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## Short Communication

# Arene complexes of Ru(II)
# Part I. Synthesis, characterization and X-ray crystal structure of $[(\eta^6\text{-}C_6H_5CH_3)RuCl(PPh_3)_2][BF_4]$

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### Abstract

The reaction of $AgBF_4$ with the Ru(II) complex, dichlorotris(triphenylphosphine)Ru(II) in toluene leads to the formation of a stable cationic complex in which the aromatic ring of the solvent molecule is bound in an $\eta^6$ manner. The complex was characterized by $^{13}C$ and $^1H$ NMR spectroscopy and its crystal structure determined. The complex crystallizes in the triclinic space group $P1$, with lattice constants $a=10.389(2)$, $b=13.743(3)$, $c=17.344(4)$ Å, $\alpha=72.15(2)$, $\beta=83.80(2)$, $\gamma=81.34(2)°$, $V=2325.2(9)$ Å$^3$, $Z=2$. Convergence to conventional $R$ values of $R=0.0735$ and $R_w=0.0950$ was obtained using 332 variable parameters and 3123 reflections with $I>3\sigma(I)$.

### Introduction

Arene complexes of ruthenium are playing increasingly important roles in organometallic chemistry as catalyst precursors for the hydrogenation of olefins, as well as useful precursors to a variety of metallacarborane complexes and hydrido(arene) systems [1]. The preparation of several ruthenium arene complexes has been described; these include 'piano stool' type complexes containing one arene ring, bis(arene) complexes of both Ru(II) and Ru(0), as well as polymeric cyclophane complexes [1, 2]. Although a substantial number of Ru–arene complexes has been prepared, detailed crystallographic investigations have been carried out on only a few. Of principal interest are the various structural distortions to the coordinated arene ring arising from electronic effects [3–5]. Also of interest are the $^{13}C$ and $^1H$ spectra of these complexes. In all instances rather substantial upfield shifts are observed, a precise explanation for which still remains to be developed [6].

### Experimental

The title complex was prepared by reacting dichlorotris(triphenylphosphine)Ru(II) with a stoichiometric amount of $AgBF_4$ in refluxing toluene and isolated as a fine yellow microcrystalline powder. Crystals suitable for X-ray diffraction work were obtained from a diethyl ether–chloroform solution. All solvents were distilled prior to use using appropriate drying agents. $^{13}C$ and $^1H$ NMR spectra were recorded at room temperature in $CDCl_3$ using a Bruker AC-200 spectrometer.

*Crystal data*

$C_{45}H_{40}BCl_6F_4P_2Ru$, $M=1043.3$, triclinic, space group $P\bar{1}$, a = 10.389(2), b = 13.743(3), c = 17.344(4) Å, $\alpha=72.15(2)$, $\beta=83.80(2)$, $\gamma=81.34(2)°$, $V=2325.2(9)$ Å$^3$, $D_{calc}=1.490$ Mg m$^{-3}$, $Z=2$, $\mu=0.793$ mm$^{-1}$, $F(000)=1054$, $T=298$ K.

*X-ray data collection, structure solution and refinement*

Intensity data collection was carried out using a Nicolet R3m/V diffractometer equipped with graphite-monochromated Mo K$\alpha$ (0.71073 Å) radiation. A total of 6517 reflections was collected and corrected for absorption, Lorentz and polarization effects. Corrections for absorption were applied numerically following careful measurement of crystal dimensions and assignment of indices to the crystal faces (minimum and maximum transmission factors, 0.931 and 0.962, respectively). The Ru atom was located from a sharped Patterson map and used as an initial phasing model. Remaining non-hydrogen atoms were located on difference Fourier maps. The structure was refined using a full matrix least-squares procedures using scattering factors that included terms for anomalous dispersion [7, 8]. The phenyl rings of the triphenylphosphine ligands were refined as rigid idealized polygons (C–C = 1.395 Å) using hydrogen atoms placed in idealized positions with fixed isotropic $U=0.08$ Å$^2$. Refinement was based on $F$ using weights of the form $w^{-1}=[\sigma^2(F)+0.0033(F^2)]$. Convergence to conventional $R$ values of $R=0.0735$ and $R_w=0.0950$ was obtained using 332 variable parameters and 3123 reflections with $I>3\sigma(I)$.

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## Results and discussion

Strong upfield shifts are seen in both the $^{13}C$ and $^1H$ NMR spectra of this complex, indicative of the presence of a $\pi$-bound molecule of toluene. In the $^{13}C$ spectrum, four resonances at 98.17, 94.49, 83.40 and 65.72 ppm (relative to TMS) corresponding to the six ring atoms of the toluene molecule are observed, and in the $^1H$ NMR spectrum three resonances are present at 4.62, 5.81 and 6.45 ppm corresponding to the *ortho*, *meta* and *para* hydrogens, respectively.

The X-ray crystal structure of this complex confirms the presence of a $\pi$-bound molecule of toluene, a view of which is provided in Fig. 1. Not shown are two molecules of cocrystallized $CHCl_3$ and the $BF_4$ counterion which possessed some degree of crystallographically imposed disorder, in addition to being disordered over two crystallographically inequivalent sites in the lattice. Atomic positional parameters are given in Table 1 and pertinent bond distances and angles are presented in Table 2.

The structure consists of a Ru(II) center to which is coordinated a molecule of toluene, two triphenylphosphine groups and a chloride ligand. Bonds to P(1) and P(2) of the triphenylphosphine groups measure 2.399(3) and 2.383(4) Å, respectively. The length of the Ru–Cl bond measures 2.389(4) Å, and interaxial angles associated with these three ligand groups range from 85.3(1) to 100.3(1)$^0$. The triphenylphosphine ligands themselves display no unexpected or particularly unusual features and are similar to those typically observed in other transition metal complexes containing these ligands.

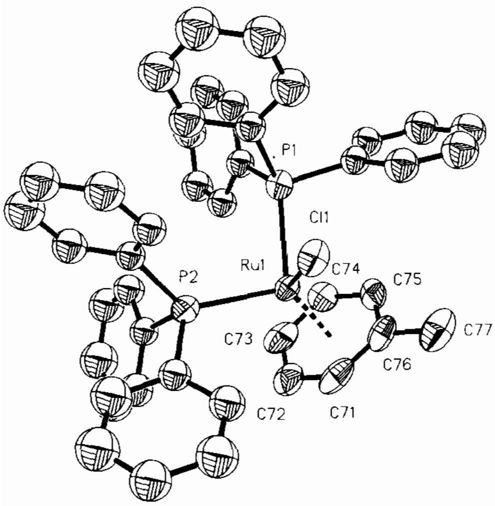

Fig. 1. A perspective view of the structure with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity; not shown is the $BF_4$ counterion and the two molecules of cocrystallized solvent.

TABLE 1. Atomic coordinates (×10$^4$) and equivalent isotropic displacement coefficients (Å$^2$×10$^3$)

| | $x$ | $y$ | $z$ | $U_{eq}$$^a$ |
|---|---|---|---|---|
| Ru(1) | 11449(1) | 4138(1) | 3021(1) | 33(1) |
| P(1) | 11736(2) | 5883(2) | 2270(2) | 41(1) |
| P(2) | 12639(2) | 3253(2) | 2130(2) | 38(1) |
| Cl(1) | 9577(2) | 4412(2) | 2257(2) | 49(1) |
| Cl(2)* | 2762(3) | 9315(3) | 4543(3) | 293(1) |
| Cl(3)* | 5637(3) | 8900(3) | 4581(2) | 87(1) |
| Cl(4)* | 4265(3) | 8975(3) | 3238(2) | 164(1) |
| Cl(5)* | 4415(3) | 7207(3) | 4570(3) | 207(1) |
| Cl(6)* | 8243(3) | 88(3) | 213(3) | 321(1) |
| Cl(7)* | 5986(3) | 892(3) | 650(3) | 258(1) |
| Cl(8)* | 7606(3) | −453(3) | 1827(3) | 395(1) |
| Cl(6A)* | 8242(3) | −626(3) | 1360(3) | 378(1) |
| Cl(7A)* | 6269(3) | 131(3) | 342(3) | 506(1) |
| Cl(8A)* | 6634(3) | 859(3) | 1566(3) | 266(1) |
| F(1)* | −424(2) | 9578(2) | 4618(2) | 322(1) |
| F(2)* | 1251(2) | 10408(2) | 4532(2) | 546(1) |
| F(3)* | 1289(2) | 8809(2) | 5296(2) | 226(1) |
| F(4)* | 5969(2) | 5958(2) | 4539(3) | 270(1) |
| F(5)* | 5197(2) | 4589(2) | 4480(3) | 210(1) |
| F(6)* | 3880(2) | 6004(2) | 4434(3) | 165(1) |
| B(1)* | 531(2) | 9707(2) | 5026(2) | 140(1) |
| B(2)* | 4953(2) | 5414(2) | 4755(2) | 221(1) |
| C(1) | 4357(3) | 8568(3) | 4238(3) | 106(1) |
| C(2) | 7424(3) | 421(3) | 928(3) | 168(1) |
| C(11) | 9356(3) | 6630(3) | 2933(2) | 61(1) |
| C(12) | 8554 | 7192 | 3386 | 73(1) |
| C(13) | 9089 | 7822 | 3729 | 73(1) |
| C(14) | 10426 | 7891 | 3618 | 67(1) |
| C(15) | 11228 | 7330 | 3164 | 50(1) |
| C(16) | 10693 | 6700 | 2822 | 44(1) |
| C(21) | 12249(3) | 6271(3) | 611(2) | 62(1) |
| C(22) | 12018 | 6723 | −207 | 78(1) |
| C(23) | 10852 | 7354 | −428 | 85(1) |
| C(24) | 9917 | 7534 | 170 | 81(1) |
| C(25) | 10149 | 7082 | 988 | 70(1) |
| C(26) | 11315 | 6451 | 1209 | 46(1) |
| C(31) | 13516(3) | 7322(3) | 1701(2) | 60(1) |
| C(32) | 14708 | 7693 | 1661 | 69(1) |
| C(33) | 15716 | 7076 | 2118 | 68(1) |
| C(34) | 15533 | 6090 | 2617 | 62(1) |
| C(35) | 14341 | 5719 | 2657 | 52(1) |
| C(36) | 13333 | 6336 | 2200 | 44(1) |
| C(41) | 11629(3) | 4090(2) | 630(2) | 48(1) |
| C(42) | 11649 | 4354 | −215 | 67(1) |
| C(43) | 12834 | 4293 | −671 | 68(1) |
| C(44) | 13998 | 3967 | −282 | 76(1) |
| C(45) | 13979 | 3703 | 562 | 60(1) |
| C(46) | 12794 | 3764 | 1018 | 40(1) |
| C(51) | 14695(3) | 1845(3) | 2901(2) | 62(1) |
| C(52) | 15945 | 1586 | 3185 | 84(1) |
| C(53) | 16810 | 2323 | 2982 | 86(1) |
| C(54) | 16426 | 3320 | 2496 | 73(1) |
| C(55) | 15176 | 3579 | 2212 | 53(1) |
| C(56) | 14311 | 2841 | 2415 | 44(1) |
| C(61) | 12752(3) | 1431(3) | 1733(2) | 76(1) |
| C(62) | 12295 | 541 | 1702 | 83(1) |
| C(63) | 11100 | 276 | 2100 | 72(1) |
| C(64) | 10362 | 901 | 2527 | 77(1) |
| C(65) | 10819 | 1791 | 2558 | 58(1) |

(*continued*)

TABLE 1. (*continued*)

| | $x$ | $y$ | $z$ | $U_{eq}$[a] |
|---|---|---|---|---|
| C(66) | 12014 | 2056 | 2161 | 47(1) |
| C(71) | 10683(3) | 2899(3) | 4083(3) | 61(1) |
| C(72) | 12025(3) | 2707(3) | 4030(3) | 57(1) |
| C(73) | 12811(3) | 3485(3) | 4006(3) | 60(1) |
| C(74) | 12162(3) | 4416(3) | 4083(3) | 47(1) |
| C(75) | 10786(3) | 4576(3) | 4196(3) | 51(1) |
| C(76) | 10025(3) | 3817(3) | 4193(3) | 54(1) |
| C(77) | 8584(3) | 3998(3) | 4274(3) | 77(1) |

[a]Equivalent isotropic $U$ defined as one third of the trace of the orthogonalized $U_{ij}$ tensor. Starred atoms were disordered and refined with fractional occupancy factors.

TABLE 2. Bond lengths (Å) and angles (°)

| | | | |
|---|---|---|---|
| Ru(1)–P(1) | 2.399(3) | Ru(1)–P(2) | 2.384(3) |
| Ru(1)–Cl(1) | 2.389(3) | Ru(1)–C(71) | 2.257(4) |
| Ru(1)–C(72) | 2.247(4) | Ru(1)–C(73) | 2.219(4) |
| Ru(1)–C(74) | 2.214(5) | Ru(1)–C(75) | 2.305(5) |
| Ru(1)–C(76) | 2.347(4) | P(1)–C(16) | 1.848(5) |
| P(1)–C(26) | 1.838(5) | P(1)–C(36) | 1.837(4) |
| P(2)–C(46) | 1.838(5) | P(2)–C(56) | 1.816(4) |
| P(2)–C(66) | 1.841(5) | C(71)–C(72) | 1.377(4) |
| C(71)–C(76) | 1.398(6) | C(72)–C(73) | 1.428(6) |
| C(73)–C(74) | 1.390(5) | C(74)–C(75) | 1.415(4) |
| C(75)–C(76) | 1.402(6) | C(76)–C(77) | 1.479(4) |
| P(1)–Ru(1)–P(2) | 100.3(1) | P(1)–Ru(1)–Cl(1) | 85.3(1) |
| P(2)–Ru(1)–Cl(1) | 89.3(1) | P(1)–Ru(1)–C(71) | 154.3(1) |
| P(2)–Ru(1)–C(71) | 105.4(1) | P(1)–C(16)–C(11) | 118.6(1) |
| P(1)–C(16)–C(15) | 121.2(1) | P(1)–C(26)–C(21) | 117.1(1) |
| P(1)–C(26)–C(25) | 122.8(1) | P(1)–C(36)–C(31) | 119.1(1) |
| P(1)–C(36)–C(35) | 120.8(1) | P(2)–C(46)–C(41) | 116.2(1) |
| P(2)–C(46)–C(45) | 123.1(1) | P(2)–C(56)–C(51) | 121.4(1) |
| P(2)–C(56)–C(55) | 118.3(1) | P(2)–C(66)–C(61) | 117.5(1) |
| P(2)–C(66)–C(65) | 122.4(1) | C(72)–C(71)–C(76) | 122.2(4) |
| C(71)–C(72)–C(73) | 121.0(4) | C(72)–C(73)–C(74) | 117.0(3) |
| C(73)–C(74)–C(75) | 121.4(4) | C(74)–C(75)–C(76) | 120.9(4) |
| C(71)–C(76)–C(75) | 117.3(3) | C(71)–C(76)–C(77) | 121.6(4) |
| C(75)–C(76)–C(77) | 121.3(3) | | |

Of particular interest are the structural features associated with the coordinated molecule of toluene. The Ru atom is separated from the centroid defined by the six atoms of the arene ring by a distance of 1.780 Å. A close inspection of the Ru–C bond lengths, which range from a minimum of 2.213(9) Å to a maximum of 2.348(7) Å, shows that the arene ring is slipped with the Ru atom being displaced toward C(73) and away from C(76) which bears the methyl group. However, in contrast to other neutral and cationic Ru(II)–arene complexes for which structural data are available, we find that the arene ring in this complex displays an essentially planar configuration with no substantial out-of-plane deformations by any of the atoms [3–5]. The methyl group is also essentially coplanar with the arene ring, being displaced by less than 0.014 Å from the least-squares plane defined by the six ring atoms. Some notable deviation in the arene C–C bond lengths are, however, evident. Within the arene ring we find that these bonds range in length from 1.378(9) to 1.427(11) Å. While all are within the 1.39 Å bond distance typically associated with aromatic systems, the pattern of alternating long and short bonds suggests that some degree of bond localization has occurred as a result of coordination. Apart from the lack of any substantial deviations in planarity of the arene ring, these results are in good agreement with the structural data reported for the unusual cationic ($\eta^6$-$C_6H_6P(C_6H_5)_3$)RuH($PPh_3$)$_2$ complex, the ($\eta^6$-$C_6H_5CH_3$)RuH($PPh_3$)$_2$ cation, as well as the two neutral arene complexes, ($\eta^6$-$C_6H_6$)Ru$Cl_2$($Ph_2PCH_3$) and ($\eta^6$-1,4-i-$C_3H_7C_6H_4$)Ru$Cl_2$($Ph_2PCH_3$) [3–5].

## Supplementary material

Lists of anisotropic thermal parameters, H atom positional parameters, as well as observed and calculated structure factor amplitudes, are available from author (L.C.P.) upon request.

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