

Regioselective Functionalisation of Tetrabromo Phenanthroline

Ruthenium Complexes

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Abstract

Structural, photophysical and -chemical characterisation and reactivity of a novel polypyridyl ruthenium complex based on 3,5,6,8-tetra-bromophenanthroline are discussed.

Signal storage at a molecular level is great challenge for chemistry.¹ The possibility of connecting different functionalities selectively to one ligand of a metal complex may open the route towards higher integrated molecular units capable of processing various external stimuli in a predesignated order. The implementation of this concept demands ligands with a multitude of potential connecting groups which can selectively be transformed.² 3-bromo- and 3,8-dibromophenanthrolines have proved useful for the preparation of mononuclear³ and multiheteronuclear complexes.⁴ These systems have found applications ranging from DNA photoprobes⁵ to metalloligands in catalysis.⁶ A very useful feature of this bromophenanthroline ruthenium complexes is their susceptibility towards nucleophilic aromatic substitution which is very well established.⁷

We have improved a bromination reaction of phenanthroline first published by Dénes and Chira⁸ which allows now the selective formation of 3,5,6,8,-tetrabromophenanthroline (Br₄phen) in an one step multigram reaction, figure 1.⁸

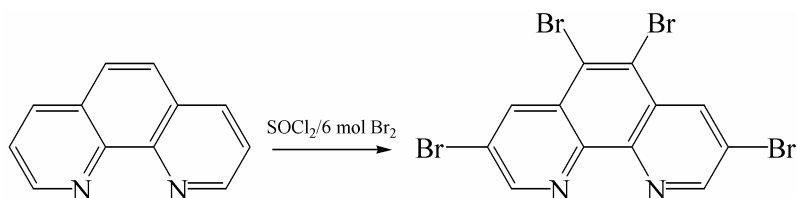


Figure 1 Improved preparation of 3,5,6,8,-tetrabromophenanthroline (Br₄phen)

Br₄phen readily forms a complex with (tbbpy)₂RuCl₂ resulting in [(tbbpy)₂Ru(Br₄phen)]²⁺, **1**. The structural characterisation using two dimensional NMR spectroscopy suggests that a symmetrical complex is formed indicated by the presence of only two signals for the four phenanthroline based protons. ¹³C, HSQC, HMBC allows the complete assignment of all signals in the ¹H- and ¹³C-NMR spectra which together with mass spectroscopy suggests that Br₄phen coordinates in a similar fashion as the unsubstituted phenanthroline. The X-ray crystallographic characterisation confirms this assumption and as apparent from table 1 shows no significant differences compared with the parent complex [(tbbpy)₂Ru(phen)]²⁺, **2** (see supporting information), the molecular structure is depicted in figure 2.

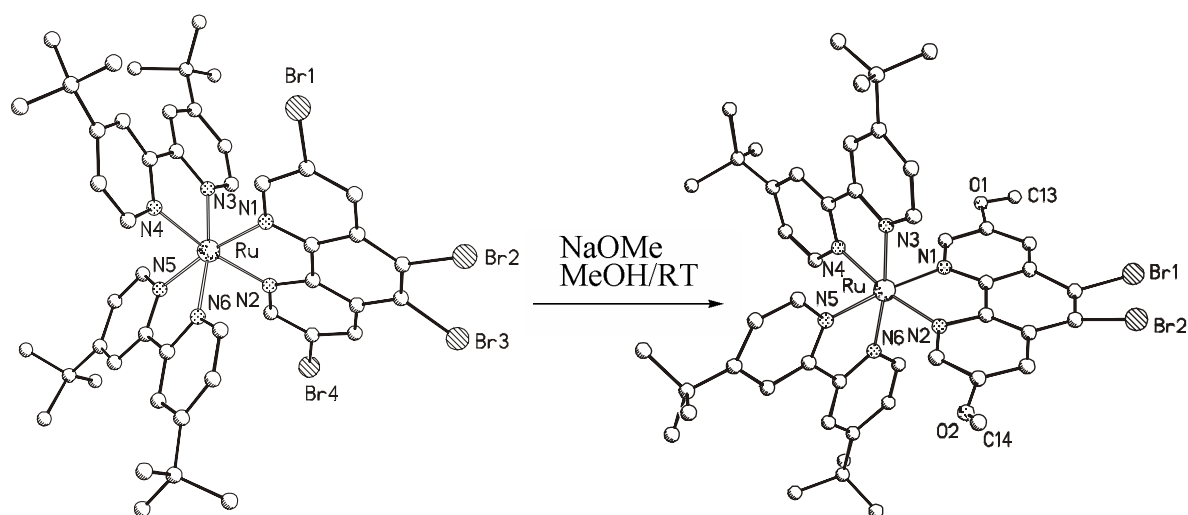


Figure 2. Regioselective nucleophilic substitution of **1** with NaOMe leading to **3**; molecular structure of **1**, Anions and hydrogen atoms omitted and structural motive of **3** confirming the regioselective substitution

Reaction of **1** with NaOMe at room temperature in methanol leads to the selective formation of one product that still contains two bromine and two new methoxy functions, confirmed by ESI-MS. The fact that all bipyridine based signals in the $^1\text{H-NMR}$ did not change their position together with only one new signal at 4.15 ppm for the methoxy function suggests the formation of a symmetrical species where substitution at the phenanthroline moiety has taken place. The regioselective formation of the 5,6-dibromo-3,8-dimethoxyphenanthroline ruthenium complex **3** could be confirmed by a structural motive depicted figure 2.

Table 1 Ru-N bond length in Å, angles in °

	1	2
Ru-N1	2.046(5)	2.055(4)
Ru-N2	2.060(5)	2.056(5)
Ru-N3	2.064(5)	2.053(4)
Ru-N4	2.052(5)	2.055(4)
Ru-N5	2.047(5)	2.060(4)
Ru-N6	2.071(5)	2.074(4)
C2-Br1	1.891(6)	----
C5-Br2	1.883(6)	----
N1-Ru-N2	79.27(19)	79.9(2)
N3-Ru-N4	78.21(19)	77.88(16)
N5-Ru-N6	78.25(19)	78.99(16)

Photophysical investigation of compounds **1** to **3** suggests that the tetrabromo-substitution lowers the electron density of the phenanthroline ligand considerably. The absorption and emission wavelength of **1** are redshifted compared with **2**, see table 2. This finding correlates well with the data obtained for the oxidation potential of RuII/III which clearly shows that the four bromine substituents significantly decrease the electron density at the metal centre (difference of 137 mV). Introduction of the methoxy groups increases the electron density as expected.⁹ The introduction of two methoxy groups has a pronounced influence on the photophysical properties which is in agreement with an electron donating substituent.

Table 2 Photophysical and electrochemical properties of complexes **1-3** in acetonitrile

Compound	E _{1/2} ox in V (vs Fc/Fc ⁺)	λ _{max} in nm	λ _{em} in nm
1	0.92	470	680
2	0.783	444	610
3	0.845	450	615

In conclusion, rutheniumpolypyridyl complexes based on the ligand Br₄phen are readily obtainable. Most importantly a regioselective nucleophilic substitutions with NaOMe at the 3,8 position is possible. It is evident from the conventional reactivity of bromine substituted aromatics that **1** and **3** are potentially very interesting synthon in itself opening the possibility to derivatise the previously not easily accessible 5,6 position. Initial investigations of the photochemical reactivity of **3** suggest that Br₂OMe₂phen is very photolabile.

Acknowledgement

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reduction of the ruthenium centre of **3** suggesting an involvement of the methoxy function as observed previously: L. O'Brien, M. Duati, S. Rau, A.L. Guckian, T.E. Keyes, N.M. Boyle, A. Serr, H. Görls, J.G. Vos, *J. Chem. Soc. Dalton Trans.* **2004**, 514.

Supporting information

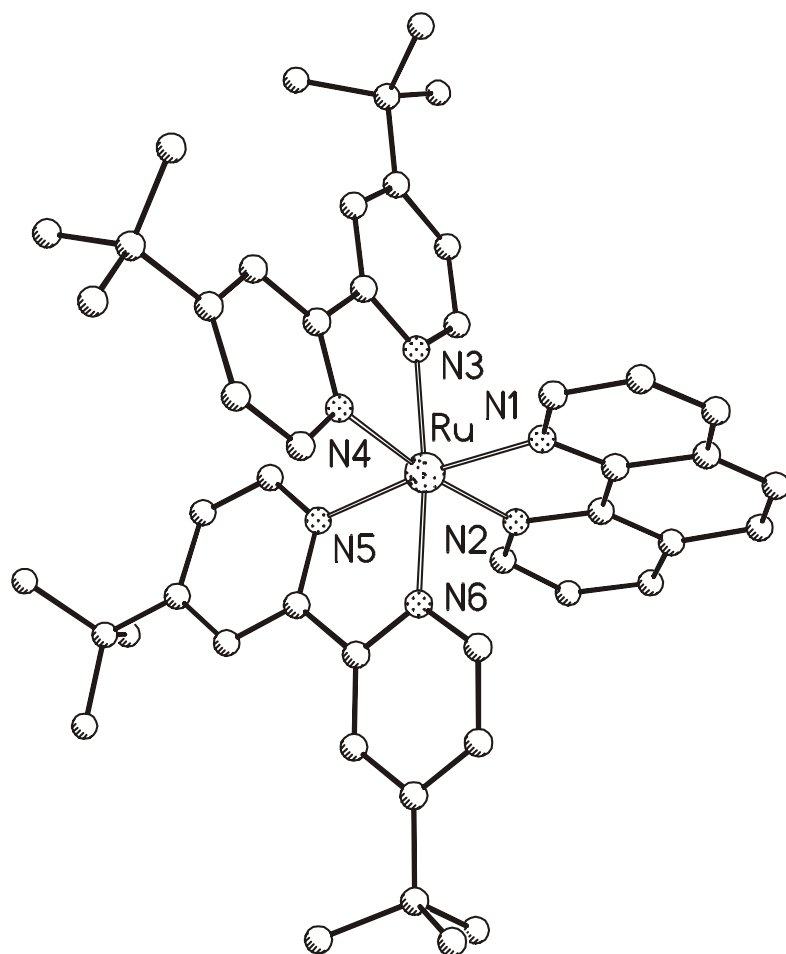


Figure S1. Molecular structure of $(tbbpy)_2Ru(phen)$, **2**, Anions and hydrogen atoms omitted (Ru-N bond length in Å, angles in °, Ru-N1 2.061(5), Ru-N2 2.056(5), Ru-N3 2.053(4), Ru-N4 2.055(4), Ru-N5 2.060(4), Ru-N6 2.074(4), N1-Ru-N2 79.9(2), N3-Ru-N4 77.88(16), N5-Ru-N6 78.99(16))

Experimental conditions

Methods and Materials

1,10-phenanthroline was received from Aldrich and used without further purification, $(tbbpy)_2RuCl_2$ was prepared according to literature methods.¹ All manipulations were carried out under Argon using standard Schlenk techniques and the used solvents were dried and distilled if not stated otherwise. The NMR spectra were recorded on a Bruker 400 MHz and

200 MHz spectrometer. The mass spectroscopy was carried out on a SSQ 170, Finigan Mat. The Electrospray mass spectroscopy was performed on a Finnigan MAT 95 XL double focussing sector field instrument (Thermo Finnigan GmbH, Bremen, Germany) adjusted to a mass resolution of about 2000.

UV-VIS spectra were obtained using a Varian Cary 1 UV-vis or a Shimadzu UV 3100 UV-vis-NIR spectrometer. Emission spectra are not corrected and were recorded using a Perkin Elmer LS50B spectrometer equipped with a Hamamatsu R928 red sensitive detector.

Electrochemical investigation

The electrochemical oxidation of the compounds was investigated in 3-electrode technique by means of cyclic square-wave voltammetry using an home-built computer controlled instrument based on the PCI-6110E data acquisition board (National Instruments). The experiments were performed in acetonitrile containing 0.25M tetra-n-butylammonium-hexafluorophosphate under a blanket of solvent-saturated argon. The ohmic resistance of the solvent which had to be compensated for was determined by measuring the impedance of the system at potentials where the faradaic current was negligibly small. The reference electrode was an Ag\AgCl electrode in acetonitrile containing 0.25M tetra-n-butylammonium chloride. The potential of this reference system was calibrated by measuring the potential of the ferrocenium/ferrocene couple at the end of each experiment. The latter was found to be at $0.803 \pm 0.001V$ throughout the measurements.

The working electrode was a 1.5 mm Pt disk electrode (Bioanalytical Systems Inc., West Lafayette, USA).

Crystal Structure Determination

The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer, using graphite-monochromated Mo-K α radiation. Data were corrected for Lorentz and polarization effects^[2,3]. **1** was corrected for absorption effects^[4].

The structures were solved by direct methods (SHELXS^[5]) and refined by full-matrix least squares techniques against Fo² (SHELXL-97^[6]). The hydrogen atoms were included at calculated positions with fixed thermal parameters. All nonhydrogen atoms were refined anisotropically^[6]. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations. The quality of the data for compound **3** is insufficient for full structural refinement. We will therefore only publish the conformation of the molecule and the crystallographic data. We will not deposit the data in the Cambridge Crystallographic Data Centre. Further informations can be obtained directly at the authors.

Synthesis

3,5,6,8,-tetrabromophenanthroline (Br₄phen):

4,0 g (20 mmol) of 1,10-phenanthroline monohydrate were dissolved in 200 ml SOCl₂. 9.3 g (120 mmol) of freshly distilled Br₂ were carefully added. This mixture was refluxed for 31 h and cooled to room temperature and the bright yellow precipitate filtered of (3,5,6,8,-tetrabromophenanthroline). The precipitate was washed with aqueous NH₃ until the washing solution was colourless. The white solid was recrystallised from toluene.

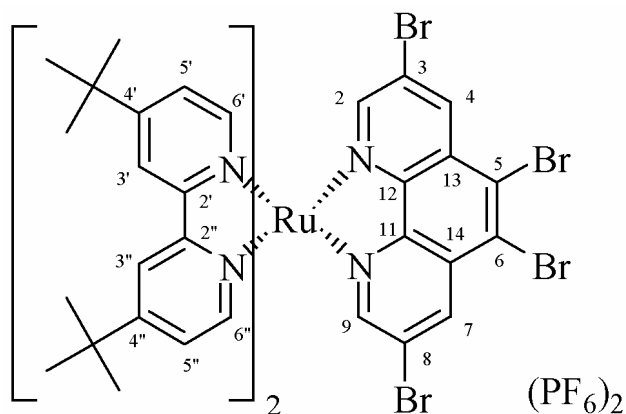
3,5,6,8,-tetrabromophenanthroline (Br₄phen) ¹H-NMR (CDCl₃): 9.16 (2H, d), 8.91 (2H, d);

¹³C-NMR (CDCl₃): 122,0; 125,1; 129,6; 139,0; 143,6; 152,4; ; MS(DCI with H₂O): 497

(M+H⁺) 417 (M-Br+H⁺), 338 (M-Br₂+H⁺), 257 (M⁺-Br₃) Yield 5.22 g (52 % of theory based on phen)

[(tbbpy)₂Ru(Br₄phen)](PF₆)₂ (1): 3,5,6,8-Tetrabromo-1,10-phenanthroline (1.15 g, 2.32 mmol) and [(tbbpy)₂RuCl₂] (1.5 g, 2.11 mmol) were refluxed in a mixture of 80 mL ethanol and 20 mL H₂O for 8 hours. The crude reaction mixture was filtered, washed twice with ethanol/H₂O (80:20), and the combined filtrate was concentrated to the half volume. Upon addition of NH₄PF₆ and stirring at room temperature for 1 hour the crude product precipitated. Recrystallisation from acetone/water gave the desired product. Crystals suitable for X-ray analysis were obtained from acetone/water.

Crystal Data for 1 ^[7]: C₄₈H₅₂Br₄N₆Ru²⁺ * 2 [PF₆]⁻, Mr = 1423.61 g mol⁻¹, bourdeaux-red prism, size 0.02 x 0.02 x 0.01 mm³, tetragonal, space group I4₁/a, a = b = 32.5281(3), c = 20.5151(4) Å, V = 21706.6(5) Å³, T = -90 °C, Z = 16, ρ_{calcd.} = 1.742 g cm⁻³, μ (Mo-Kα) = 33.74 cm⁻¹, psi-scan, transmin: 0.5565, transmax: 0.7367, F(000) = 11264, 20023 reflections in h(-42/42), k(-29/29), l(-19/26), measured in the range 2.66° ≤ Θ ≤ 27.49°, completeness Θ_{max} = 99.8 %, 12423 independent reflections, R_{int} = 0.053, 7520 reflections with F_o > 4σ(F_o), 652 parameters, 0 restraints, R_{1obs} = 0.065, wR_{2obs}² = 0.135, R_{1all} = 0.129, wR_{2all}² = 0.163, GOOF = 1.018, largest difference peak and hole: 1.217 / -1.151 e Å⁻³.



¹ H-NMR	in d ₆ -DMSO 400MHz		in d ₆ acetone 400 MHz	
	Proton	Chemical Shift (ppm)	Chemical Shift (ppm)	Integration, multiplicity
CH ₃ (<i>tert</i> -butyl)	1.362	18H, s	1.300	18H, s
CH ₃ (<i>tert</i> -butyl)	1.391	18H, s	1.388	18H, s
5'	7.310	2H, d(lc)	7.600	2H, d(lc)
6'',6'	7.527	4H, m	7.857	4H, m
5''	7.599	2H, d(lc)	7.359	2H, d(lc)
2,9	8.055	2H, s(lc)	8.340	2H, s(lc)
3'	8.788	2H, s(lc)	8.838	2H, s(lc)
3''	8.792	2H, s(lc)	8.801	2H, s(lc)
4,7	8.997	2H, s(lc)	8.988	2H, s(lc)

¹³C-NMR in d₆-DMSO 400MHz

Carbon	Chemical shift (ppm)
CH ₃ (<i>tert</i> -butyl)	29.962
CH ₃ (<i>tert</i> -butyl)	30.001
C(<i>tert</i> -butyl)	35.378
C(<i>tert</i> -butyl)	35.508
3',3''	121.741
11,12	122.572
5'	124.261
5''	124.685
13,14	126.074

5,6	130.765
4,7	138.459
3,8	145.802
6' or 6''	150.732 and 151.974
2,9	153.667
2' or 2''	156.006 and 156.610
4' or 4''	161.934 and 162.267

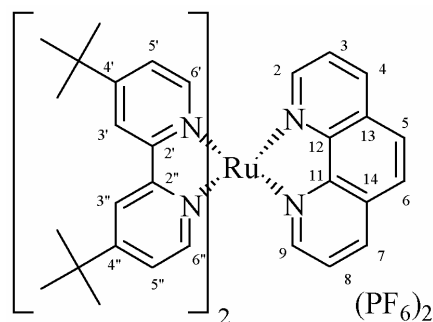
MS (Micro-ESI in CHCl₃ + Methanol); m/z(relative intensity) with matching isotop pattern
1279(100) (**1** + PF₆), 1201(34) (**1**-Br + PF₆), 567(51) (**1**²⁺)

Synthesis of [(tbbpy)₂Ru(phen)](PF₆)₂ **2**:

1,10-phenanthroline (0.018 g, 0.09 mmol) and [(tbbpy)₂RuCl₂] (0.06 g, 0.085 mmol) were reacted and purified according to **1**. Yield 96 mg (95%). Crystals suitable for X-ray analysis were obtained from acetone/water.

Crystal Data for 2 ^[7]: [C₄₈H₅₆N₆Ru]²⁺ * 2 [PF₆]⁻ * 2 C₃H₆O, Mr = 1224.15 g mol⁻¹, red-brown prism, size 0.12 x 0.10 x 0.09 mm³, triclinic, space group P-1, a = 12.1999(7), b = 13.3243(7), c = 18.989(1) Å, α = 76.854(2), β = 74.819(3), γ = 78.206(3)°, V = 2866.3(3) Å³, T = -90 °C, Z = 2, ρ_{calcd.} = 1.418 g cm⁻³, μ (Mo-Kα) = 4.13 cm⁻¹, psi-scan, transmin: 0.9521, transmax: 0.9637, F(000) = 1264, 19624 reflections in h(-15/15), k(-17/14), l(-24/24), measured in the range 2.11° ≤ Θ ≤ 27.44°, completeness Θ_{max} = 97.4 %, 12753 independent reflections, R_{int} = 0.062, 6757 reflections with F_o > 4σ(F_o), 664 parameters, 0 restraints, R_{1obs} = 0.074, wR_{2obs} = 0.194, R_{1all} = 0.138, wR_{2all} = 0.220, GOOF = 0.955, largest difference peak and hole: 1.402 / -1.062 e Å⁻³.

¹ H-NMR	in d ₃ -Acetonitrile 400MHz	
proton	Chemical Shift (ppm)	Integration, multiplicity
CH ₃ (<i>tert</i> -butyl)	1.322	18H, s
CH ₃ (<i>tert</i> -butyl)	1.437	18H, s
5''	7.200	2H, d(lc)
6''	7.405	2H, d
5'	7.463	2H, d(lc)



6'	7.705	2H, d
3,8	7.753	2H, m
2,9	8.058	2H, s(lc)
5,6	8.299	2H, s
3''	8.456	2H, s(lc)
3'	8.504	2H, s(lc)
4,7	8.613	2H, s(lc)

¹³C-NMR in d₃-acetonitrile 200MHz

δ in ppm 164.16; 164.01; 158.73; 158.44; 153.83; 152.71; 149.35; 138.09; 132.59; 129.68; 127.66; 126.22; 126.06; 123.07; 123.00; 122.00; 36.96; 36.85; 31.38, 31.14

MS FAB in nba m/z(relative intensity) with matching isotop pattern

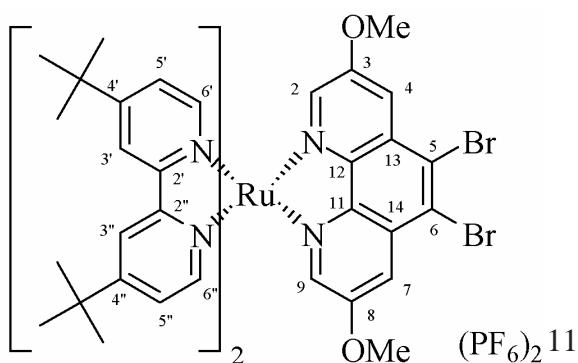
980(22) 2+PF₆; 834(15) 2

Synthesis of [(tbbpy)₂Ru(OMe₂Br₂phen)](PF₆)₂ **3**:

200 mg of **1**, 0.14 mmol, were dissolved in 100 ml of a freshly prepared 1 M solution of NaOMe in MeOH. The solution was stirred for 6 h and 200 ml H₂O were added. The pH of the solution was slowly adjusted to 7 by adding diluted HCl. The resulting opaque orange solution was extracted with CH₂Cl₂ until colorless and the solvent was removed from the combined organic phases. The precipitate was dissolved in a minimal amount of EtOH and concentrated aqueous NH₄PF₆ added. The precipitate was recrystallised from aceton/water. Yield 170 mg (90%)

Crystal Data for 3 : C₅₂H₆₁Br₂F₁₂ N₆O₂P₂ Ru, Mr = 1304.72 gmol⁻¹, red prism, size 0.02 x 0.02 x 0.01 mm³, monoclinic, space group P2₁/n, a = 13.983(3), b = 39.063(5), c = 10.4711(15) Å, β = 100.945(13)°, V = 5615.4(17) Å³, T = -153 °C, Z = 4, ρ_{calcd.} = 1.543 gcm⁻³, μ (Mo-Kα) = 6.22 cm⁻¹, F(000) = 2654, 21731 reflections in h(-15/13), k(-45/45), l(-12/12), measured in the range 1.52° ≤ Θ ≤ 14.56°, completeness Θ_{max} = 72.1 %, 6903 independent reflections.

¹ H-NMR in d ₆ -aceton 400MHz		
proton	Chemical Shift (ppm)	Integration, multiplicity
CH ₃ (<i>tert</i> -butyl)	1.367	18H, s



CH ₃ (<i>tert</i> -butyl)	1.428	18H, s
CH ₃ (OMe)	2.831	6H, s
5''	7.397	2H, d(lc)
5'	7.618	2H, d(lc)
6''	7.828	2H, d
2,9	7.845	2H, s(lc)
6'	7.939	2H, d
4,7	8.174	2H, s(lc)
3''	8.844	2H, s(lc)
3'	8.879	2H, s(lc)

MS FAB in nba m/z(relative intensity) with matching isotop pattern

1181(5) **3**+PF₆; 1035(5) **3**

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- (7) CCDC 216455 and 216456 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via 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 deposit@ccdc.cam.ac.uk).