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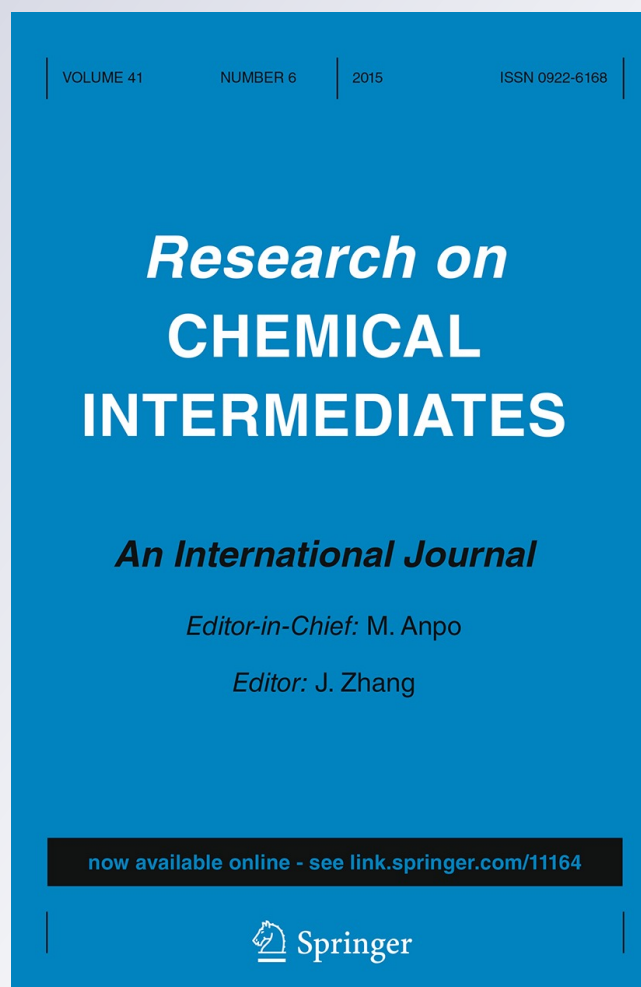
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Hexakis(benzonitrile)ruthenium(II) bis[tetrafluoroborate(1-)] : a precursor to ruthenium organometallic compounds

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Abstract The new compound, $[\text{Ru}(\text{NCC}_6\text{H}_5)_6][\text{BF}_4]_2$, has been synthesized by reaction of the polymeric species $[\{\text{RuCl}_2(\text{COD})\}_x]$ ($\text{COD} = 1,5\text{-cyclooctadiene}$) with benzonitrile under reflux and characterized by elemental analysis, IR, NMR spectroscopic analyses, and single crystal X-ray diffraction. The Ru(II) atom is coordinated by six N atoms from six benzonitrile ligands in distorted octahedral coordination geometry. The compound was crystallized in the monoclinic space group $P2_1/c$ with unit-cell dimensions $a = 10.7536(11) \text{ \AA}$, $b = 18.6582(18) \text{ \AA}$, $c = 20.311(2) \text{ \AA}$, $\beta = 91.864(2)^\circ$, $V = 4073.2(7) \text{ \AA}^3$ and final R of 0.0429.

Keywords Ruthenium · Benzonitrile · Spectroscopic analysis · Reaction intermediate · X-ray crystallography

Introduction

The ease with which the acetonitrile (NCMe) ligand in ruthenium(II)–acetonitrile complexes can be replaced is responsible for their wide application as precursors for the synthesis of ruthenium(II) organometallic compounds [1–4]. A large number of active compounds have been synthesized using these acetonitrile solvate precursors, ranging from nanoclusters applied in catalysis [5–7] to compounds with medicinal

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and biological activities [8–14]. Notable among these precursors is the hexakis(acetonitrile)ruthenium(II) $[1]^{2+}$ [$1 = \text{Ru}(\text{NCMe})_6$]. The non-isolable $[1]$ has been precipitated from solutions as $[1][\text{BF}_4]_2$ [15] and $[1][\text{ZnCl}_4]$ [16]. However, these two complexes have not received the expected prominent use as starting materials for the synthesis of ruthenium(II) organometallic compounds. This is most likely because $[1][\text{BF}_4]_2$ requires many steps to synthesize. On the other hand, the ruthenium(II) zincate analogue $[1][\text{ZnCl}_4]$ contains a counter anion $[\text{ZnCl}_4]^{2-}$ capable of initiating side reactions with the incoming ligand(s). To address these shortcomings, and with the understanding that the benzonitrile (NCPH) complexes are more soluble in common organic solvents, we have therefore developed a convenient synthetic route to the preparation of NCPH analogue $[2][\text{BF}_4]_2$ ($[2 = \text{Ru}(\text{NCPH})_6]$) as a possible alternative to $[1][\text{BF}_4]_2$. Reported synthesis of $[2][\text{BF}_4]_2$ involved a combination of both electrochemical and chemical techniques in a series of steps starting from RuCl_3 [17]. The electrochemical route yielded $[\text{RuX}_2(\text{NCPH})_4]$ as the lowest halide-containing moiety which was then subjected to a reaction with $\text{Ag}(\text{I})$ to remove a further halide resulting in $[\text{RuX}(\text{NCPH})_5]^+$. The last halide was then removed by the reaction of $[\text{RuX}(\text{NCPH})_5]^+$ with hot concentrated triflic acid under strict anaerobic conditions to obtain $[\text{Ru}(\text{NCPH})_6]^{2+}$. One major problem associated with the use of concentrated triflic acid is that it has the capacity to catalyze the polymerization of benzonitrile [17]. To prevent polymerization, more benzonitrile is usually added to the reaction mixture and subsequent dilution with dry ether. The complex $[2][\text{BF}_4]_2$ has also been synthesized from the substitution reaction of $[\text{Ru}(\text{H}_2\text{O})_6]^{2+}$ with benzonitrile, but the preparation of $[\text{Ru}(\text{H}_2\text{O})_6]^{2+}$ is not easy, requiring very tedious purification procedures [18]. In the present study, $[2][\text{BF}_4]_2$ was obtained pure in a single step starting with the polymer $[\{\text{RuCl}_2(\text{COD})\}_x]$.

Experimental

Materials and physical measurements

The reagents $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ and benzonitrile were commercially sourced from Acros Organics. The starting material $[\{\text{RuCl}_2(\text{COD})\}_x]$ [19] was synthesized according to a literature method. Melting point was obtained on a Kofler hot-stage apparatus and was uncorrected. Infrared spectrum was recorded in the solid state (ATR) on a Bruker Tensor 27 FTIR spectrophotometer. High-resolution ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker Avance 400 MHz NMR spectrometer at 100 K. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ chemical shifts were calibrated to solvent peaks which are reported relative to TMS. Microanalyses were undertaken at the Institute of Material Science, University of Connecticut, USA.

X-ray diffraction analysis

A yellow crystal of dimension $0.33 \times 0.22 \times 0.09 \text{ mm}^3$ was selected for the single-crystal X-ray diffraction analysis. The crystal of $[2][\text{BF}_4]_2$ was mounted on a

Cryoloop with Paratone-N oil and data were collected at 90 K with a Bruker APEX II CCD using Mo K alpha radiation. Data were corrected for absorption with SADABS [20] and the structure solved by direct methods. All non-hydrogen atoms were refined anisotropically by full matrix least squares on F^2 . Hydrogen atoms on benzonitrile were found from a Fourier difference map and were then fixed in position with suitable riding parameters.

Synthesis of hexakis(benzonitrile)ruthenium(II) bis[tetrafluoroborate(1-)]

A suspension of $[\{\text{RuCl}_2(\text{COD})\}_x]$ (1.0 g, 3.57 mmol) and two equivalents of AgBF_4 (1.4 g, 7.14 mmol) in benzonitrile (30 ml) were refluxed for 24 h. The brown solution was filtered hot and allowed to cool to room temperature, whereupon a yellow precipitate settled at the bottom of the flask. The yellow precipitate was collected, washed several times with ethanol, and dried in vacuo to obtain a yellow powder. The compound was recrystallized by a slow diffusion of diethyl ether into a dichloromethane solution. Yield: 2.48 g, 78 %; m.p. ($^\circ\text{C}$): 208–212; ^1H NMR (CD_2Cl_2) δ (ppm) 7.61–8.30 (m, C_6H_5); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2), δ (ppm) 110.03 (s, CN), 126–135 (m, C_6H_5); IR $\nu(\text{CN})$ 2,279 cm^{-1} . Elemental analysis for $\text{C}_{42}\text{H}_{30}\text{B}_2\text{F}_8\text{N}_6\text{Ru}$, Calcd. (Found): C, 56.44 (56.65); H, 3.36 (3.48); N, 9.41 (9.73).

Results and discussion

The literature synthesis of $[1][\text{BF}_4]_2$ and the zincate salt $[1][\text{ZnCl}_4]$ requires three or more steps to proceed with an overall reported yield of 80 % for $[1][\text{BF}_4]_2$ [21] and 36 % for $[1][\text{ZnCl}_4]$ [15]. Even with an improved synthetic procedure recently reported by Underwood et al. [15], $[1][\text{BF}_4]_2$ was obtained in 66 % yield. The synthesis of the new precursor, $[2][\text{BF}_4]_2$ requires just a single step, and results in a product without a counter ion capable of ligand coordination. The complex, $[2][\text{BF}_4]_2$, was prepared by treatment of the polymer $\{\text{RuCl}_2(\text{COD})\}_x$ with two equivalents of AgBF_4 in refluxing benzonitrile for 24 h with an overall yield of 78 % compared to 66 % reported for $[1][\text{BF}_4]_2$ in Ref. [15]. The yellow complex, $[2][\text{BF}_4]_2$, is stable in air and has been characterized by ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR and IR spectroscopy as well as by elemental analysis. The experimental results of the elemental analysis of the complex are in close agreement with the calculated values, which confirms the identity of the prepared complex. The characteristic nitrile stretching frequency was observed at 2,279 cm^{-1} in the IR spectrum of $[2][\text{BF}_4]_2$ which is higher in frequency than in the free nitrile at 2,229 cm^{-1} [22], in line with coordination through the N atom of the NCPH ligand [1]. Appearance of a single ν_{CN} band in the infrared spectra of $[2][\text{BF}_4]_2$ at 2,279 cm^{-1} suggest a *trans* arrangement of the NCPH ligands around the ruthenium ion [17]. In the ^1H NMR spectrum of $[2][\text{BF}_4]_2$, the NCPH protons were observed as multiplets between 7.61 and 8.30 ppm in the expected ratio of 2:2:1. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum displays a single line at 110.03 ppm which was assigned to the CN carbon while the aromatic carbons were present as four distinct lines between 126 and 135 ppm.

X-ray crystallographic analysis of $[2][\text{BF}_4]_2$

Crystals of $[2][\text{BF}_4]_2$ suitable for X-ray diffraction studies were obtained by a slow diffusion of diethyl ether into a solution of the compound in CH_2Cl_2 . The compound crystallized as yellow prisms and its single crystal X-ray diffraction data were collected at 100 K. The ORTEP diagram that shows the atomic numbering scheme for $[2][\text{BF}_4]_2$ is shown in Fig. 1. The selected bond distances and angles are given in Table 1 while a summary of the crystal data is collected in Table 2. The crystal structure of analogous homoleptic Ru(II) complex, $[1][\text{BF}_4]_2$, with acetonitrile ligands has been reported [15], but the structure of $[2][\text{BF}_4]_2$ is the first with six NCPH ligands coordinated to a ruthenium center. The structure of $[2][\text{BF}_4]_2$ consists of a discrete cation and anion with six N-bonded NCPH ligands coordinated in a distorted octahedral arrangement to the central Ru^{2+} ion with two BF_4 anions outside the coordination sphere. The six NCPH ligands are coordinated to the ruthenium center through the nitrogen atom as proposed from its IR spectrum. The six-coordinate ruthenium atom has the NCPH ligands slightly deviated from linear geometry with average Ru–N–C angle of $175.9(2)^\circ$. Compound $[2][\text{BF}_4]_2$ crystallizes with a unit cell in the monoclinic space group $P2_1/c$ with unit cell dimensions $a = 10.7536(11) \text{ \AA}$, $b = 18.6582(18) \text{ \AA}$, $c = 20.311(2) \text{ \AA}$, $\beta = 91.864(2)^\circ$, where as the acetonitrile analogue $[1][\text{BF}_4]_2$ crystallized with a unit cell in the same monoclinic space group $P2_1/c$ but with smaller unit cell dimensions $a = 8.0993(16) \text{ \AA}$, $b = 8.1969(16) \text{ \AA}$, $c = 15.877(3) \text{ \AA}$ and $\beta = 92.78(3)^\circ$. The angles around the Ru atom in $[2][\text{BF}_4]_2$ are all close to 90° in line with the octahedral coordination arrangement. The six phenyl rings in the structure have the average C–C bond distance of $1.390(6) \text{ \AA}$ and C–C–C bond angles of 120.04° which are within the accepted values of $1.394 \text{ \AA}$ and 120° for phenyl rings [23]. The average Ru–N bond distance found in this structure ($2.019 \text{ \AA}$) is slightly shorter than the average value in $[1][\text{BF}_4]_2$ ($2.022 \text{ \AA}$) [15] which suggests a stronger Ru–N bond interaction in $[2][\text{BF}_4]_2$.

The average Ru–N bond length of $2.019(2) \text{ \AA}$ in $[2][\text{BF}_4]_2$ is shorter than the sum of their covalent radii, $2.17 \text{ \AA}$ [24], which suggests a strong mutual attraction between Ru and N [25]. The N–Ru–N angles between mutually trans NCPH ligands are $177.48(8)^\circ$, $177.74(7)^\circ$, and $179.59(9)^\circ$. However, no chemical interactions were observed between the BF_4 anions and the $[\text{Ru}(\text{NCPH})_6]^{2+}$ cations as was observed in the $[\text{Ru}(\text{NCMe})_6]^{2+}$ analogue [15]. Compound $[2][\text{BF}_4]_2$ can be used as an alternative to $[\text{Ru}(\text{NCMe})_6]^{2+}$ in the synthesis of active organometallic compounds, in particular as those of tris(benzonitrile)ruthenium(II) complexes with trinitrogen donor ligands [15], and work is ongoing in this regard.

Conclusions

The paper described a convenient route to the preparation of a reaction intermediate $[\text{Ru}(\text{NCPH})_6][\text{BF}_4]_2$ analogous to the known $[\text{Ru}(\text{NCMe})_6][\text{BF}_4]_2$ derivative which are potential candidates in the synthesis of active ruthenium organometallic compounds. The complex was isolated as a bright yellow air-stable solid and has

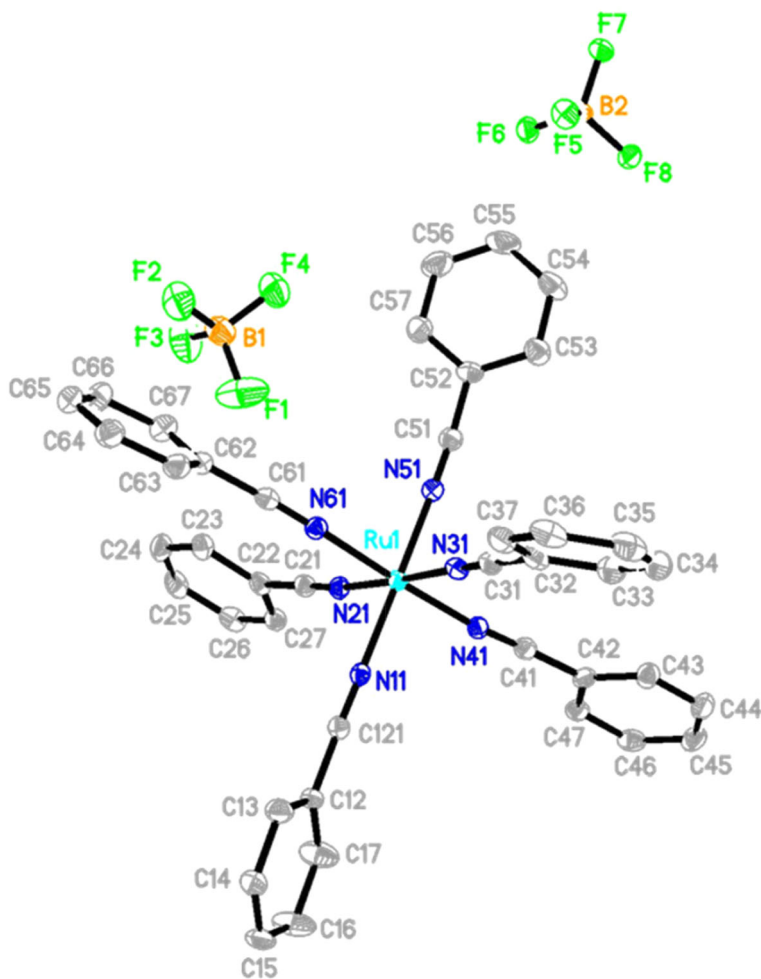


Fig. 1 ORTEP diagram of $[\text{Ru}(\text{NCPh})_6][\text{BF}_4]_2$ with ellipsoids drawn at 50 % probability. Hydrogen atoms have been omitted for clarity

Table 1 Selected bond lengths (Å) and angles (°) for $[\text{Ru}(\text{NCPh})_6][\text{BF}_4]_2$

Ru1–N51	2.004(2)	N11–C121	1.143(4)	C41–C42	1.441(4)
Ru1–N61	2.018(2)	N21–C21	1.134(3)	C21–C22	1.439(4)
Ru1–N41	2.018(2)	N31–C31	1.139(3)	C51–C52	1.443(4)
Ru1–N21	2.022(2)	B1–F1	1.375(5)	B1–F2	1.387(4)
N51–Ru1–N61	89.33(8)	N41–Ru1–N61	177.74(7)	B1–F3	1.400(4)
N41–Ru1–N31	89.23(9)	N11–Ru1–N51	179.59(9)	C31–C32	1.442(4)
N61–Ru1–N21	86.90(9)	C21–N21–Ru1	172.50(2)	C21–C22	1.439(4)
N21–Ru1–N31	177.48(8)	C51–N51–Ru1	178.30(2)	C42–C43	1.400(4)
N21–C21–C22	177.6(3)	N51–C51–C52	174.6(3)	C62–C63	1.402(4)

Table 2 Summary of crystal data and structure refinement for [2][BF₄]₂

Empirical formula	C ₄₂ H ₃₀ B ₂ F ₈ N ₆ Ru
Formula weight	893.41
Temperature	100(2)°K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	
a	10.7536(11) Å
b	18.6582(18) Å
c	20.311(2) Å
β	91.864(2)°
Volume	4,073.2(7) Å ³
Z	4
Density (calculated)	1.457 g/cm ³
Absorption coefficient	0.460 mm ⁻¹
F (000)	1,800
Crystal size	0.33 × 0.22 × 0.09 mm ³
Theta range for data collection	1.89°–28.55°
Reflections collected	32,398
Independent reflections	9412 [R(int) = 0.0464]
Completeness to theta = 25.00°	99.3 %
Data/restraints/parameters	9412/0/532
Goodness-of-fit on F ²	1.006
Final R indices [I > 2σ(I)]	R1 = 0.0429, wR2 = 0.1232
R indices (all data)	R1 = 0.0565, wR2 = 0.1460
Largest diff. peak and hole	1.640 and −0.881 e Å ⁻³

been characterized by IR and NMR spectroscopic techniques, elemental analysis, and X-ray crystallographic diffraction analysis. The potential of this compound as a viable precursor to the synthesis of active organometallic compounds of ruthenium is a subject of ongoing research.

Supplementary material

CCDC 860692 contains the supplementary crystallographic data for complex [2][BF₄]₂. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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