPh{2,6-$(MeO)_2C_6H_3$}{2-O-6-MeO_6H_3}] **3b**.

Studies of the reactivity difference of various phosphines with ruthenium(II) arene complexes, and investigations on the mechanisms of these reactions are now in progress.

A listing of additional bond distances, angles thermal parameters, and tables of observed and calculated structure factors are available from the authors.



Scheme 1. Reactions of $[(\eta^6\text{-arene})RuCl_2]_2$ **1** with aromatic phosphines containing methoxy groups in 2,6-positions.

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[4] Elemental analysis was in agreement with the calculated value.

[5] **2a** (51%). ^{1}H NMR($CDCl_3$; 250 MHz): δ 1.72 (d, $J_{PH} = 1.5$ Hz, C_6Me_2), 2.26 (d, $J_{PH} = 1.5$ Hz, C_6Me_4), 3.46, 3.49 (s, 6H, *Me*O), 4.30 (d, $J_{PH} = 3.2$ Hz, 2H, C_6H_2), 5.6–7.5 (m, Ph). ^{31}P{H} NMR ($CDCl_3$; 100 MHz): δ 48.32. UV-vis(CH_2Cl_2): λ_{max} 324(3.76) nm. **2b** (52%). ^{1}H NMR($CDCl_3$; 250 MHz): δ 0.89 (d, $J_{HH} = 7.0$ Hz, $CHMe_2$), 1.89 (s, *Me*), 2.41 (sep, $CHMe_2$), 3.47, 3.51 (s, 6H, *Me*O), 5.30 (s, CH_2Cl_2), 5.6–7.5 (m, *Ph*). UV-vis(CH_2Cl_2): λ_{max} 322 (log ϵ 3.89), 374 (3.15) nm.

[6] Crystal data: $C_{32}H_{35}O_6PRu$, M 647.7, monoclinic, space group $P2_1/n$ (No. 14), $a = 17.79(2)$, $b = 15.43(1)$, $c = 20.93(1)$ Å, $\beta = 91.25(8)°$, $V = 5734(1)$ Å, $Z = 8$, $\lambda(MoK\alpha) = 0.71073$ Å. Data were collected on a Rigaku AFC5s diffractometer in the range $55° > 2\theta > 3°$ (14135 reflections collected, 13607 independent reflections). The structure was solved by direct methods and refinement was by full-matrix least-squares techniques (all non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in calculated positions) to $R = 0.056$ and $R_w = 0.069$ ($w = 1/\sigma^2(F_o)$) for 6835 reflections ($I > 3.0\sigma(I)$).

[7] **3a** (65%). ^{1}H NMR ($CDCl_3$; 250 MHz, diastereometers A* and A**): δ 1.05, 1.06 (d, $J_{HH} = 6.9$ Hz, C_6Me_4)*, 1.12, 1.15 (d, $J_{HH} = 7.2$ Hz, C_6Me_4)**, 1.94**, 1.97* (s, *Me*), 2.75 (m, $CHMe_2$), 3.09**, 3.26*, 3.27**, 3.32*, 3.35**, 3.76* (s, *Me*O), 5.27 (s, CH_2Cl_2), 4.6–8.3 (m, *Ph*). ^{31}P{H} NMR($CDCl_3$; 100 MHz): 31.56**, 39.00*. UV-vis(CH_2Cl_2): λ_{max} 291sh (3.88), 3.19sh (3.70), 466sh (2.52) nm. **3b** (66%). ^{1}H NMR ($CDCl_3$; 250 MHz, diastereomers A* and A**): δ 1.58, 2.04 (s, C_6Me_2)*, 2.18, 2.19 (d, $J_{PH} = 1.8$ Hz, C_6Me_2)*, 3.27 (s, 2*Me*O)*, 3.38 (s, *Me*O)*, 1.68, 1.93 (s, C_6Me_2)**, 2.11, 2.30 (d, $J_{PH} = 2.4$ Hz, C_6Me_2)**, 3.05 (s, *Me*O)**, 3.22 (s, 2*Me*O)**, 3.78 (s, *Me*O), 4.5–8.1 (m, *Ph*). ^{31}P{H} NMR($CDCl_3$; 250 MHz): δ 36.94*, 39.61**.

[8] Crystal data: $C_{32}H_{36}O_4Cl_3PRu$ (with one CH_2Cl_2 molecule), triclinic, space group $P\bar{1}$ (No. 2), $a = 12.33(1)$, $b = 14.246(8)$, $c = 11.236(9)$ Å, $\alpha = 91.47(8)$, $\beta = 117.28(6)$, $\gamma = 111.70(6)°$, $V = 1584(2)$ Å^3, $z = 2$. Data were collected on a Rigaku AFC5s diffractometer in the range $50° > 2\theta > 3°$ (14135 reflections collected, 5903 independent reflections). The structure was solved by direct methods and refinement was by full-matrix least-squares techniques (all non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in calculated positions) to $R = 0.040$ and $R_w = 0.047$ ($w = 1/\sigma^2(F_o)$) for 4517 reflections ($I > 3.0\sigma(I)$).

[9] The crystal that an X-ray analysis was carried out on is shown to be a pair of diasetereomers.

[10] **4a** (24%). ^{1}H NMR($CDCl_3$; 250 MHz): δ 1.79 (s, C_6Me_2), 2.08 (d, $J_{PH} = 2.3$ Hz, C_6Me_2), 3.2 (s, *Me*O), 4.5–8.0 (m, *Ph*). ^{31}P{H} NMR ($CDCl_3$; 100 MHz): δ 19.73. **5a** (43%). ^{1}H NMR($CDCl_3$; 250 MHz): δ 1.65 and 1.98 (s, C6, Me_2), 2.14 (d, $J_{PH} = 2.4$ Hz, C_6Me), 2.2 (d, $J_{PH} = 1.5$ Hz, C_6Me), 3.40 (s, O*Me*), 4.7–8.0 (m, *Ph*).

[11] **6** CH_2Cl_2 (45%). ^{1}H NMR($CDCl_3$; 250 MHz): δ 3.17 (s, *Me*O), 4.53 (s, *Me*O), 5.27 (s, CH_2Cl_2), 6.5–7.5 (m, *Ph*). ^{31}P NMR (CD_3Cl; 100 MHz): δ 61.1. UV-vis(CH_2Cl_2): λ_{max} 279^{sh} (3.88), 320 (3.43), 516 (2.74) nm.