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Self-Assembly of New Arene-Ruthenium Rectangles Containing Triptycene Building Block and Their Application in Fluorescent Detection of Nitro Aromatics

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Abstract

A suite of two new tetraruthenium metallarectangles **5** and **6** have been obtained from [2 + 2] selfassemblies between dipyridylethynyltriptycene **2** and one of the two dinuclear arene ruthenium clips, $[\operatorname{Ru}_2(\mu \cdot \eta^4 - OO \cap OO)(\eta^6 - p - \operatorname{cymene})_2][OTf]_2$; $(OO \cap OO = \operatorname{oxalate} 3; 6, 11 - \operatorname{dihydroxy-5}, 12$ naphthacenedionato (dotq) **4**; OTf = triflate). These molecular rectangles are fully characterized by ¹H NMR spectroscopy, electrospray mass spectrometry. A single crystal of **6** was suitable for X-ray diffraction structural characterization. These new metallarectangles showed fluorescence behavior in solution, have been examined for emission quenching effects with various aromatic compounds, and show high quenching selectivity and sensitivity towards nitroaromatics, particularly picric acid and trinitrotoluene. Excited-state charge transfer from the rectangles to nitro aromatic substrates can be used to develop selective fluorescent sensors for nitro aromatics.

Keywords

Fluorescent; Ruthenium; Self-assembly; Nitro aromatics; Metalla-rectangle

1. Introduction

The design and study of discrete supramolecular structures through abiological selfassembly is an active field of research fuelled by the single-step formation of complicated

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Appendix A. Supplementary material

CCDC 986299 contains the supplementary crystallographic data for complex 6. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with 1 H, 13 C NMR and ESI-MS spectral of ligand 2, complexes (5 and 6). Fluorescence quenching spectra of complexes with different quenchers.

structural motifs and incorporation of constituent building blocks with the desired functionalities.¹ Of the various self-assembly protocols, metal-ligand coordination driven self-assembly is especially appealing and effective.² Its highly directional and predictable nature provides limitless possibilities to design novel molecular materials. With the tremendous progress that has been made in the preparation and characterization of metallosupramolecules, attention is now being focused on fully exploring and developing their sensor and host-guest properties.^{3,4}

Nitroaromatics, especially trinitrotoluene (TNT), dinitrotoluene (DNT), and picric acid (PA), are the primary constituents of many unexploded land mines worldwide.⁵ Nitroaromatics used in organic synthesis, drug analysis, rocket fuel, fireworks, and matches release contaminants into the environment that are toxic to living organisms.⁶ It is of great interest to develop efficient fluorescent sensors that rapidly detect nitroaromatic compounds in an effort to prevent terrorism and reduce environmental problems associated with explosive residues. Recently, optical detection techniques based on fluorimetric assays for sensing nitroaromatics have attracted a great deal of attention.⁷ The pioneer work of Swager et al. in developing poly(phenylene ethynylene)s polymers has been extensively employed for sensing nitroaromatics.⁸ The response characteristics of these materials depend on the strength of the chemical (or physical) interaction between the analyte and photoactive polymer, and the permeability of analyte in the polymer. To increase the permeability of fluorescent poly(phenylene ethynylene)s polymer films, sterically demanding pentiptycene and triptycene moieties were incorporated, allowing nitroaromatics to quench polymer fluorescence more rapidly and efficiently. Additionally, the incorporation of rigid three dimensional pentiptycene and triptycene molecules into the polymeric backbone prevents low quantum yields due to π -stacking, excimer formation, and self-quenching.^{8b,c and e} Pentiptycene and triptycene containing fluorescent-conjugated organic polymers have been employed extensively as sensing materials. The potential of pentiptycene and triptycene containing conjugated metal-organic discrete assemblies of finite shapes and sizes as sensors for nitroaromatics has not yet been explored.

Herein, we report the synthesis of two new [2 + 2] metal-organic discrete assemblies **5** and **6** by coordination driven self-assembly. The assemblies include oxalate and 6,11dihydroxy-5,12-naphthacenedionato-based *O*,*O*-bridging ligands between the Ru centers of acceptors **3** and **4**, respectively, with new dipyridylethynyltriptycene donor **2** used as a bridging donor unit. Ethynyl spacer and triptycene functionalities were integrated into donor **2** to endow supramolecules **5** and **6** with photoluminescent properties that are exploited for detection of electron-poor guests like nitro-aromatics. The triptycene functionality also prevents the self-quenching of initial fluorescence intensity in solution that occurs due to intermolecular stacking.

2. Experimental Section

2.1. Materials and physical measurements

1,4-Diethynyl-9,10-dihydro-9,10-[1',2']benzeno-anthracene **1**, was synthesized following the reported procedure.⁹ Arene-ruthenium acceptor clips 3^{10} and 4^{11} were synthesized under a dry nitrogen atmosphere by standard Schlenk technique following the reported procedures.

Solvents were dried and distilled according to the standard literature procedures.¹² ¹H and ¹³C NMR spectra were recorded on a Bruker 300 MHz spectrometer. The chemical shifts (δ) in ¹H NMR are reported relative to residual solvent signals. ESI-MS spectra for compound **2** were recorded on Triple Quadrupole LC-Mass spectrometry (Finnigan TSQ Quantum Ultra EMR). ESI-MS spectra for self-assemblies **5** and **6** were recorded on a Micromass QuattroII triple-quadrupole mass spectrometer using electrospray ionization with a Mass Lynx operating system. Absorption spectra were recorded by a CARY 100 Conc UV/Vis spectrophotometer. Elemental analyses were performed using an Elemental GmbH Vario EL-3 instrument. Fluorescence titration studies were carried out on a HORIBA FluoroMax-4 fluorometer.

2.2. Fluorescence Quenching Titration Study

A 2 mL stock solution $(5.0 \times 10^{-6} \text{ M})$ of macrocycles **5** and **6** were placed in a 1 cm wide quartz cell. Quenchers (1,3,5-trinitrobenzene, picric acid, 2,4-dinitrophenol, nitrobenzene, $benzoquinone and benzoic acid) stock solution <math>(1.0 \times 10^{-4} \text{ M})$ was added in an incremental fashion. The whole titration experiment was carried out at 298 K, and each titration measurement was repeated at least three times to obtain concordant values. For all measurements, macrocycle **5** was excited at $\lambda_{ex} = 283$ nm, and the corresponding emission intensity was monitored from 300 nm. Both excitation and emission slit widths were 3 nm. No change in emission spectra shape was noted except for significant gradual quenching of the initial fluorescence intensity of **5** and **6** upon titration with electron-deficient nitroaromatics. Analysis of normalized fluorescence emission intensity (I_0/I) as a function of increasing quenchers concentration ([Q]) was well described by the Stern-Volmer equation: $I_0/I = 1 + K_{SV}[G]$. Stern-Volmer constants were calculated from the slope of Stern-Volmer plots.

2.3. Synthesis of compounds

2.3.1. Synthesis of compound 1,4-bis(pyridin-4-ylethynyl)-9,10-dihydro-9,10-[1,2]benzene anthracene 2—The flask containing Pd(PPh₃)₂Cl₂ (0.057 g, 0.08 mmol) and copper(I) iodide (0.025 g, 0.13 mmol) was evacuated and then filled with nitrogen. In sequence, deoxygenated triethylamine (10 mL), a deoxygenated solution of 4-iodopyridine (0.389 g, 1.9 mmol) in anhydrous THF (5 mL), and a deoxygenated solution of compound **1** (0.250 g, 0.83 mmol) in triethylamine (5 mL) were added to the flask via cannula. After 12 h at 50 °C, the reaction mixture was poured into a flask containing dichloromethane (20 mL) and saturated NH₄Cl (20 mL) solution. The organic layer was separated, washed with water, dried over Na₂SO₄, and concentrated. Residue was purified by column chromatography (neutral alumina, methanol/ dichloromethane, 2/98, v/v) to afford **2** as a pale yellow solid. Yield 85%. M. p. 179-181 °C. ¹H NMR (300 MHz, CDCl₃): δ = 8.71 (d, *J* = 6.9 Hz, 4H), 7.52 (d, *J* = 6.8 Hz, 4H), 7.47- 7.49 (m, 4H), 7.20 (s, 2H), 7.05-7.08 (m, 4H), 5.95 (s, 2H). ¹³C NMR (75 MHz, CDCl₃): δ = 150.0, 147.7, 144.1, 131.1, 128.2, 125.7, 125.6, 124.1, 118.2, 91.4, 91.1, 52.1. MS (ESI): m/z calcd = 456.16, found = 457.17. Anal. Calcd for C₃₄H₂₀N₂: C, 89.45; H, 4.42; N, 6.14. Found: C, 89.07; H, 4.67; N, 5.99.

2.3.2. Synthesis of metallarectangle 5—A CH₂Cl₂ (1 mL) solution of donor 2 (0.017 g, 0.04 mmol) was added dropwise to a CH₃OH solution (1 mL) of ruthenium acceptor **3**

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(0.034 g, 0.04 mmol). The mixture was then stirred for 48 h at room temperature. The reaction mixture was filtered and solvent was removed under reduced pressure. The resulting solid was washed with diethyl ether and then dried to furnish **5** as a yellow powder. Yield 90%. ¹H NMR (300 MHz, CD₃NO₂): δ = 8.13 (d, *J* = 5.8 Hz, 8H, H_i), 7.66-7.69 (m, 16H, H_g and H_h), 7.18-7.21 (m, 8H, H_f), 6.11 (s, 4H, H_e), 5.94 (d, *J* = 6.4 Hz, 8H, H_{cym}), 5.78 (d, *J* = 6.4 Hz, 8H, H_{cym}), 5.54 (s, 4H, H_d), 2.85-2.96 (m, 4H, H_c), 2.27 (s, 12H, H_b), 1.42 (d, *J* = 7.0 Hz, 24H, H_a) ppm; ¹³C NMR (75 MHz, CD₃NO₂): δ = 185.7, 154.1, 149.4, 145.5, 135.9, 129.2, 127.1, 125.4, 118.9, 105.6, 102.9, 100.5, 96.1, 91.2, 84.9, 83.3, 52.9, 32.7, 22.6, 18.5; MS (ESI) for **5** (C₁₁₆H₉₆F₁₂N₄O₂₀Ru₄S₄): 726.44 [**5**–3OTf]³⁺. Anal. Calcd for C₁₁₆H₉₆F₁₂N₄O₂₀Ru₄S₄: C, 53.05; H, 3.68; N, 2.13; Found: C, 50.34; H, 3.59; N, 2.30.

2.3.3. Synthesis of metallarectangle 6—A CH₂Cl₂ (1 mL) solution of donor 2 (0.017 g, 0.04 mmol) was added dropwise to a CH₃OH solution (1 mL) of ruthenium acceptor **4** (0.042 g, 0.01 mmol). The mixture was then stirred for 48 h at room temperature. The reaction mixture was filtered and then solvent was removed under reduced pressure. The resulting solid was washed with diethyl ether and then dried to furnish **6** as a green powder. Yield 94%. ¹H NMR (300 MHz, CD₃NO₂): δ = 8.82-8.85 (m, 8H, H_k), 8.71 (d, *J* = 6.8 Hz, 8H, H_j), 7.99-8.02 (m, 8H, H_i), 7.53 (d, *J* = 6.8 Hz, 8H, H_h), 7.19-7.22 (m, 8H, H_g), 6.57-6.60 (m, 8H, H_f), 6.54 (s, 4H, H_e), 6.02 (d, *J* = 6.2 Hz, 8H, H_{cym}), 5.79-5.82 (m, 12H, H_{cym} and H_d), 3.10-3.15 (m, 4H, H_c), 2.34 (s, 12H, H_b), 1.42 (d, *J* = 6.8 Hz, 24H, H_a) ppm; ¹³ C NMR (75 MHz, CD₃NO₂): δ = 170.8, 153.2, 149.4, 145.3, 135.2, 134.3, 128.9, 128.5, 126.8, 125.2, 118.8, 108.6, 105.3, 101.0, 95.2, 91.2, 85.3, 84.0, 52.8, 32.1, 22.7, 18.1; MS (ESI) for **6** (C₁₄₈H₁₁₂F₁₂N₄O₂₀Ru₄S₄): 859.93 [**6**–30Tf]³⁺.

2.4. Single-crystal X-ray Crystallography

A single crystal of rectangle **6** was mounted onto a loop, and the data were collected at 100 K on an ADSC Quantum 210 CCD diffractometer with synchrotron radiation ($\lambda = 0.80000$ Å) at Macromolecular Crystallography Beamline 6B1, Pohang Accelerator Laboratory (PAL), Pohang, Korea. The raw data were processed and scaled using the program HKL2000. The structure was solved by direct methods, and refinements were carried out with full-matrix least-squares on F2 with appropriate software implemented in the SHELXTL program package.

X-ray data for **6**: $C_{83}H_{80}F_6N_2O_{13}Ru_2S_2$, formula weight = 1693.75, Monoclinic, wavelength = 0.80000 Å, T = 100(2) K, space group = $P2_1/n$, unit cell dimensions a = 17.581(4) Å, $a = 90^\circ$, b = 25.642(5) Å, $\beta = 113.73(3)^\circ$, c = 19.481(4) Å, $\gamma = 90^\circ$, V = 8040(3) Å3, Z = 4, ρ calcd = 1.399 g cm⁻³, absorption coefficient = 0.681 mm⁻¹, F(000) = 3480, crystal size = $0.35 \times 0.20 \times 0.15$ mm³, theta range for data collection = 1.49 to 25.07°, index ranges = -20 h 20, -28 k 28, -22 l 22, reflections collected = 40281, independent reflections = 10910 [R(int) = 0.0208], completeness to theta = 25.00°, 77.1 %, absorption correction = semi-empirical from equivalents, max. and min. transmission = 0.9047 and 0.7965, refinement method = full-matrix least-squares on F², data / restraints / parameters = 10910 / 170 / 976, goodness-of-fit on F²= 1.682, final R indices [I>2sigma(I)] R1 = 0.1287, wR2 = 0.3693, R indices (all data) R1 = 0.1421, wR2 = 0.3829, largest diff. peak and hole = 1.146 and -0.701 e.Å⁻³.

3. Results and Discussion

Ligand **2** was synthesized in 85% yield by coupling with 4-iodopyridine and 1,4diethynyl-9,10-dihydro-9,10-[1',2']benzenoanthracene **1** in the presence of Pd(0)/CuI catalyst (Scheme 1).

Solutions containing equimolar amounts of $[Ru_2(\mu \cdot \eta^4 - C_2O_2)(MeOH)_2(\eta^6 - p - cymene)_2]$ $[O_3SCF_3]_2$ (**3**) or $[Ru_2(\mu - \eta^4 - C_{18}H_8O_4)(\eta^6 - p - cymene)_2][O_3SCF_3]_2$ (**4**) and dipyridylethynyltriptycene donor **2** in CH₂Cl₂/CH₃OH were stirred for 48 h at room temperature. This resulted in the quantitative self-assembly of **5** and **6**, respectively (Scheme 2). Analytically pure rectangles were isolated as crystalline solids upon addition of diethyl ether to concentrated reaction mixtures. All rectangles were fully characterized by ¹H, ¹³C NMR, electrospray mass spectrometry (ESI-MS), and UV-Vis absorption and emission. A single crystal of complex **6** was used to determine its solid-state structure via X-ray crystallography.

In ¹H NMR spectra of **5** and **6**, the signals corresponding to the H_a nuclei on the pyridine rings undergo upfield shifts ($\Delta \delta = 0.1$ -0.6 ppm) relative to compound **2**, indicating metal pyridine coordination. Likewise, the aromatic proton signals of the triptycene functional group of rectangles **5** and **6** showed significant upfield shifts due to increased electron density upon coordination. The aromatic proton resonances of *p*-cymene ligands were observed as two doublets at $\delta = 6.02$ and 5.79-5.82 ppm, while the signals for naphthacenedione protons were observed as two multiplets at $\delta = 8.82$ -8.85 and 7.99-8.02ppm for **6**. The appearance of prominent peaks in the ESI-MS spectra of the multiply charged ions for **5** at m/z = 726.44 [**5**-30Tf]³⁺ and for **6** at 859.93 [**6**-30Tf]³⁺ indicate the formation of [2+2] self-assembled products. The observed peaks are isotopically resolved and agreed well with their theoretically predicted patterns (Figure S5 and S6, Supporting Information).

3.1. Crystal structure of 6

The molecular structure of **6** was further confirmed by X-ray crystallography (Figure 1 and Table 1). Single crystals of rectangle **6** were obtained by slow evaporation of Et₂O into a concentrated solution of the complex in methanol. X-Ray diffraction analysis revealed that complex **6** had a tetranuclear rectangular architecture. The molecular structure of **6** consisted of two dipyridylethynyltriptycene units linked by two $[Ru_2(\mu - \eta^4 - C_{18}H_8O_4)(\eta^6 - p - cymene)_2]^{2+}$ building blocks to form a M₄L₂ rectangle. Each Ru center was coordinated to one *p*-cymene moiety in a η^6 fashion with a dotq bridging ligand and one pyridyl group of the dipyridylethynyltriptycene linker. This resulted in molecular rectangle **6**, which contained two diethyl ether molecules inside the rectangular molecular cavity with overall dimensions of 8.35 Å × 20.65 Å.

3.2. Detection of Nitroaromatics by Fluorescence Quenching

Fluorescence quenching-based detection of chemical explosives has been employed extensively due to the high sensitivity, easy visualization, and short response time required for detecting chemical explosives.¹³ The electron-deficient character of nitroaromatic

explosives makes them efficient fluorescence quenchers through photo-induced electron transfer (PET) processes. The strategy used to design new fluorescent metallarectangles **5** and **6** involved the following unique features: (a) triptycene and ethynyl functionalities were introduced to create fluorescent and π -electron rich assemblies; (b) open spaces in the metallarectangles were suitable to accommodate small electron-deficient nitroaromatics; (c) triptycene molecules and bulky capped *p*-cymene moieties on each ruthenium metal center help to avoid intermolecular stacking and reduce self-quenching of initial fluorescence intensity in solution.

The electronic absorption spectra of metallarectangles in methanol solutions $(1.0 \times 10^{-5} \text{ M})$ exhibit intense bands at $\lambda_{abs} = 282$ and 350 nm for **5** and $\lambda_{abs} = 280$, 351, 572, and 614 for **6** (Supporting information, Figure S7). High-energy bands observed at 330 nm in the spectra of **2** were also present in each of the rectangles. This suggests that the $\pi \rightarrow \pi^*$ transitions expected for an extended aromatic system of dipyridyl ligand were preserved upon self-assembly. The photoexcitation of **5** in methanol solution $(1.0 \times 10^{-6} \text{ M})$ at 283 nm resulted in emission around 375 nm, whereas **6** showed emission bands at 379 nm. To demonstrate the ability of metallarectangles **5** and **6** at sensing electron-deficient nitroaromatic solution. Titration of a $1.0 \times 10^{-6} \text{ M}$ methanolic solution of **5** (Figure 2) and **6** (Figure 3) with a $1.0 \times 10^{-4} \text{ M}$ methanolic solution of picric acid and 1,3,5-trinitrobenzene showed gradual quenching of the initial fluorescence intensity.

Emission of metallarectangles **5** and **6** was above 350 nm whereas picric acid absorbs irradiation below 300 nm. This evidence ruled out the possibility of energy transfer from excited rectangles to explosives quenched due to a lack of overlap between the emission of supramolecular rectangles and absorption of picric acid. Thus, the observed fluorescence quenching is due to photoinduced electron transfer from the excited state of metallarectangles to the ground state of nitroaromatics. The main reason for facile electron transfer is the presence of conjugated labile π -electrons in the fluorophore and the strong oxidant tendency of 1,3,5-trinitobenzene and picric acid.

3.2.1. Analysis of normalized fluorescence intensity (I_0/I) as a function of picric acid and 1,3,5-trinitrobenzene concentration—Stern-Volmer constants $K_{SV} = 3.7 \times 10^5 \text{ M}^{-1}$ and $2.2 \times 10^5 \text{ M}^{-1}$ were obtained from the slope of a linear Stern-Volmer plots for picric acid and 1,3,5-trinitrobenzene with metallarectangle **5**, respectively (Figure 2). The R² values 0.882 and 0.977 were obtained from the Stern-Volmer plots for picric acid and 1,3,5-trinitrobenzene with metallarectangle **5**, respectively. Stern-Volmer constants $K_{SV} = 1.2 \times 10^5 \text{ M}^{-1}$ and $4.2 \times 10^5 \text{ M}^{-1}$ were obtained from the slope of a linear Stern-Volmer constants $K_{SV} = 1.2 \times 10^5 \text{ M}^{-1}$ and $4.2 \times 10^5 \text{ M}^{-1}$ were obtained from the slope of a linear Stern-Volmer plot for picric acid and 1,3,5-trinitrobenzene with metallarectangle **6**, respectively (Figure 3). The R² values 0.922 and 0.983 were obtained from the Stern-Volmer plots for picric acid and 1,3,5-trinitrobenzene with metallarectangle **6**, respectively.

The investigation was extended to nitro-aromatics known as electron-poor molecules, such as nitrobenzene and 2,4-dinitrophenol (Figure S8, S9, S12 and S13, Supporting Information). The results indicate that the increased electron-withdrawing nature of nitro-aromatics may induce enhanced π - π interactions with π -electron rich molecular rectangles **5**

and **6**. The selectivity of **5** and **6** for nitroaromatic compounds over other electron-deficient aromatic systems such as benzoic acid (BA) and benzoquinone (BQ) was also investigated. No significant quenching was noticed with polar aromatics such as benzoic acid (Figure S11 and S15, Supporting Information). The weak quenching response towards carboxylic acid also ruled out the possibility of simple acid–base reactions of analytes with molecular rectangles.

The fluorescence quenching results suggest that metallarectangles **5** and **6** only have quenching responses for nitroaromatic analytes in comparison to other tested aromatic compounds due to their low reduction potential value compared to nitroaromatics. This result support proposed quenching mechanism, in which electron-deficient nitroaromatics act as fluorescence quenchers via photoinduced electron transfer from the electron-rich fluorophores.

4. Conclusions

In conclusion, we herein report the synthesis and characterization of metallarectangles **5** and **6** prepared via directional self-assembly of a dinuclear Ru-acceptor and a new dipyridyl donor. The incorporation of ethynyl and triptycene functionalities creates assemblies fluorescent and π -electron rich. These new, electron-rich, and photoluminescent metallarectangles have been examined for emission quenching effects with various aromatic compounds. The metallarectangles show high quenching selectivity and sensitivity towards nitroaromatics, particularly picric acid and 1,3,5-trinitrobenzene. Conjugated organic polyethynyl compounds have been used as potential sensors for chemical explosives. Our unique self-assembled organometallic rectangles **5** and **6** can be used as molecular sensors to detect picric acid and 1,3,5-trinitrobenzene.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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- Triptycene and ethynyl functionalities containing new ligand has been synthesized.
- Fluorescent and π -electron rich metallarectangles **5** and **6** were synthesized.
- Presence of triptycene prevents self-quenching by avoiding intermolecular stacking.
- Metallarectangles **5** and **6** show high emission quenching selectivity for nitroaromatics.



Scheme 1. Synthesis of dipyridylethynyltriptycene donor 2.



Scheme 2. Synthesis of metallarectangles 5 and 6.





Figure 1.

(a) Molecular structure of **6** showing two encapsulated diethyl ether molecules. (b) Side view. Color code: green, Ru; blue, N; red, O; grey, oxygen. H atoms are not shown for clarity.



Figure 2.

Quenching of initial fluorescence intensity of 6 $(1.0 \times 10^{-6} \text{ M})$ upon gradual addition of picric acid and 1,3,5-trinitrobenzene in methanol $(1.0 \times 10^{-4} \text{ M})$ at room temperature and corresponding Stern-Volmer plots.



Figure 3.

Quenching of initial fluorescence intensity of **5** (1.0×10^{-6} M) upon gradual addition of picric acid and 1,3,5-trinitrobenzene in methanol (1.0×10^{-4} M) at room temperature and corresponding Stern-Volmer plots.

O(3)-Ru(2)-N(2)

Table 1

Selected bond lengths [Å] and angles [°] for 6

85.1(3)

Bonds		Length [A]	Bond		Length [A]	
Ru(1)-N(1) and Ru(1)#-N(1)#		2.109(8)	Ru(1)-O(1)		2.109(8)	
Ru(1)-O(2)		2.039(6)	Ru(2)-N(2) and Ru(2)#-N(2)#		2.115(10)	
Ru(2)-O(3)		2.018(7)	Ru(2)-O(4)		2.026(6)	
					-	
Bonds	Angle [°]	Bonds		Angle [°]	_	
O(1)-Ru(1)-O(2)	85.8(2)	O(1)-Ru(1)-N	(1)	82.5(3)		
O(2)-Ru(1)-N(1)	82.3(3)	O(3)-Ru(2)-O	0(4)	84.5(2)		

O(4)-Ru(2)-N(2)

82.1(3)