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Synthesis and Crystallographic Characterisation of the Heterodimetallic Complex [(Dibenzo-18-crown-6)K(μ-Cl)$_3$Ru(η^6-*p*-cymene)]

Carsten A. Vock,[a] Rosario Scopelliti,[a] and Paul J. Dyson*[a]

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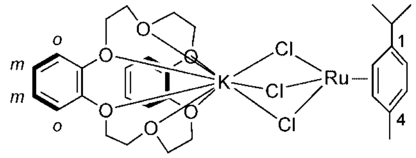
The triple-chlorido-bridged heterodimetallic dinuclear complex [(dibenzo-18-crown-6)K(μ-Cl)$_3$Ru(η^6-*p*-cymene)] containing an (η^6-arene)Ru^{II} fragment and a Group 1 metal crown ether fragment was synthesized and characterized by spectroscopy and X-ray crystallography. The solid-state structure clearly reveals the presence of the triple-chlorido-bridged dinuclear complex, whereas NMR investigations in different deuteriated solvents reveal the presence of an essentially 1:1 mixture of **1** and starting materials, indicating the presence of a dynamic equilibrium.

Introduction

Dinuclear homometallic cationic ruthenium(II) complexes of the general type [(η^6-arene)Ru(μ-Cl$_3$)(η^6-arene)]$^+$ were first described in the early 1970s by Bennett and Smith.[1] Subsequently, these compounds were explored in more detail by Stephenson et al.,[2] with an emphasis on synthetic and electrochemical aspects. A series of crystallographic analyses[3] in combination with theoretical investigations,[4] have also been reported, and applications in hydrogen transfer reactions were reported.[5]

In recent years, dimetallic complexes involving the (η^6-arene)Ru^{II} fragment and another transition metal fragment have been widely explored, and impressive applications in catalysis have been observed. For example, the metathesis catalysts Ru(=CHR)Cl$_2$(PCy$_3$)$_2$ (R = CHCPh$_2$ or Ph), react quantitatively with the bridged dimers [M(η^6-*p*-cymene)-Cl$_2$]$_2$ (M = Ru or Os) to form dimetallic complexes in which the two metal centres are bridged by two chlorido ligands;[6] the resulting dimetallic complexes were found to have higher activities than the mononuclear complexes. Moreover, dimetallic complexes, in which two metal fragments are connected by three halogenido bridges also exhibit interesting properties. Their potential as precursors in catalytic reactions has been demonstrated in Oppenauer-type oxidation reactions of alcohols[7] and for atom-transfer radical reactions.[8] The dimetallic precursors are composed of two transition metal fragments; prominent examples for metal combinations in these heterodimetallic complexes are Ru–Rh[7] and Ru–Ir.[7c,9] However, to the best of our knowledge, halogenido-bridged dimetallic complexes, in which one metal fragment is ruthenium and the other is a main group metal, have not been reported. Herein, we describe the synthesis and characterisation of the first triple-chlorido-bridged Ru^{II}–alkali metal heterodimetallic dinuclear complex (Scheme 1).



1

Scheme 1. [(Dibenzo-18-crown-6)K(μ -Cl)$_3$Ru(η^6-*p*-cymene)] (**1**) including NMR numbering scheme.

Results and Discussion

Treatment of [Ru(η^6-*p*-cymene)Cl$_2$]$_2$ with a slight excess of [(dibenzo-18-crown-6)K][Cl] (freshly prepared from dibenzo-18-crown-6 and KCl in MeOH/H$_2$O) in CH$_2$Cl$_2$ at room temperature and subsequent precipitation by addition of ethyl acetate and slow evaporation of CH$_2$Cl$_2$ in vacuo afforded [(dibenzo-18-crown-6)K(μ-Cl)$_3$Ru(η^6-*p*-cymene)]·EtOAc (**1**·EtOAc) in moderate yield as orange-brown solid. NMR studies in CD$_2$Cl$_2$ revealed the presence of a mixture of essentially equal amounts of a new species and starting material [Ru(η^6-*p*-cymene)Cl$_2$]$_2$, indicating a dynamic equilibrium in solution, as recently described for the salt [Ph$_4$P][Ru(η^6-*p*-cymene)Cl$_3$].[10] However, for the system described herein, the equilibrium is not strongly dependent on the solvent, since measurements in CDCl$_3$ and C$_6$D$_6$ lead only to marginal changes in the starting material/product ratio. In comparison, for [Ph$_4$P][Ru(η^6-*p*-cymene)Cl$_3$],[10] changing the solvent from CD$_2$Cl$_2$ to CDCl$_3$ led to an al-

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[a] Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne (EPFL),
1015 Lausanne, Switzerland
Fax: +41-21-693-98-85
E-mail: paul.dyson@epfl.ch

most complete shift of the equilibrium towards the starting material.

Crystallization by layering a CH_2Cl_2 solution of the obtained material with ethyl acetate and storage at 4 °C for several days yielded orange crystals of **1**·EtOAc that were suitable for X-ray analysis. An ORTEP plot of the structure is depicted in Figure 1. Crystal data and data of the structure refinement are presented in Table 1. Compound **1** crystallizes as discrete molecules in space group $P2_1/n$. The coordination around the Ru^{II} centre is defined by an η^6-*p*-cymene ligand [Ru–centroid 1.653(3) Å] and by three chlorido bridges [Ru–Cl_{av}, 2.437(2) Å]. The potassium ion lies in the middle of the crown ether and is displaced by 1.216 Å towards the chlorido ligands and the Ru ion [Ru···K, 4.066(2) Å]. The potassium ion completes its ninefold coordination with the three bridging chlorido ligands [K–Cl_{av}, 3.232(2) Å], these distances being slightly longer than those found in solid KCl [3.146 Å].[11] The K–O distances within the crown ether show a wide range of values [2.938(4)–3.127(4) Å] and, compared to those found in a similar molecule,[12] clearly bear out the reduced flexibility of this ligand with respect to the classical 18-crown-6. The solvent molecule lies in the large cavity formed by the crown ether, and it shows short K···C interactions [3.555(8) Å; K···H_{Me}, 3.07 Å]. Some weak CH···O hydrogen bonds are observed between the complex and the ethyl acetate of a neighbouring asymmetric unit.

Table 1. Crystallographic parameters for **1**·EtOAc.

	1·EtOAc
Empirical formula	$C_{34}H_{46}Cl_3KO_8Ru$
Formula mass	829.23
Colour and shape of crystal	orange, long needle
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 15.129(4) Å, α = 90° b = 17.702(6) Å, β = 118.573(16)° c = 15.667(4) Å, γ = 90°
Volume	3684.8(17) Å^3
Z	4
Density (calculated)	1.495 Mg/m^3
Absorption coefficient	0.804 mm^{-1}
F(000)	1712
Crystal size	0.83 × 0.34 × 0.30 mm
θ range for data collection	3.29–25.03°
Index ranges	$-17 \le h \le 17$ $-21 \le k \le 21$ $-18 \le l \le 18$
Reflections collected	47956
Independent reflections	6412 [R(int) = 0.1301]
Completeness to θ = 25.03°	98.8%
Absorption correction	semiempirical from equivalents (SADABS)
Max./min. transmission	1.0000/0.5927
Refinement method	full-matrix least squares on F^2
Data/restraints/parameters	6412/0/424
Goodness-of-fit on F^2	1.109
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0499, wR_2 = 0.1082
R indices (all data)	R_1 = 0.0819, wR_2 = 0.1295
Largest difference peak/hole	1.220/–1.056 e·Å^{-3}

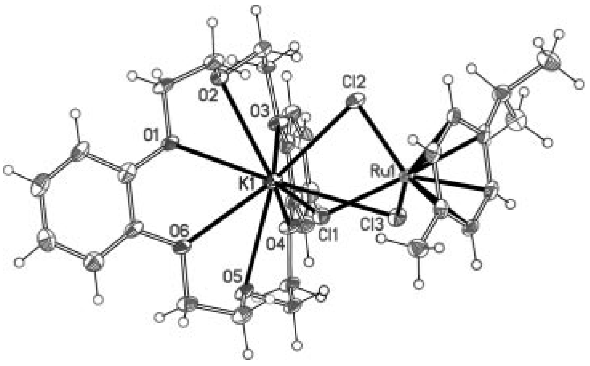

Figure 1. ORTEP representation of **1**·EtOAc; EtOAc solvent has been omitted for clarity; thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: Ru1–Cl1 2.4334(15), Ru1–Cl2 2.4302(14), Ru1–Cl3 2.4460(14), K1–Cl1 3.2350(19), K1–Cl2 3.2268(18), K1–Cl3 3.2342(18), K1–O1 3.099(4), K1–O2 2.952(4), K1–O3 2.952(4), K1–O4 2.938(4), K1–O5 2.943(4), K1–O6 3.127(4); Cl2–Ru1–Cl1 86.40(5), Cl1–Ru1–Cl3 87.11(5), Cl2–Ru1–Cl3 87.51(5), O2–K1–O1 101.41(10), O1–K1–O6 49.52(9), O1–K1–Cl2 97.70(8), O1–K1–Cl3 150.38(8).

(Arene)ruthenium(II) compounds are playing an increasingly important role in organometallic chemistry,[13] and as far as we are aware the structural motif of the (arene)ruthenium(II) compound described herein is unique. The structure demonstrates that under certain conditions Group 1 metal ions can interact with the (arene)ruthenium(II) unit. The implications of such an observation are potentially far-reaching as the Noyori-type transfer hydrogenation catalysts based on the (arene)ruthenium(II) unit are activated in the presence of KOH.[14] It has previously been shown that attaching a crown ether to the arene ring in these catalysts influences the rate of the reaction depending on the nature of the ion, viz. Na^+, K^+ or Cs^+.[15] (Arene)ruthenium(II) compounds have also been immobilised in materials which contain Group 1 ions, such as clays,[16] and again, interactions between the two units could be present. (Arene)ruthenium(II) complexes are also being increasingly evaluated in medicinal applications,[17] and again, in a physiological environment interactions with ions such as Na^+ or K^+ could prove to be important, activating the compounds towards reaction with biomolecular targets.

Experimental Section

Synthesis and Spectroscopic Characterization: $[RuCl_2$(η^6-*p*-cymene)$]_2$ was synthesized according to a literature protocol.[18] All other reagents and solvents were obtained from commercial sources and used without further purification. ^1H and ^{13}C NMR spectra were recorded with a Bruker 400 MHz spectrometer at room temperature in CD_2Cl_2. NMR spectra were referenced to internal solvents as follows: $\delta(CH_2Cl_2, {}^1H) = 5.35$ and $\delta(CD_2Cl_2, {}^{13}C) = 53.45$. Elemental analyses were conducted at the EPFL.

Synthesis of [(Dibenzo-18-crown-6)K(μ-Cl)$_3$Ru(η^6-*p*-cymene)]·EtOAc (1·EtOAc): To a solution of KCl (49.0 mg, 0.657 mmol, 2.12 equiv.) in H_2O (1 mL) and MeOH (10 mL), dibenzo-18-crown-6 (237 mg, 0.658 mmol, 2.12 equiv.) was added, and the resulting mixture was stirred at room temperature for 75 min. The solvent was removed in vacuo. The white solid residue was dissolved in

CH_2Cl_2 (10 mL), [Ru(η^6-*p*-cymene)Cl_2]$_2$ (190 mg, 0.310 mmol) was added, and the mixture was stirred at room temperature for 1 h. The solution was filtered, and the residue was washed with CH_2Cl_2 (2 × 5 mL). EtOAc (30 mL) was added to the combined filtrates, and CH_2Cl_2 was removed in vacuo. After standing at room temperature overnight, the formed voluminous precipitate was filtered, washed with EtOAc (2 × 10 mL) and dried in vacuo, affording **1** as an orange-brown solid (271 mg, 0.327 mmol, 53 %). Crystals of the solvated compound **1**·EtOAc suitable for X-ray analysis were obtained by layering a CH_2Cl_2 solution of the obtained product with EtOAc and storing at 4 °C for several days. ^1H NMR (400 MHz, CD_2Cl_2): δ = 1.29 [d, J = 7.0 Hz, 6 H, 1-CH(CH_3)$_2$], 2.14 (s, 3 H, 4-CH_3), 2.99 [sept, J = 7.0 Hz, 1 H, 1-CH(CH$_3$)$_2$], 4.05 (br. t, J = 4.2 Hz, 8 H, 4 × OCH_2CH$_2$OC$_6$H$_4$ of dibenzo-18-crown-6), 4.17 (br. t, J = 4.2 Hz, 8 H, 4 × OCH$_2$CH_2OC$_6$H$_4$ of dibenzo-18-crown-6), 5.12 (d, J = 5.8 Hz, 2 H, 2-H, 6-H), 5.35–5.37 (m, 2 H, 3-H, 5-H), 6.91 (m$_c$, 8 H, 2 × OC$_6$$H_4$O). ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 18.47 (4-CH$_3$), 21.98 [1-CH(CH$_3$)$_2$], 30.76 [1-CH(CH$_3$)$_2$], 67.26 (4 × OCH$_2$CH$_2$OC$_6$H$_4$ of dibenzo-18-crown-6), 69.05 (4 × OCH$_2$-CH$_2$OC$_6$H$_4$ of dibenzo-18-crown-6), 79.17 (C-2, C-6), 81.84 (C-3, C-5), 96.30 (C-4), 100.9 (C-1), 111.7 (4 × *ortho*-C of dibenzo-18-crown-6), 120.9 (4 × *meta*-C of dibenzo-18-crown-6), 147.8 (4 × CO of dibenzo-18-crown-6). $C_{30}H_{38}Cl_3KO_6Ru$·1.5 EtOAc (873.30): calcd. C 49.51, H 5.77; found C 49.87, H 5.43.

Crystallography: Diffraction data for **1** were measured with a Bruker-Nonius kappa diffractometer equipped with an APEX II CCD using Mo-K_α radiation. Data were reduced by EvalCCD[19] and then corrected for absorption by a semiempirical method.[20] The structure was solved by direct methods,[21] and refined using full-matrix least squares on F^2 with all non-H atoms anisotropically defined. Hydrogen atoms were placed in calculated positions using the "riding model". Structure solution, refinement, geometrical calculations and geometrical representations were carried out with SHELXTL.[22] CCDC-643569 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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