

Isocyanide ligation at ruthenium(II) complexes with chelating tertiary amine and porphyrin ligands. Structural and electrochemical studies

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Abstract

Reaction of $[\text{Ru}(\text{Me}_3\text{tacn})(\text{PMe}_3)_2(\text{O}_2\text{CCF}_3)]\text{PF}_6$ with one equivalent of *t*-BuNC or 4-cyano-1-isocyano-2,6-diisopropylbenzene (*L'*) in refluxing 1,2-dichloroethane gave $[\text{Ru}(\text{Me}_3\text{tacn})(\text{PMe}_3)(\text{t-BuNC})(\text{O}_2\text{CCF}_3)]\text{PF}_6$ (**1**)·PF₆ and $[\text{Ru}(\text{Me}_3\text{tacn})(\text{PMe}_3)(\text{L}')(\text{O}_2\text{CCF}_3)]\text{PF}_6$ (**3**)·PF₆, respectively. In the presence of zinc amalgam, reactions of $[\text{Ru}(\text{Me}_3\text{tacn})(\text{H}_2\text{O})_2(\text{O}_2\text{CCF}_3)](\text{OTf})_2$, *trans*- $[\text{Ru}(\text{16-TMC})\text{Cl}_2]\text{Cl}$ and *cis*- $[\text{Ru}(2,2,2\text{-tet-Me}_6)\text{Cl}_2]\text{PF}_6$ with an excess of *t*-BuNC in 1,2-dichloroethane, followed by anion metathesis, afforded $[\text{Ru}(\text{Me}_3\text{tacn})(\text{t-BuNC})_2(\text{O}_2\text{CCF}_3)]\text{PF}_6$ (**2**)·PF₆, *trans*- $[\text{Ru}(\text{16-TMC})(\text{t-BuNC})_2](\text{ClO}_4)_2$ (**4**)·(ClO₄)₂ and *cis*- $[\text{Ru}(2,2,2\text{-tet-Me}_6)(\text{t-BuNC})_2](\text{PF}_6)_2$ (**5**)·(PF₆)₂, respectively. Treatment of $[\text{Ru}(\text{Por})(\text{CO})(\text{MeOH})]$ (Por = TPP, 4-MeO-TPP or 4-F-TPP) with an excess of *t*-BuNC or *L'* gave $[\text{Ru}(\text{TPP})(\text{t-BuNC})_2]$ (**6**) or $[\text{Ru}(4\text{-MeO-TPP})(\text{L}')_2]$ (**7**) and $[\text{Ru}(4\text{-F-TPP})(\text{L}')_2]$ (**8**), respectively. **1**·PF₆–**5**·(PF₆)₂ display a quasi-reversible Ru(III/II) couple at potentials ranging from +0.65 to +1.42 V vs. FeCp₂^{+/0}. The *E*_{1/2}(Ru^{III/II}) of **5**·(PF₆)₂ (+1.42 V vs. FeCp₂^{+/0}) is notably high compared with that of **4**·(ClO₄)₂ (+0.65 V), reflecting the strong π-back-bonding in the *cis*-bis(*tert*-butyl isocyanide)ruthenium(II) complex. Irrespective of the overall charge, the cationic complex **4** and the neutral complexes **6**–**8** all exhibit a virtually linear RNC–Ru–CNR moiety. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Isocyanide complexes; Ruthenium; Crystal structures; Porphyrins; Electrochemistry; Tertiary amine

1. Introduction

When compared with phosphines [1], alkyl- and aryl-isocyanides [2] are less commonly encountered as auxiliary ligands in organometallic chemistry. Our interest in transition metal isocyanide complexes stemmed from the recent report that functionalized isocyanides [3] are versatile bridging ligands for the formation of organometallic supermolecules [4]. Because of the linear –N≡C moiety, isocyanide ligands are relatively not sterically demanding upon coordination to metal ions [5]. With proper design of peripheral functional groups, their complexes can act as building blocks for

oligomeric materials or extended solids [6]. Recently, 1,4-diisocyanobenzene [7], 1,4-dicyanobenzene [6c] and CN–C₆H₂–R₂–2,6-CN-4 (R = H or CH₃) [8] have been employed as bridging ligands in the synthesis of organometallic polymers [2,9]. Indeed, Mayr and co-workers have synthesized $[\text{FeI}_2(\text{CN}-\text{C}_6\text{H}_2-\text{Me}_2-2,6-\text{CN}-4)_4]$ and demonstrated the usefulness of this complex as a building block for molecular materials [8]. Because ruthenium(II) is a good π-donor, there would be considerable π-back-bonding effect in ruthenium-(II)–isocyanide complexes. Therefore, we envisage that substantial electronic delocalization would be observed in polymeric ruthenium(II)–isocyanide solids. In this work, we report the synthesis, crystal structures and characterization of the ruthenium(II) complexes obtained from ligation of *tert*-butyl isocyanide and 4-cyano-1-isocyano-2,6-diisopropylbenzene (*L'*) to ruthenium(II) ion containing the chelating tertiary amines and porphyrin ligands.

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2. Results and discussion

2.1. Synthesis and characterization

Reaction of $[\text{Ru}(\text{Me}_3\text{tacn})(\text{PMe}_3)_2(\text{O}_2\text{CCF}_3)]\text{PF}_6$ (Me_3tacn = 1,4,7 - trimethyl - 1,4,7 - triazacyclononane) with one equivalent of *t*-BuNC or 4-cyano-1-isocyano-2,6-diisopropylbenzene (*L'*) in refluxing 1,2-dichloroethane gave $[\text{Ru}(\text{Me}_3\text{tacn})(\text{PMe}_3)(t\text{-BuNC})(\text{O}_2\text{CCF}_3)]\text{PF}_6$ (**1**)·PF₆ or $[\text{Ru}(\text{Me}_3\text{tacn})(\text{PMe}_3)(\text{L}')(\text{O}_2\text{CCF}_3)]\text{PF}_6$ (**3**)·PF₆, respectively in good yields. In an attempt to prepare the bis(isocyanide) complexes, a mixture of **1**·PF₆ or **3**·PF₆ and a fivefold excess of isocyanide ligand in 1,2-dichloroethane was stirred at elevated temperature. **1**·PF₆ or **3**·PF₆, however, was recovered. Presumably the PMe_3 ligand in $[\text{Ru}(\text{Me}_3\text{tacn})(\text{PMe}_3)(t\text{-BuNC})(\text{O}_2\text{CCF}_3)]^+$ or $[\text{Ru}(\text{Me}_3\text{tacn})(\text{PMe}_3)(\text{L}')(\text{O}_2\text{CCF}_3)]^+$ is inert toward further substitution reaction. Therefore, $[\text{Ru}(\text{Me}_3\text{tacn})(\text{PMe}_3)_2(\text{O}_2\text{CCF}_3)]\text{PF}_6$ is not a good precursor for the preparation of the ruthenium(II)-bis(isocyanide) complex. We turned to another precursor $[\text{Ru}^{\text{III}}(\text{Me}_3\text{tacn})(\text{H}_2\text{O})_2(\text{O}_2\text{CCF}_3)](\text{OTf})_2$ [10] (OTf^- = trifluoromethanesulphonate). In the presence of zinc amalgam, this complex reacted with an excess of *t*-BuNC in 1,2-dichloroethane to give $[\text{Ru}(\text{Me}_3\text{tacn})(t\text{-BuNC})_2(\text{O}_2\text{CCF}_3)]^+$ (**2**), which was isolated as a PF_6^- salt. However, the complex $[\text{Ru}(\text{Me}_3\text{tacn})(\text{L}')_2(\text{O}_2\text{CCF}_3)]^+$ could not be obtained by a similar method, presumably the sterically demanding isopropyl substituents on *L'* prevent formation of the target complex (Scheme 1).

Our success in the preparation of *trans*- $[\text{Ru}(16\text{-TMC})(\text{C}\equiv\text{C}\text{Ar})_2]$ [11] (16-TMC = 1,5,9,13-tetramethyl-1,5,9,13-tetraazacyclohexadecane) prompted us to study the analogous isoelectronic ruthenium complexes with $\text{C}\equiv\text{N}-\text{R}$ ligands. *trans*- $[\text{Ru}(16\text{-TMC})(t\text{-BuNC})_2]^{2+}$ (**4**) was prepared by reacting $[\text{Ru}(16\text{-TMC})\text{Cl}_2]\text{Cl}$ with an excess of *t*-BuNC in the presence of Zn amalgam in refluxing methanol. This procedure, however, did not give any $\text{Ru}(16\text{-TMC})$ complex of *L'*. *cis*- $[\text{Ru}(2,2,2\text{-tet-Me}_6)(t\text{-BuNC})_2]^{2+}$ (2,2,2-tet-Me₆ = *N,N,N',N'*-3,6-hexamethyl-3,6-diazaoctane-1,8-diamine) (**5**) was also obtained from reaction of *cis*- $[\text{Ru}(2,2,2\text{-tet-Me}_6)\text{Cl}_2]\text{PF}_6$, *t*-BuNC and zinc amalgam. As we have not been successful in preparing $\text{Ru}(\text{II})$ complexes of *L'* containing the 16-TMC ligand, we changed to the preparation of the $\text{Ru}(\text{Por})$ (*Por* = porphyrinato dianion) complex of *L'*. Treatment of $[\text{Ru}(\text{Por})(\text{CO})(\text{MeOH})]$ (*Por* = *meso*-tetraphenylporphyrinato (TPP), *meso*-tetrakis(4-methoxyphenyl)porphyrinato (4-MeO-TPP) or *meso*-tetrakis(4-fluorophenyl)porphyrinato (4-F-TPP)) with a large excess of *t*-BuNC or *L'* gave the bisaxially coordinated complexes $[\text{Ru}(\text{TPP})(t\text{-BuNC})_2]$ (**6**), $[\text{Ru}(4\text{-MeO-TPP})(\text{L}')_2]$ (**7**) and $[\text{Ru}(4\text{-F-TPP})(\text{L}')_2]$ (**8**), respectively. All the isocyanide complexes prepared are

air stable in the solid state and in solution at ambient temperature.

2.2. NMR spectroscopy

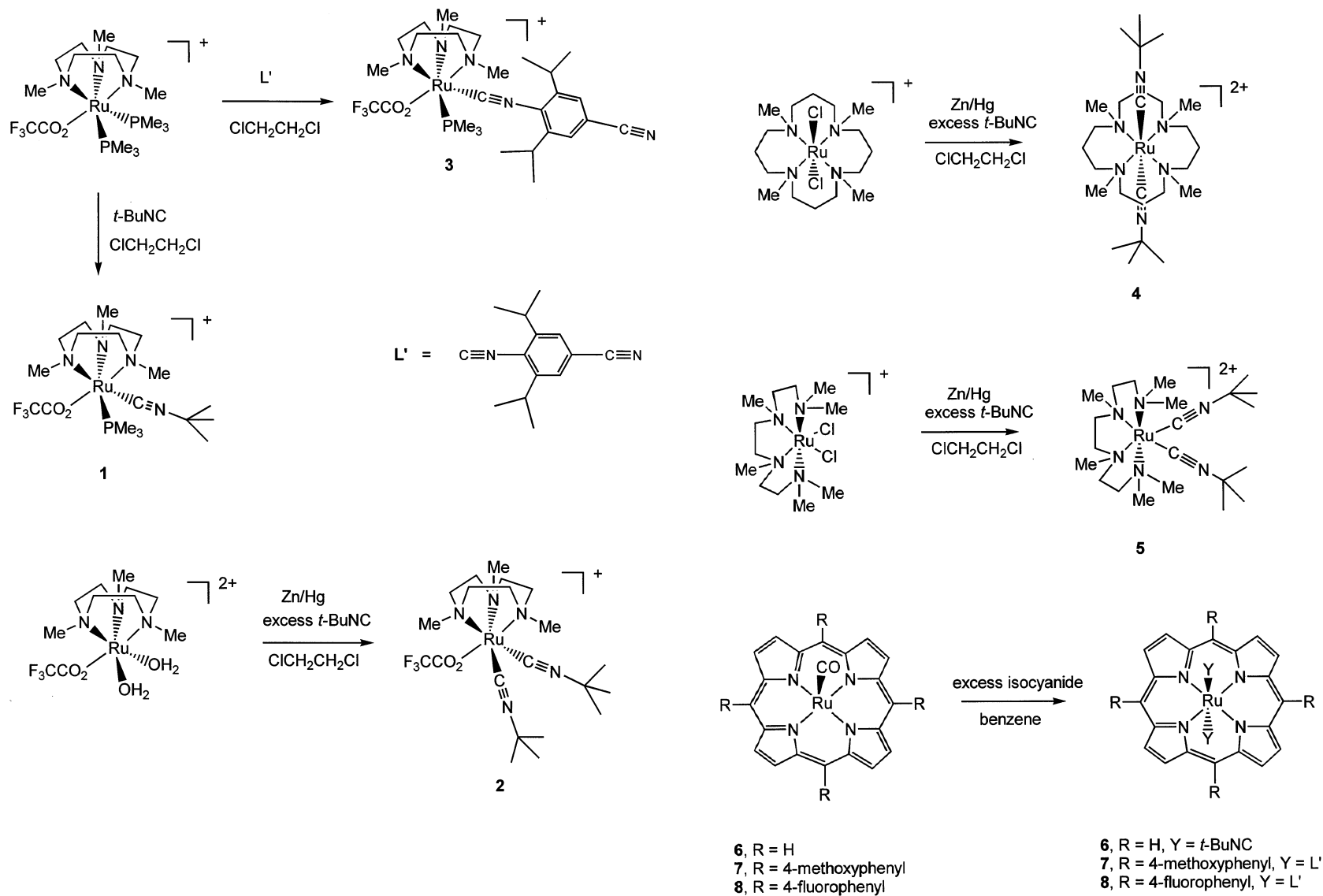
The ^1H -NMR spectrum of **1**·PF₆ displays a sharp singlet for $\text{NC}(\text{CH}_3)_3$, a doublet for $\text{P}(\text{CH}_3)_3$ and multiplets for Me_3tacn protons in an integral ratio of 9:9:21 whereas **2**·PF₆ shows only one sharp singlet for the *t*-BuNC protons and multiplets for Me_3tacn protons in a ratio of 18:21. These results reveal that in **1**, there is only one *t*-BuNC per Me_3tacn ligand but in **2**, there is a plane of symmetry bisecting the two *t*-BuNC and the Me_3tacn ligands. Complex **3**·PF₆ exhibits a septet for $\text{CH}(\text{CH}_3)_2$, a doublet for $\text{C}(\text{CH}_3)_2$, a doublet for $\text{P}(\text{CH}_3)_3$ and multiplets for Me_3tacn protons in an integral ratio of 2:12:9:21, suggesting that there is only one *L'* per Me_3tacn . The ^1H -NMR spectra of **4**·(ClO_4)₂ and **5**·(PF_6)₂ show a singlet for *t*-BuNC in accordance with pseudo- D_{4h} and C_2 symmetry, respectively. Integration reveals that in **4** and **5** there are two *t*-BuNC per chelating tertiary amine ligand. As observed in other metalloporphyrins [12,13], the proton signals of the axial ligands in **6–8** are significantly upfield shifted (**6** by 1.88 ppm for *t*-BuNC; and **7** and **8** by > 1.00 ppm for *i*-propyl and aryl protons) when compared to those of free ligands due to the porphyrin ring current effect. Integration shows that there are two isocyanide ligands in **6–8** which also display a single resonance for the pyrrolic protons.

Notably, the ^{13}C signals for the bound *t*-BuN≡C in **5** and Ar–N≡C in **8** were found at 152.2 and 164.0 ppm, respectively. The $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra of cationic complexes **1** and **3** show a single resonance at 2.8 and 0.4 ppm, respectively, which fall in the range observed for coordinated PMe_3 [10].

2.3. IR and UV-vis spectroscopy

Selected IR spectral data of **1**·PF₆–**8** are summarized in Table 1. Complexes **1**·PF₆–**3**·PF₆ exhibit bands at ca. 2110 and 1690 cm^{-1} attributable to the stretches of –N≡C in bound isocyanide and C=O in the $\eta^1\text{-O}_2\text{CCF}_3$ ligand, respectively. Similar bands are observed for $[\text{Ru}(\text{Me}_3\text{tacn})(\text{CNC}_6\text{H}_3\text{Me}_2\text{-2,6})_2(\text{O}_2\text{CCF}_3)]\text{PF}_6$ (2125 and 2145 cm^{-1} for $\nu(\text{N}\equiv\text{C})$ and 1695 cm^{-1} for $\nu(\text{C}=\text{O})$) [14] and $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(t\text{-BuNC})_2\text{Cl}]$ (2110 and 2046 cm^{-1} for $\nu(\text{N}\equiv\text{C})$) [12].

Complexes **4**·(ClO_4)₂ and **6** show only one intense –N≡C stretch in accordance with a *trans* configuration of the bis-(alkyl isocyanide) ligands while **2**·PF₆ and **5**·(PF_6)₂ show two –N≡C stretches at ca. 2115 and 2158 cm^{-1} , which are comparable to those of $[\text{Ru}(\text{Me}_3\text{tacn})(\text{CNC}_6\text{H}_3\text{Me}_2\text{-2,6})_2(\text{O}_2\text{CCF}_3)]\text{PF}_6$ [14] and



Scheme 1. (Coordination of L' via the isocyano group.)

Table 1
Selected IR spectral data (from Nujol mull)

Compound	$\nu(-N\equiv C)$ (cm ⁻¹)	$\nu(-C\equiv N)$ (cm ⁻¹)	$\nu(C\equiv O)$ (cm ⁻¹)
<i>t</i> -BuNC	2138		
4-Cyano-1-isocyano-2,6-diisopropylbenzene (L')	2123	2230	
[Ru(Me ₃ tacn)(<i>t</i> -BuNC)(O ₂ CCF ₃)(PMe ₃)]PF ₆ (1)·PF ₆	2112		1689
[Ru(Me ₃ tacn)(<i>t</i> -BuNC) ₂ (O ₂ CCF ₃)]PF ₆ (2)·PF ₆	2110, 2154		1694
[Ru(Me ₃ tacn)(L')(O ₂ CCF ₃)(PMe ₃)]PF ₆ (3)·PF ₆	2048	2233	1693
[Ru(Me ₃ tacn)(CNC ₆ H ₃ Me ₂ -2,6) ₂ (O ₂ CCF ₃)]PF ₆ [14]	2125, 2145		1695
<i>trans</i> -[Ru(16-TMC)(<i>t</i> -BuNC) ₂](ClO ₄) ₂ (4)·(ClO ₄) ₂	2120		
<i>cis</i> -[Ru(2,2,2-tet-Me ₆)(<i>t</i> -BuNC) ₂](PF ₆) ₂ (5)·(PF ₆) ₂	2115, 2158		
[Ru(TPP)(<i>t</i> -BuNC) ₂] (6) ^a	2119		
[Ru(4-MeO-TPP)(L') ₂] (7) ^a	2077	2231	
[Ru(4-F-TPP)(L') ₂] (8) ^a	2079	2234	

^a From KBr pellets.

[Ru(η^5 -C₅Me₅)(*t*-BuNC)₂Cl] [12]. On the other hand, the IR spectra of **3**·PF₆, **7** and **8** display bands at ca. 2077 and 2231 cm⁻¹ attributed to the $-N\equiv C$ and $-C\equiv N$ stretches in L', respectively. The $-N\equiv C$ stretching frequencies of the ruthenium complexes prepared in this work are only slightly lower than those of the free isocyanide ligands indicating that π -back-bonding to the coordinated isocyanide ligands is not as important as expected. The larger decrease in $\nu(-N\equiv C)$ values observed for the complexes of aryl isocyanide L' as compared to those of *t*-BuNC implies that aryl isocyanide is a better π -acceptor than alkyl isocyanide [15]. Complexes **7** and **8** show similar $\nu(-N\equiv C)$ values although the MeO and F substituents are expected to exert opposite electronic effect. The $\nu(-C\equiv N)$ values of **3**·PF₆, **7** and **8** are close to that of free ligand L' suggesting that the peripheral cyanide group remains unperturbed.

As observed for [Ru(NH₃)₄(C₇H₇NC)]²⁺ [16], which gives a metal-to-ligand charge transfer (MLCT) band at 244 nm, complexes **1**, **2**, **3** and **5** exhibit similar electronic transition(s) at ca. 250–320 nm. For example, complex **3**·PF₆ exhibits an intense absorption band at 317 nm, attributed to Ru^{II} $\rightarrow$ $\pi^*(L')$ transition. For the porphyrin complexes **6**–**8**, the $d_\pi(Ru) \rightarrow \pi^*$ (isocyanide) transitions are probably mixed with the $\pi \rightarrow \pi^*$ transition of the porphyrin ring and therefore could not be located [17].

2.4. Electrochemical studies

Electrochemistry of the title ruthenium(II)–isocyanide complexes has been examined by cyclic voltammetry (CV) and the electrochemical data are listed in Table 2. Complexes **1**·PF₆–**5**·(PF₆)₂ display a quasi-reversible oxidation couple at potentials ranging from +0.65 to +1.42 V. The peak current is comparable to that of the Cp₂Fe^{+/0} couple measured at the same concentration under identical conditions; hence a one-electron process is implied. These couples are tenta-

tively assigned to be Ru(III/II). Oxidation of **1**·PF₆ occurs at a slightly lower potential than that of **2**·PF₆, presumably PMe₃ is a better σ -donor but a weaker π -acceptor than *t*-BuNC. On the other hand, L' is a better π -acceptor than *t*-BuNC, thereby making **3**·PF₆ more resistant toward oxidation than **1**·PF₆. Moreover, as PhC $\equiv$ C⁻ is a much better σ -donor than *t*-BuNC, *trans*-[Ru(16-TMC)(C $\equiv$ CC₆H₅)₂] (–0.74 V) [11] is much easier to oxidize than **4**·(ClO₄)₂. It is noteworthy that the $E_{1/2}(Ru^{III/II})$ of *cis*-[Ru(2,2,2-tet-Me₆)(*t*-BuNC)₂](PF₆)₂ **5**·(PF₆)₂ is notably high compared to that of **4**·(ClO₄)₂ although the $\nu(-N\equiv C)$ values of both complexes are similar.

It can be seen from Table 2 that both **7** and **8** exhibit two reversible oxidation couples in the potential range +0.20 to +0.90 V. In the absence of a strong π -acid ligand such as terminal carbonyl [18], the first oxidation couple is assignable to Ru(II/III) while the second one is ascribed to the oxidation of the porphyrin ring and formation of a Ru(III)–cation radical complex, [Ru^{III}(Por)(L')₂]⁺ (Por = 4-MeO-TPP, 4-F-TPP). The

Table 2
Selected electrochemical data^a

Complex	$E_{1/2}$ (Ru ^{III/II})	$E_{1/2}$ (Ru ^{II/I})
1 ·PF ₆	+0.73	
2 ·PF ₆	+0.89	
3 ·PF ₆	+0.89	
4 ·(ClO ₄) ₂	+0.65	
5 ·(PF ₆) ₂	+1.42	
7	+1.30 ^{b,c} +0.71 ^b +0.25	–2.01 ^c
8	+1.56 ^{b,c} +0.86 ^b +0.33	–2.02 ^c

^a $E_{1/2}$ (V vs. Cp₂Fe^{+/0}, scan rate = 100 mV s⁻¹) in acetonitrile at 298 K with 0.1 M NBu₄PF₆ as supporting electrolyte.

^b Formation of cationic radical (see text).

^c Irreversible couple.

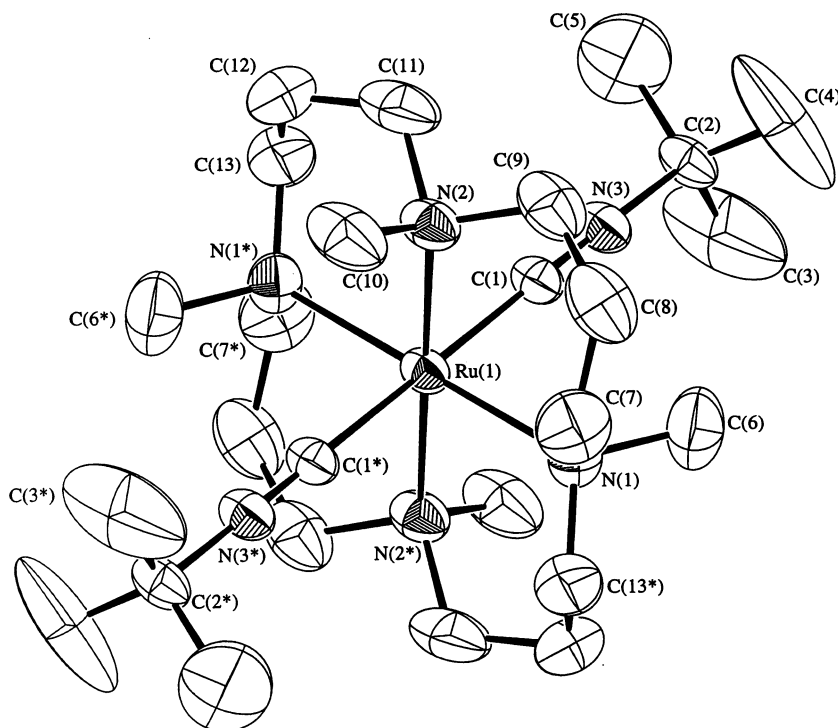


Fig. 1. Perspective view of complex **4** with the atomic numbering scheme. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at 40% probability.

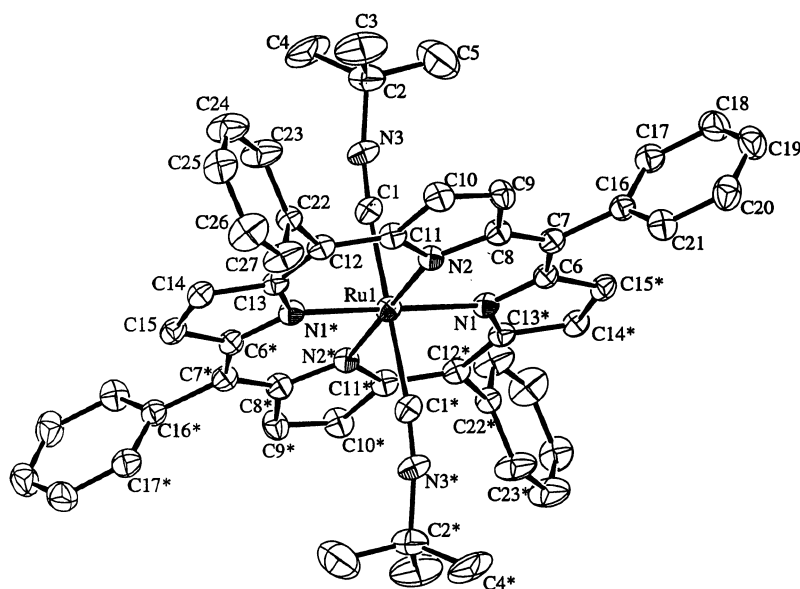


Fig. 2. Perspective view of complex **6** with the atomic numbering scheme. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at 40% probability.

irreversible oxidation wave at +1.30 V for **7** or +1.56 V for **8** suggests that the Ru(III)-dication is unstable on the CV time scale. In addition, **7** and **8** undergo an irreversible reduction at −2.01 V which can be attributed to the formation of highly unstable $[\text{Ru}^{\text{I}}(\text{Por})(\text{L}')_2]^-$ [18]. In general, the oxidation couples of **8** were found at higher potentials than those of **7**,

reflecting the stronger electron withdrawing effect of −F substituent compared to the −OMe group.

2.5. Crystal structures

Figs. 1–4 show perspective views of complexes **4** and **6–8**, respectively. Crystal data are collected in Table 3

while selected bond distances and angles are listed in Table 4. As shown from the perspective view of **4**, the ruthenium atom resides in a distorted octahedral environment and is coordinated by four equatorial nitrogen atoms of 16-TMC and two *t*-BuN≡C ligands in a *trans*-configuration. The crystal structure of **4** consists of one CH₃CN molecule as the solvent of crystallization. The six-membered chelate rings of the Ru(16-TMC) fragment are all in chair forms with the *N*-methyl groups adopting the 'two up, two down' configuration as in *trans*-[Ru(16-TMC)(C≡CC₆H₅)₂] [11]. The Ru–C distance observed for **4** (1.989(7) Å) falls in the normal range for Ru–C bonds [19] and is comparable to those in *cis*-[Ru(Me₃taen)(CNC₆H₃Me₂-2,6)₂(O₂CCF₃)]PF₆ (1.921(4) and 1.912(4) Å) [14] and *trans*-[Ru(16-TMC)(C≡CC₆H₅)₂] (2.077(4) Å) [11] as expected since 2,6-Me₂C₆H₃NC, *t*-BuNC and PhC≡C[−] are isoelectronic.

It can be seen from Figs. 2–4 that the ruthenium

atoms in **6–8** reside in a pseudo octahedral environment; all are situated at the centre of the mean plane defined by the four nitrogen atoms of the porphyrin ligands and bonded to the two axial isocyanide ligands. The crystal structures of **7** and **8** consist of three and five benzene molecules, respectively, as the solvent of crystallization. The Ru–C distances of **6** (molecule 1: 2.015(5) Å), **7** (1.980(4) Å) and **8** (1.988(5) Å) are within the range observed for Ru–C bond [14,19] and comparable to that of **4**. It is apparent that the Ru–C and RuC≡NR distances [14,20] found in this work are not sensitive to the nature of the macrocyclic ligand, irrespective of 16-TMC and porphyrinato anion. It is interesting to note that the RNC–Ru–CNR fragment is essentially linear in these structures. For example, the Ru–C(1)–N(3) and C(1)–N(3)–C(2) angles in **4** are 178.8(7) and 179.4(7)°, respectively. As L' can act as a bridging ligand, **7** and **8** are potential building blocks for extended solids or molecular materials.

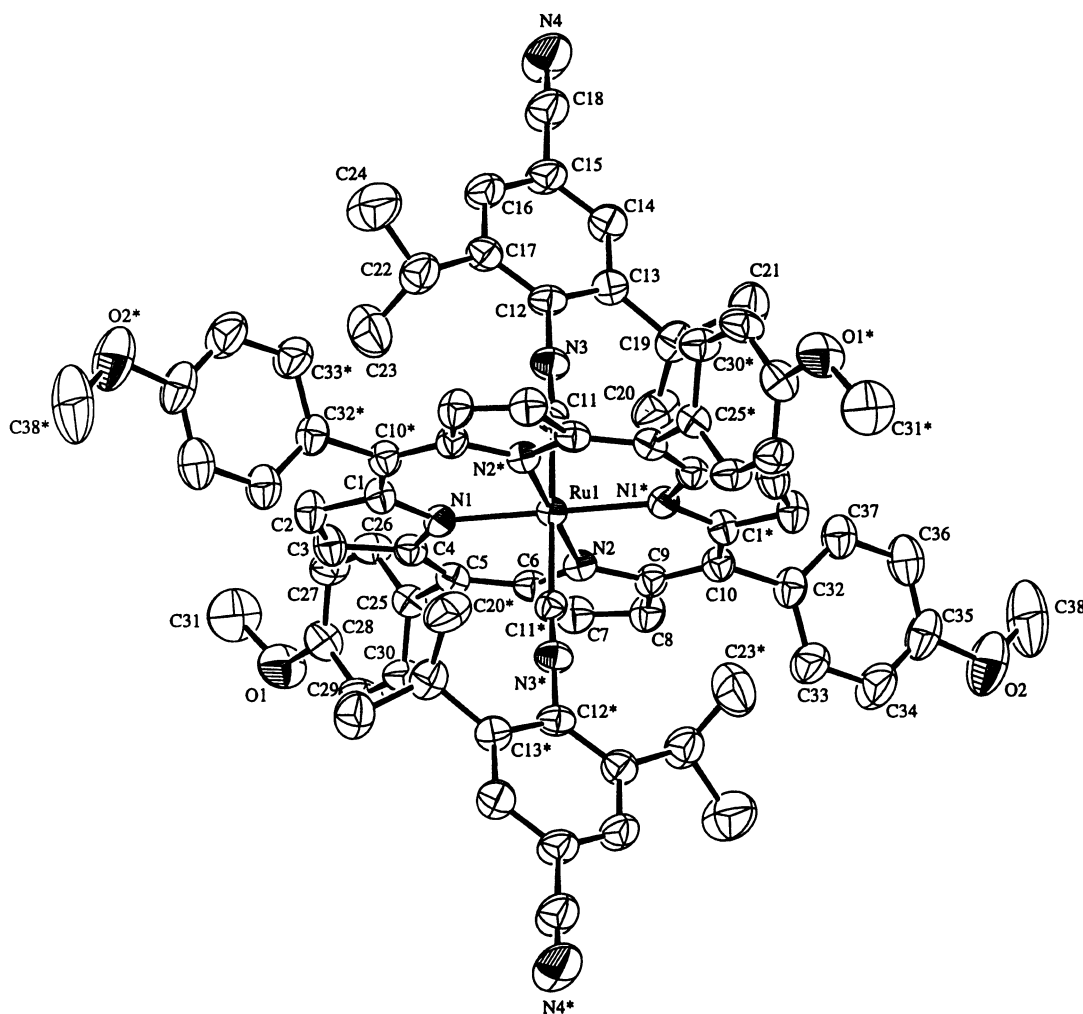


Fig. 3. Perspective view of complex **7** with the atomic numbering scheme. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at 40% probability.

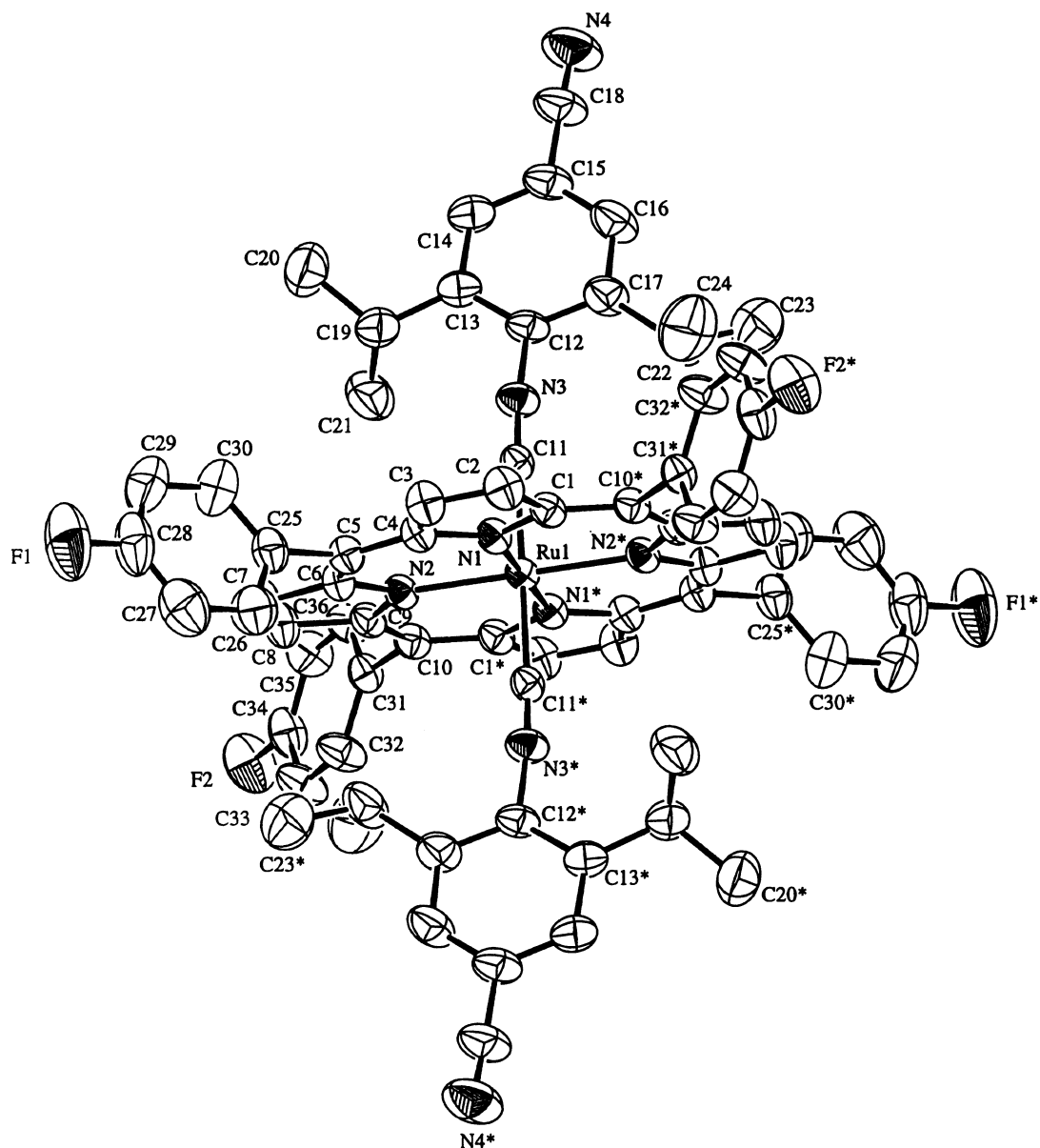


Fig. 4. Perspective view of complex **8** with the atomic numbering scheme. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at 40% probability.

3. Conclusions

A series of ruthenium(II) mono- and bis-isocyanide complexes supported by chelating tertiary amine and porphyrinato ligands have been synthesized. They are air stable in the solid state and in solution at ambient temperature and show a quasi-reversible Ru(II/III) couple. It is worth noting that the *cis*-[Ru^{II}(*t*-BuNC)₂]²⁺ moiety in **5** is much more resistant to oxidation compared to *trans*-[Ru^{II}(*t*-BuNC)₂]²⁺ in **4**. Results from X-ray diffraction studies reveal that the Ru–C and RuC≡NR distances are evidently insensitive to the overall electronic charges of the metal complexes and within the normal range. It is apparent that **6–8** consist of

virtually linear RN≡C–Ru–C≡NR moieties, which are essential for making 1-D polynuclear assemblies and supramolecular structures via peripheral –CN groups.

4. Experimental

4.1. General procedures

All reactions were performed under a nitrogen atmosphere using standard Schlenk techniques unless otherwise stated. Solvents were dried by standard methods and distilled before use. 4-Cyano-1-isocyano-2,6-diisopropylbenzene (L') was a donation from Dr M.-X. Li

[8]. $[\text{Ru}(\text{Me}_3\text{tacn})(\text{H}_2\text{O})_2(\text{O}_2\text{CCF}_3)](\text{OTf})_2$ [10], $[\text{Ru}(\text{Me}_3\text{tacn})(\text{PMe}_3)_2(\text{O}_2\text{CCF}_3)]\text{PF}_6$, *trans*- $[\text{Ru}(16\text{-TMC})\text{-Cl}_2]\text{Cl}$, *cis*- $[\text{Ru}(2,2,2\text{-tet-Me}_6)\text{Cl}_2]\text{PF}_6$ [21], $[\text{Ru}(\text{TPP})(\text{CO})(\text{MeOH})]$ [22], $[\text{Ru}(4\text{-MeO-TPP})(\text{CO})(\text{MeOH})]$ and $[\text{Ru}(4\text{-F-TPP})(\text{CO})(\text{MeOH})]$ [23] were prepared by published procedures. Zinc powder (BDH), mercury(II) chloride (Merck), ammonium hexafluorophosphate (Aldrich) and *tert*-butyl isocyanide (Aldrich) were used as received.

^1H -, $^{13}\text{C}\{^1\text{H}\}$ - and $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra were recorded on Jeol 270, Bruker DPX-300, and Bruker DRX-500 FT-NMR spectrometers. Chemical shifts were referenced to Me_4Si (for ^1H , ^{13}C) and 85% H_3PO_4 (for ^{31}P). In the $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra, multiplets for 16-TMC were observed because of the flexible nature of the propylene groups, and the chemical shifts listed correspond to the most intense signals. Fast atom bombardment (FAB) mass spectra were obtained on a Finnigan MAT 95 mass spectrometer with a 3-nitrobenzyl alcohol matrix. Infrared spectra were recorded from Nujol mulls or KBr pellets on a Bio-Rad FTIR spectrometer. UV–vis spectra were recorded on Perkin–Elmer Lambda 19 and Milton Roy (Spectronic 3000 Array) diode array spectrophotometers. Elemental analyses were performed by the Butterworth Laboratories Ltd., Teddington, UK.

Cyclic voltammetry was performed with a Bioanalyt-

ical Systems (BAS) model 100 B/W electrochemical analyser. A conventional two-compartment electrochemical cell was used. The glassy carbon electrode was polished with 0.05 μm alumina on a microcloth, sonicated for 5 min in deionized water and rinsed with acetonitrile before use. An Ag/AgNO_3 (0.1 M in CH_3CN) electrode was used as reference electrode. All solutions were degassed with argon before experiments. $E_{1/2}$ values were taken from the average of the cathodic and anodic peak potentials for the oxidative and reductive waves. The $E_{1/2}$ value of the ferrocenium/ferrocene couple ($\text{Cp}_2\text{Fe}^{+/0}$) measured in the same solution was used as an internal reference.

4.2. $[\text{Ru}(\text{Me}_3\text{tacn})(\text{PMe}_3)(t\text{-BuNC})(\text{O}_2\text{CCF}_3)]\text{PF}_6$ (**1**)· PF_6

A mixture of $[\text{Ru}(\text{Me}_3\text{tacn})(\text{PMe}_3)_2(\text{O}_2\text{CCF}_3)]\text{PF}_6$ (0.10 g, 0.14 mmol) and *t*-BuNC (1.0 cm^3) in 1,2-dichloroethane (10 cm^3) was refluxed under a nitrogen atmosphere for 12 h. After cooling, the solvent was removed in vacuo. The solid residue was washed with diethyl ether (10 $\text{cm}^3 \times 5$) and dried to give a pale yellow solid. Diffusion of diethyl ether into an acetone solution gave a yellow crystalline solid. Yield = 0.06 g (56%). Anal. Calc. for $\text{C}_{19}\text{H}_{39}\text{N}_4\text{F}_9\text{O}_2\text{P}_2\text{Ru}$: C, 33.10; H,

Table 3
Crystal data for **4**· $(\text{ClO}_4)_2\cdot\text{CH}_3\text{CN}$ and **6**· $8.5\text{C}_6\text{H}_6$

	4 · $(\text{ClO}_4)_2\cdot\text{CH}_3\text{CN}$	6	7 · $3\text{C}_6\text{H}_6$	8 · $5\text{C}_6\text{H}_6$
Formula	$\text{C}_{26}\text{H}_{54}\text{N}_6\text{O}_8\text{Cl}_2\text{Ru}\cdot\text{CH}_3\text{CN}$	$\text{C}_{54}\text{H}_{46}\text{N}_6\text{Ru}$	$\text{C}_{76}\text{H}_{68}\text{N}_8\text{O}_4\text{Ru}\cdot 3\text{C}_6\text{H}_6$	$\text{C}_{72}\text{H}_{56}\text{F}_4\text{N}_8\text{Ru}\cdot 5\text{C}_6\text{H}_6$
M_r	791.78	880.07	1492.83	1600.92
Crystal size, mm	$0.35 \times 0.20 \times 0.10$	$0.30 \times 0.20 \times 0.10$	$0.30 \times 0.20 \times 0.10$	$0.20 \times 0.15 \times 0.15$
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$\text{C}2/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a (Å)	18.832(3)	11.651(2)	12.352(4)	11.525(4)
b (Å)	10.772(3)	14.039(2)	12.773(3)	14.034(4)
c (Å)	18.605(3)	15.292(2)	14.780(3)	14.872(4)
α (°)		78.71(2)	103.13(2)	68.17(2)
β (°)	96.43(2)	67.82(2)	93.67(2)	72.14(2)
γ (°)		90.31(2)	115.96(2)	84.33(2)
V (Å ³)	3750(1)	2262.7(8)	2006(1)	2125(1)
Z	4	2	1	1
D_{calc} (g cm ⁻³)	1.402	1.292	1.236	1.251
$\mu(\text{Mo-K}\alpha)$ (cm ⁻¹)	6.13	3.90	2.52	2.46
$F(000)$	1664	912	782	834
$2\theta_{\text{max}}$ (°)	50.0	50.9	50.0	50.0
No. of data measured	3615	24277	6115	7838
No. of unique data	3497	7544	5767	7503
No. of observed data ($I > 3\sigma(I)$)	2024	5108	4408	4469
No. of variables	211	553	439	445
R^a , wR^b	0.050, 0.068	0.045, 0.061	0.048, 0.065	0.051, 0.067
GoF	2.35	1.37	1.88	1.74
Residual ρ (e Å ⁻³)	+0.71, -0.38	+0.62, -0.71	+0.83, -0.45	+0.61, -0.39

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$.

^b $wR = [\sum w||F_o| - |F_c||^2 / \sum w|F_o|^2]^{1/2}$.

Table 4
Selected bond distances (Å) and angles (°) for **4**-(ClO₄)₂ and **6–8**

Complex 4 -(ClO ₄) ₂					
Ru–N(1)	2.246(6)	Ru–N(2)	2.255(5)	Ru–C(1)	1.989(7)
N(3)–C(1)	1.143(8)	N(3)–C(2)	1.469(8)	N(1)–C(6)	1.470(1)
N(1)–Ru–N(1*)	180.0	Ru–C(1)–N(3)	178.8(7)		
N(1)–Ru–N(2)	91.1(2)	N(1)–Ru–N(2*)	88.9(2)		
N(1)–Ru–C(1)	88.9(2)	N(1)–Ru–C(1*)	91.1(2)		
C(1)–Ru–C(1*)	180.0	N(2)–Ru–C(1)	88.6(2)		
N(2)–Ru–C(1*)	91.4(2)	C(1)–N(3)–C(2)	179.4(7)		
Complex 6					
	Molecule 1		Molecule 2		
Ru–N(1)	2.057(3)		2.065(4)		
Ru–N(2)	2.073(3)		2.063(3)		
Ru–C(1)	2.015(5)		2.011(5)		
N(3)–C(1)	1.153(6)		1.151(6)		
N(1)–Ru–N(1*)	180.0		180.0		
N(1)–Ru–N(2)	91.0(1)		90.2(1)		
N(1)–Ru–C(1)	90.1(2)		93.2(2)		
C(1)–Ru–C(1*)	180.0		180.0		
C(1)–N(3)–C(2)	167.8(5)		167.6(5)		
Ru–C(1)–N(3)	170.6(4)		169.3(4)		
Complex 7					
Ru–N(1)	2.057(3)	Ru–N(2)	2.049(3)	Ru–C(11)	1.980(4)
N(3)–C(11)	1.154(5)	N(4)–C(18)	1.120(7)		
N(1)–Ru–N(1*)	180.0	C(11)–Ru–C(11*)	180.0		
N(1)–Ru–N(2)	90.2(1)	C(11)–N(3)–C(12)	178.3(4)		
N(1)–Ru–C(11)	92.8(1)	Ru–C(11)–N(3)	173.7(4)		
Complex 8					
Ru–N(1)	2.058(4)	Ru–N(2)	2.060(4)	Ru–C(11)	1.988(5)
N(3)–C(11)	1.156(6)	N(4)–C(18)	1.115(7)		
N(1)–Ru–N(1*)	180.0	N(1)–Ru–N(2)	90.1(1)		
N(1)–Ru–C(11)	86.4(2)	C(11)–Ru–C(11*)	180.0		
C(11)–N(3)–C(12)	173.9(5)	Ru–C(11)–N(3)	174.2(4)		

5.70; N, 8.12. Found: C, 33.37; H, 5.79; N, 7.92. ¹H-NMR (300 MHz, (CD₃)₂CO): 1.52 (d, *J*_{PH} = 8.6 Hz, 9H, P(CH₃)₃), 1.63 (s, 9H, C(CH₃)₃), 2.90–3.39 (m, 21H, Me₃tacn). ¹³C{¹H}-NMR (500 MHz, (CD₃)₂CO): 17.4 (d, *J*_{PC} = 28.7 Hz, P(CH₃)₃), 31.0 (C(CH₃)₃), 52.1, 53.1, 58.3 (Me₃tacn), 58.5 (C(CH₃)₃), 58.8, 59.2, 60.1, 61.0, 63.0, 63.2 (Me₃tacn). ³¹P{¹H}-NMR (202 MHz, (CD₃)₂CO): 2.8. Infrared (Nujol, cm^{−1}): ν(−N≡C) 2112s; ν(C=O) 1689s. FAB MS (*m/z*): 545, [M⁺]. UV–vis λ_{max}, nm (log ε_{max}) in CH₃CN: 236 (3.71), 258 (3.24), 540 (1.41).

4.3. [Ru(Me₃tacn)(*t*-BuNC)₂(O₂CCF₃)]PF₆ (**2**)·PF₆

A mixture of [Ru(Me₃tacn)(H₂O)₂(O₂CCF₃)](OTf)₂ (0.10 g, 0.15 mmol), *t*-BuNC (1.0 cm³) and zinc amalgam (1 g) in 1,2-dichloroethane (10 cm³) was stirred at ambient temperature under a nitrogen atmosphere for 12 h. The solution was filtered and concentrated to ca. 5 cm³. A saturated solution of NH₄PF₆ in 1,2-dichloroethane was added to give a pale yellow precipitate, which was filtered and washed with diethyl ether

(10 cm³ × 3). Recrystallization by diffusion of diethyl ether into an acetone solution gave a yellow crystalline solid. Yield = 0.05 g (72%). Anal. Calc. for C₂₁H₃₉N₅F₉O₂PRu: C, 36.21; H, 5.64; N, 10.05. Found: C, 36.18; H, 5.40; N, 10.01. ¹H-NMR (300 MHz, CDCl₃): 1.54 (s, 18H, C(CH₃)₃), 2.86–3.23 (m, 21H, Me₃tacn). ¹³C{¹H}-NMR (500 MHz, CDCl₃): 31.0 (C(CH₃)₃), 51.3, 57.6 (Me₃tacn), 58.1 (C(CH₃)₃), 58.2, 59.0, 61.3 (Me₃tacn). Infrared (Nujol, cm^{−1}): ν(−N≡C) 2110s, 2154s; ν(C=O) 1693s. FAB MS (*m/z*): 552, [M⁺]. UV–vis λ_{max}, nm (log ε_{max}) in CH₃CN: 237 (3.90), 316 (2.54).

4.4. [Ru(Me₃tacn)(PMe₃)(L')(O₂CCF₃)]PF₆ (**3**)·PF₆

A mixture of [Ru(Me₃tacn)(PMe₃)₂(O₂CCF₃)]PF₆ (0.10 g, 0.14 mmol) and L' (0.05 g, 0.24 mmol) in 1,2-dichloroethane (10 cm³) was refluxed under a nitrogen atmosphere for 12 h. After cooling, the solvent was removed in vacuo. The solid residue was washed with diethyl ether (10 cm³ × 5) and dried to give a pale yellow solid. Recrystallization by diffusion of diethyl

ether into an acetone solution gave a yellow crystalline solid. Yield = 0.07 g (85%). Anal. Calc. for $C_{28}H_{46}N_5F_9O_2P_2Ru$: C, 41.08; H, 5.61; N, 8.55. Found: C, 41.27; H, 5.62; N, 8.35. 1H -NMR (500 MHz, $CDCl_3$): 1.24 (d, $J_{HH} = 6.8$ Hz, 12H, $C(CH_3)_2$), 1.50 (d, $J_{HH} = 8.5$ Hz, 9H, $P(CH_3)_3$), 2.91–3.40 (m, 21H, Me_3tacn), 3.55 (septet, $J_{HH} = 6.8$ Hz, 2H, $CH(CH_3)_2$), 7.48 (s, 2H, H_{aryl}). $^{13}C\{^1H\}$ -NMR (500 MHz, $CDCl_3$): 17.8 (d, $J_{PC} = 29.2$ Hz, $P(CH_3)_3$), 22.3 ($C(CH_3)_2$), 23.8 ($C(CH_3)_2$), 52.9, 58.4, 59.3, 59.4, 59.9, 60.6, 60.7, 62.2, 64.0 (Me_3tacn), 111.8 ($-C\equiv N$), 118.2 (C_{aryl}), 118.3, 118.4 (O_2CCF_3), 127.5, 128.1, 147.0 (C_{aryl}), 173.1 ($-N\equiv C$). $^{31}P\{^1H\}$ -NMR (202 MHz, CD_2Cl_2): 0.37. Infrared (Nujol, cm^{-1}): $\nu(-N\equiv C)$ 2048s, $\nu(-C\equiv N)$ 2233w; $\nu(C=O)$ 1698s. FAB MS (m/z): 674, $[M^+]$; 598, $[M-PM_3]^+$. UV-vis λ_{max} , nm (log ϵ_{max}) in CH_3CN : 239 (4.43), 317 (4.22), 539 (0.81).

4.5. *trans*-[Ru(16-TMC)(*t*-BuNC) $_2$](ClO $_4$) $_2$ (4)·(ClO $_4$) $_2$

A mixture of [Ru(16-TMC)Cl $_2$]Cl (0.1 g, 0.20 mmol), *t*-BuNC (1.0 cm 3) and zinc amalgam (1 g) in methanol (10 cm 3) was refluxed under a nitrogen atmosphere for 12 h. After cooling, the solution was filtered and concentrated to ca. 5 cm 3 . A saturated solution of NaClO $_4$ in methanol was added to afford a pale yellow solid. Diffusion of diethyl ether into an acetone solution gave a yellow crystalline solid. Yield = 0.08 g (53%). Anal. Calc. for $C_{26}H_{54}N_6Cl_2O_8Ru$: C, 41.60; H, 7.25; N, 11.19. Found: C, 41.64; H, 7.21; N, 11.17. 1H -NMR (300 MHz, CD_3CN): 1.94 (m, 16H, NCH_2), 2.12 (s, 18H, $C(CH_3)_3$), 2.53 (s, 12H, NCH_3), 3.00–3.20 (m, 8H, CH_2). $^{13}C\{^1H\}$ -NMR (500 MHz, CD_3CN): 20.3 (NCH_2CH_2), 29.3 ($C(CH_3)_3$), 51.1 (NCH_3), 61.47, 70.06 (NCH_2). Infrared (Nujol, cm^{-1}): $\nu(-N\equiv C)$ 2120s. FAB MS (m/z): 552, $[M^{2+}]$; 469, $[M-t-BuNC]^2+$. UV-vis λ_{max} , nm (log ϵ_{max}) in CH_3CN : 236 (4.55).

4.6. *cis*-[Ru(2,2,2-tet-Me $_6$)(*t*-BuNC) $_2$](PF $_6$) $_2$ (5)·(PF $_6$) $_2$

A mixture of *cis*-[Ru(2,2,2-tet-Me $_6$)Cl $_2$]PF $_6$ (0.1 g, 0.18 mmol), *t*-BuNC (1.0 cm 3) and zinc amalgam (1 g) in methanol (10 cm 3) was stirred at ambient temperature under a nitrogen atmosphere for 8 h. The pale yellow solution was filtered and evaporated to dryness. The residue was washed with *n*-hexane (10 cm 3 × 2) and dried in vacuo. Recrystallization by diffusion of diethyl ether into an acetone solution gave a yellow crystalline solid. Yield = 0.08 g (56%). Anal. Calc. for $C_{22}H_{48}N_6F_{12}P_2Ru$: C, 33.55; H, 6.10; N, 10.67. Found: C, 33.49; H, 6.14; N, 10.63. 1H -NMR (300 MHz, CD_2Cl_2): 0.86 (s, 6H, NCH_3), 0.87 (s, 6H, NCH_3), 1.27 (s, 6H, NCH_3), 1.62 (s, 18H, $C(CH_3)_3$), 2.64–3.15 (m, 12H, CH_2). $^{13}C\{^1H\}$ -NMR (500 MHz, CD_2Cl_2):

13.6, 22.5 (NCH_3), 30.5 ($C(CH_3)_3$), 31.4 (NCH_3), 52.2 ($C(CH_3)_3$), 59.1, 61.7, 63.4 (NCH_2), 152.2 ($-N\equiv C$). Infrared (Nujol, cm^{-1}): $\nu(-N\equiv C)$ 2115, 2158. FAB MS (m/z): 498, $[M^{2+}]$; 413, $[M-t-BuNC]^2+$. UV-vis λ_{max} , nm (log ϵ_{max}) in CH_3CN : 236 (3.77), 280 (3.04), 338 (2.86).

4.7. [Ru(TPP)(*t*-BuNC) $_2$] (6)

This complex was prepared by a modified procedure [24]. To a suspension of [Ru(TPP)(CO)(MeOH)] (0.21 g, 0.27 mmol) in benzene (10 cm 3) was added *t*-BuNC (1.0 cm 3). The resulting dark-red solution was stirred at ambient temperature for 2 h. All volatiles were removed in vacuo and the solid residue was washed with *n*-hexane (10 cm 3 × 5) and dried in vacuo. Purple crystals suitable for X-ray crystallography were obtained by diffusion of *n*-pentane into a benzene solution. Yield = 0.23 (97%). Anal. Calc. for $C_{54}H_{46}N_6Ru$: C, 73.70; H, 5.23; N, 9.55. Found: C, 73.66; H, 5.26; N, 9.51. 1H -NMR (300 MHz, $CDCl_3$): −0.44 (s, 18H, $C(CH_3)_3$), 7.66 (dd, $J_{HH} = 1.7, 3.2$ Hz, 12H, H_m and H_p), 8.13 (d, $J_{HH} = 3.7$ Hz, 8H, H_o), 8.40 (s, 8H, H_β). $^{13}C\{^1H\}$ -NMR (500 MHz, CD_2Cl_2): 29.0 ($C(CH_3)_3$), 53.5 ($C(CH_3)_3$), 121.1, 126.2, 126.7, 131.2, 134.1, 143.4, 143.5 (C_{aryl}). Infrared (KBr, cm^{-1}): $\nu(-N\equiv C)$ 2119. FAB MS (m/z): 880, $[M^+]$; 797, $[M-t-BuNC]^+$. UV-vis λ_{max} , nm (log ϵ_{max}) in CH_2Cl_2 : 263 (4.74), 399 (4.82), 417 (5.62), 527 (4.18).

4.8. [Ru(4-MeO-TPP)(L') $_2$] (7)

[Ru(4-MeO-TPP)(CO)(MeOH)] (0.09 g, 0.10 mmol) was suspended in benzene (10 cm 3) under an argon atmosphere. L' (0.05 g, 0.25 mmol) was added and the resulting solution was stirred at ambient temperature for 18 h. All volatiles were removed in vacuo and the solid residue was washed with *n*-hexane (20 cm 3 × 3). Red crystals were obtained by diffusion of *n*-pentane into a benzene solution. Yield = 0.10 g (81%). Anal. Calc. for $C_{76}H_{68}N_8O_4Ru$: C, 72.55; H, 5.41; N, 8.90. Found: C, 72.52; H, 5.36; N, 8.86. 1H -NMR (300 MHz, CD_2Cl_2): −0.12 (d, $J_{HH} = 6.80$ Hz, 24H, $C(CH_3)_2$), 0.15 (m, 4H, $CH(CH_3)_2$), 4.05 (s, 12H, OCH_3), 6.54 (s, 4H, H_{aryl}), 7.22 (d, $J_{HH} = 8.6$ Hz, 8H, H_m), 7.97 (d, $J_{HH} = 8.6$ Hz, 8H, H_o), 8.54 (s, 8H, H_β). $^{13}C\{^1H\}$ -NMR (500 MHz, CD_2Cl_2): 20.5 ($CH(CH_3)_2$), 29.0 ($CH(CH_3)_2$), 55.9 (OCH_3), 111.0 ($-C\equiv N$), 112.3, 118.4, 121.1, 126.8, 128.7, 131.8, 135.3, 136.0, 144.5, 145.0, 159.5 (C_{aryl}). Infrared (KBr, cm^{-1}): $\nu(-N\equiv C)$ 2077, $\nu(-C\equiv N)$ 2231. FAB MS (m/z): 1258, $[M^+]$; 1046, $[M-L]^+$; 834, $[M-2L]^+$. UV-vis λ_{max} , nm (log ϵ_{max}) in CH_3CN : 256 (4.86), 336 (4.42), 416 (5.60), 537 (4.15).

4.9. [Ru(4-F-TPP)(L')₂] (8)

The procedure was the same as that for **7** except [Ru(4-F-TPP)(CO)(MeOH)] was used. Yield = 0.12 g (87%). Anal. Calc. for C₇₂H₅₆F₄N₈Ru: C, 71.35; H, 4.62; N, 9.25. Found: C, 71.78; H, 4.77; N, 9.09. ¹H-NMR (300 MHz, CD₂Cl₂): −0.12 (d, *J*_{HH} = 6.80 Hz, 24H, C(CH₃)₂), 0.13 (septet, *J*_{HH} = 6.80 Hz, 4H, CH(CH₃)₂), 6.55 (s, 4H, H_{aryl}), 7.40 (tm, 8H, H_m), 8.01 (qm, 8H, H_o), 8.52 (s, 8H, H_β). ¹³C{¹H}-NMR (500 MHz, CD₂Cl₂): 20.5 (CH(CH₃)₂), 29.0 (CH(CH₃)₂), 111.3 (−C≡N), 113.6, 118.2, 120.5, 127.0, 128.7, 131.9, 135.6, 139.5, 144.4, 144.9, 162.0 (C_{aryl}), 164.0 (−N≡C). Infrared (KBr, cm^{−1}): ν(−N≡C) 2079, ν(−C≡N), 2234. FAB MS (*m/z*): 1211, [M]⁺; 998, [M−L]⁺; 786, [M−2L]⁺. UV–vis λ_{max}, nm (log ε_{max}) in CH₂Cl₂: 261 (4.86), 326 (4.48), 417 (5.51), 538 (4.25).

4.10. Structural determination of 4·(ClO₄)₂·CH₃CN and 6·8·5C₆H₆

Crystals of 4·(ClO₄)₂·CH₃CN and 6·8·5C₆H₆ were grown by diffusion of diethyl ether or *n*-pentane into an acetone or a benzene solution, respectively. The crystals were mounted on a glass fibre and diffraction data were collected at 301 K on a MAR (6) or Rigaku AFC7R (4·(ClO₄)₂·CH₃CN, 7·3C₆H₆ and 8·5C₆H₆) diffractometer using graphite monochromatized Mo−K_α radiation (λ = 0.71073 Å). All the structures were solved by direct methods (SIR92) [25], expanded by Fourier techniques and refined by full-matrix least-squares using the texsan [26] program on a Silicon Graphics Indy computer. Crystal data and details of collection and refinement are shown in Table 3.

For 4·(ClO₄)₂·CH₃CN, all non-H atoms were refined anisotropically and H atoms at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms were not refined. The H atoms of the CH₃CN solvent molecule in 4·(ClO₄)₂·CH₃CN were not included. For **6**, one crystallographic asymmetric unit consists of two halves of a molecule with Ru(1) and Ru(2) at special positions at 0, 0, 0 and 1/2, 1/2, 1/2, respectively. All 62 non-H atoms were refined anisotropically and 46 H atoms at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms were not refined. Starred atoms have coordinates at −*x*, −*y*, −*z*. For both 7·3C₆H₆ and 8·5C₆H₆, one crystallographic asymmetric unit consists of half of one formula unit. One of the benzene molecules is generated by a centre of symmetry. In the least-squares refinement, all non-H atoms of the porphyrinato ligand and C atoms of the benzene molecules were refined anisotropically, and H atoms at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms were not refined.

5. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 133434, 133435, 133436 and 133437 for compounds 4·(ClO₄)₂·CH₃CN, 6·7·3C₆H₆ and 8·5C₆H₆, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

- [1] (a) H.A. Mayer, W.C. Kaska, Chem. Rev. 94 (1994) 1239. (b) K.M. Pietrusiewicz, M. Zabolcka, Chem. Rev. 94 (1994) 1375.
- [2] P.M. Treichel, Adv. Organomet. Chem. 11 (1973) 21.
- [3] (a) W.P. Fehlhammer, M. Fritz, Chem. Rev. 93 (1993) 1243. (b) F.E. Hahn, Angew. Chem. Int. Ed. Engl. 32 (1993) 650.
- [4] E. Singleton, H.E. Oosthuizen, Adv. Organomet. Chem. 22 (1983) 209.
- [5] Y. Yamamoto, Coord. Chem. Rev. 32 (1980) 193.
- [6] (a) J.-M. Lehn, Supramolecular Chemistry, VCH, Weinheim, Germany, 1995. (b) T. Iwamoto, in: J.L. Atwood, J.E.D. Davies, D.D. MacNicol (Eds.), Inclusion Compounds, vol. 5, Oxford University Press, Oxford, 1991, p. 177. (c) M.C. Etter, Acc. Chem. Res. 23 (1990) 120. (d) J.C. MacDonald, G.M. Whitesides, Chem. Rev. 94 (1994) 2383.
- [7] (a) A.M. Bradford, E. Kristof, M. Rashidi, D.-S. Yang, N.C. Payne, R.J. Puddephatt, Inorg. Chem. 33 (1994) 2355. (b) R. Tannenbaum, Chem. Mater. 6 (1994) 550. (c) M. Hanack, S. Deger, A. Lange, Coord. Chem. Rev. 83 (1988) 115. (d) I. Feinstein-Jeffe, F. Frolow, L. Wackerle, A. Goldman, A. Efraty, J. Chem. Soc. Dalton Trans. (1988) 469.
- [8] L.-F. Mao, A. Mayr, Inorg. Chem. 35 (1996) 3183.
- [9] (a) K.-M. Park, R. Kuroda, T. Iwamoto, Angew. Chem. Int. Ed. Engl. 32 (1993) 884. (b) A.K. Brimah, E. Siebel, R.D. Fisher, N.A. Davies, D.C. Apperley, R.K. Harris, J. Organomet. Chem. 475 (1994) 85. (c) B.F. Abrahams, M.J. Hardie, B.F. Hoskins, R. Robson, E.E. Sutherland, J. Chem. Soc. Chem. Commun. (1994) 1049. (d) N. Kimizuka, T. Handa, I. Ichinose, T. Kunitake, Angew. Chem. Int. Ed. Engl. 33 (1994) 2483. (e) M. Ohba, H. Okawa, T. Ito, A. Ohto, J. Chem. Soc. Chem. Commun. (1995) 1545. (f) M. Zhou, B.W. Pfennig, J. Steiger, V.D. Van Engen, A.B. Bocarsly, Inorg. Chem. 29 (1990) 2456.
- [10] S.M. Yang, M.C.W. Chan, K.K. Cheung, C.M. Che, S.-M. Peng, Organometallics 16 (1997) 2819.
- [11] M.Y. Choi, M.C.W. Chan, S.B. Zhang, K.K. Cheung, C.M. Che, K.Y. Wong, Organometallics 18 (1999) 2074.
- [12] F.M. Conroy-Lewis, S.J. Simpson, J. Organomet. Chem. 322 (1987) 221.
- [13] (a) E. Galardon, P.L. Maux, L. Toupet, G. Simonneaux, Organometallics 17 (1998) 565. (b) L.K. Woo, D.A. Smith, Organometallics 11 (1992) 2234.

- [14] S.M. Yang, W.C. Cheng, S.M. Peng, K.K. Cheung, C.M. Che, *J. Chem. Soc. Dalton Trans.* (1995) 2955.
- [15] (a) U. Keppeler, W. Kobel, H.-U. Siehl, M. Hanack, *Chem. Ber.* 118 (1985) 2095. (b) P. Fantucci, L. Naldini, F. Caariati, V. Valenti, C. Bussetto, *J. Organomet. Chem.* 64 (1974) 109. (c) A.C. Sarapu, R.F. Fenske, *Inorg. Chem.* 14 (1975) 247.
- [16] L. Dozsa, J.E. Sutton, H. Taube, *Inorg. Chem.* 21 (1982) 3997.
- [17] P.A. Stuzhin, S.I. Vagin, M. Hanack, *Inorg. Chem.* 37 (1998) 2655.
- [18] K.M. Kakish, *Prog. Inorg. Chem.* 34 (1986) 435.
- [19] M.O. Albers, D.C. Liles, E. Singleton, J.E. Stead, M.M. de, V. Steyn, *Organometallics* 5 (1986) 1262.
- [20] Y. Yamamoto, T. Tanase, T. Date, Y. Koide, K. Kobayashi, *J. Organomet. Chem.* 386 (1990) 365.
- [21] C.K. Li, C.M. Che, W.F. Tong, W.T. Tang, K.Y. Wong, T.F. Lai, *J. Chem. Soc. Dalton Trans.* (1992) 2109.
- [22] (a) M. Tsutsui, D. Ostfeld, L.M. Hoffman, *J. Am. Chem. Soc.* 93 (1971) 1820. (b) M. Tsutsui, D. Ostfeld, J.N. Francis, L.M. Hoffman, *J. Coord. Chem.* 1 (1971) 115. (c) D. Cullen, E. Meyer Jr., T.S. Srivastava, M. Tsutsui, *J. Chem. Soc. Chem. Commun.* (1972) 584.
- [23] D.P. Rillema, J.K. Nagle, L.F. Barringer Jr., T.J. Meyer, *J. Am. Chem. Soc.* 103 (1981) 56.
- [24] T. Boschi, G. Bontempelli, G.A. Mazzocchin, *Inorg. Chim. Acta* 37 (1979) 155.
- [25] A. Altomare, M. Cascarano, C. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polidori, M. Camalli, *SIR92, J. Appl. Crystallogr.* 27 (1994) 435.
- [26] *texsan: Crystal Structure Analysis Package, Molecular Structure Corp., The Woodlands, TX, 1985 and 1992.*