

Syntheses and molecular structures of mononuclear ruthenium carbonyl complexes containing 2,1-naphthoquinone-2-oximato ligands

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Abstract

The reaction between $[\text{Ru}_3(\text{CO})_{12}]$ and 2,1-naphthoquinone-2-oxime or known as 2-nitroso-1-naphthol afforded two isomeric mononuclear ruthenium carbonyl complexes *trans*- $[\text{Ru}(\eta^2\text{-OC}_{10}\text{H}_6\text{NO})_2(\text{CO})_2]$ **1** and *cis*- $[\text{Ru}(\eta^2\text{-OC}_{10}\text{H}_6\text{NO})_2(\text{CO})_2]$ **2**, in which the two bidentate 2-naphthoquinone-1-oximato ligands chelated on the ruthenium centre in different spacial orientation via the coordination of naphtholic oxygen and oxime nitrogen atoms. Both **1** and **2** adopt a *cis*-dicarbonyl configuration and the carbonyl groups can be replaced by the N-donor ligands in the presence of trimethylamine-*N*-oxide via the reaction intermediates, *trans*- $[\text{Ru}(\eta^2\text{-OC}_{10}\text{H}_6\text{NO})_2(\text{CO})(\text{NMe}_3)]$ **4** and *cis*- $[\text{Ru}(\eta^2\text{-OC}_{10}\text{H}_6\text{NO})_2(\text{CO})(\text{NMe}_3)]$ **3a** respectively. Complexes **1**, **3a** and **4** have been fully characterised by spectroscopic methods and their molecular structures were established by X-ray crystallographic analyses. © 1997 Elsevier Science S.A.

1. Introduction

The chemistry of nitro and nitroso arene towards transition metal carbonyl complexes have been extensively investigated [1,2]. In particular, the nitroso derivatives are studied with enthusiasm due to the ease of the formation of the nitrene species, which are believed to be an intermediate for the reduction of nitrobenzene to aniline [3]. Recently, we have shown that the reaction of the nitrene cluster $[\text{Ru}_3(\text{CO})_{10}(\mu_3\text{-NPh})]$ with excess nitrosobenzene gave $[\text{Ru}_3(\text{CO})_7(\mu_3\text{-NPh})_2(\mu\text{-}\eta^2\text{-ONPh})_2]$ [4], in which the incoming nitrosobenzene moieties cleaved the metal–metal bonds and coordinated to the metal framework via both the nitrogen and oxygen atoms of the nitroso groups in a $\mu\text{-}\eta^2$ fashion. As a continuation, nitroso-arenes with *ortho*-substituents such as nitrosonaphthols were further investigated since they can tautomerise to give the corresponding naphthoquinone–oxime [5]. In addition, the coordination chemistry of nitrosonaphthol is also limited to a few metal complexes such as $[\text{Cu}(2\text{-nqo})_2]$ [6] and $[\text{pyH}][\text{Ir}(1\text{-nqo})\text{pyCl}_3]$ [7] (1-nqo = 1-nitroso-2-

naphthol). Although Charalambous et al. have demonstrated that the reaction between $[\text{Fe}(\text{CO})_5]$ and nitrosonaphthols [8] results in the reductive deoxygenation of the nitroso group, there is no report concerning the reactivity of nitrosonaphthol towards transition metal carbonyl clusters. Herein, we present two mononuclear ruthenium carbonyl complexes containing 2,1-naphthoquinone-2-oximato ligand from the reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with 2-nitroso-1-naphthol.

2. Results and discussion

The reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with 2-nitroso-1-naphthol (2-nqoH) in tetrahydrofuran (THF) afforded two intense red bands which were characterised as complexes **1** and **2** with approximately equal yield upon TLC separation. These two compounds are stable in solution and in the solid state. The mass spectra of both **1** and **2** showed parent ion peaks with isotopic distribution consistent with the formula $[\text{Ru}(\text{C}_{10}\text{H}_6\text{NO}_2)_2(\text{CO})_2]$. The IR spectra of **1** and **2** are essentially identical in the region of the carbonyl absorptions and exhibit two strong bands which are consistent with a *cis*-dicarbonyl arrangement [9]. In order

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to elucidate their molecular structures so as to find out the coordination geometry of the ligands, X-ray analysis was carried out on a dark red crystal of complex **1**, grown from a THF/*n*-hexane mixture at room temperature.

The molecular structure and selected bond parameters of complex **1** is shown in Fig. 1 and Table 1, respectively. The structure is consistent with its ¹H NMR spectrum as the two 2,1-naphthoquinone-2-oximato (2-nqo) ligands are equivalent and related by a non-crystallographic C₂ axis. The geometry of the central Ru atom is approximately octahedral with the two carbonyl ligands adopting a *cis* configuration [C(1)–Ru–C(2) 90.4(7)°]. The remaining co-ordination sites are occupied by two 2-nqo ligands via the naphtholic oxygen [mean Ru–O 2.062(8) Å] and oxime nitrogen atoms [mean Ru–N 2.065(1) Å] to form a five-membered ring with mean N–Ru–O angle of 79.8(4)°. This type of coordination mode is quite common in metal complexes containing bidentate naphthoquinone–oxime moieties such as [Cu(2-nqo)₂]·H₂O [6], [Cu(1-nqo)₂]·2(CH₃)₂CO [10], [pyH][Ir(1-nqo)pyCl₃] [7] and [Cu(1-nqo)(PPh₃)₂] [11]. The average N–O bond distance [1.255(1) Å] of the nitrosyl groups is within the range of most metal complexes with N-bounded nitrosyl group. The two *trans* nitrosyl groups are slightly deviated from linearity [N(1)–Ru–N(2) 167.8(5)°] while the two carbonyl groups are mutually *trans* [average O–Ru–CO 174.5(6)°] to the naphtholic oxygen atoms. However, we have no evidence for the formation of another expected isomer of compound **1**, in which the two naphtholic groups are *trans* to each other. The two

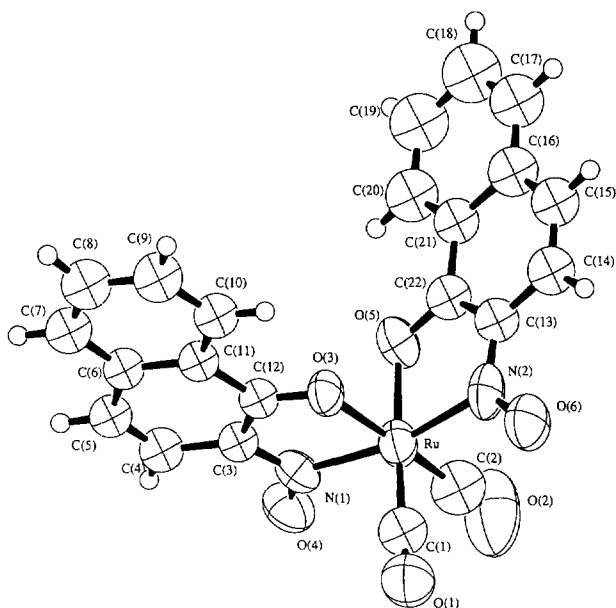


Fig. 1. Molecular structure of *trans*-[Ru(η^2 -OC₁₀H₆NO)₂(CO)₂] **1**, showing the atom-numbering scheme.

Table 1
Selected bond lengths (Å) and angles (°) of complex **1**

Ru–O(3)	2.050(8)	Ru–O(5)	2.074(9)
Ru–N(1)	2.06(1)	Ru–N(2)	2.07(1)
Ru–C(1)	1.90(2)	Ru–C(2)	1.87(2)
C(1)–O(1)	1.13(2)	C(2)–O(2)	1.12(2)
O(3)–C(12)	1.29(1)	O(5)–C(22)	1.30(1)
N(1)–O(4)	1.25(1)	N(2)–O(6)	1.26(1)
N(1)–C(3)	1.36(2)	N(2)–C(13)	1.35(2)
C(3)–C(12)	1.42(2)	C(13)–C(22)	1.43(2)
O(3)–Ru–O(5)	85.5(3)	N(1)–Ru–N(2)	167.8(5)
N(1)–Ru–O(3)	79.6(4)	N(2)–Ru–O(5)	80.0(5)
Ru–N(1)–O(4)	125.4(9)	Ru–N(2)–O(6)	125(1)
O(3)–Ru–C(2)	175.5(6)	O(5)–Ru–C(1)	173.6(6)
C(1)–Ru–C(2)	90.4(7)		

2-nqo ligands are essentially planar with maximum deviation of 0.27(1) Å and 0.13(1) Å from their ideal plane, while the dihedral angle between these two ligand planes is 75.7°.

Unfortunately, attempts to isolate the single crystals of **2** failed in most of the common solvent mixture systems including either of the following combination, such as diethyl ether, *n*-hexane, benzene, dichloromethane, chloroform and THF. From the ¹H NMR spectrum of **2**, the presence of two sets of proton signals for the two 2-nqo ligands suggested that the two 2-nqo ligands are situated in different chemical environments. Together with a *cis*-dicarbonyl arrangement, the two 2-nqo ligands should adopt a configuration with both naphtholic oxygen atoms and oxime nitrogen atoms *cis* to each other similar to the ligands arrangement in [Ru(1-nqo)₂(py)₂] [12]. In order to confirm the proposed structure of **2**, a substitution reaction of the carbonyl ligand was carried out by adding a N-donor ligand (L) into a chloroform solution of **2**. However, no reaction occurred even though the reaction mixture was heated under refluxing temperature for 2 h. Then, one equivalent of trimethylamine-*N*-oxide was added and an instantaneous colour change to dark purple was observed. Chromatographic separation afforded the mono-substituted product *cis*-[Ru(η^2 -OC₁₀H₆NO)₂(CO)(L)] **3b** (where L = NC₅H₄CH=NC₆H₄OC₁₆H₃₃) as the major product in addition to a minor product which was characterised as *cis*-[Ru(η^2 -OC₁₀H₆NO)₂(CO)(NMe₃)] **3a**. Nevertheless, crystallisation of **3b** has met with little success while crystals of **3a** can be obtained from slow evaporation of a solution mixture of *n*-hexane and CH₂Cl₂ at –20°C.

The molecular structure of complex **3a** is depicted in Fig. 2 while the respective bond lengths and angles are shown in Table 2. The molecular geometry of **3a** also adopts an approximate octahedral coordination around the ruthenium metal centre similar to that of **1**. Both

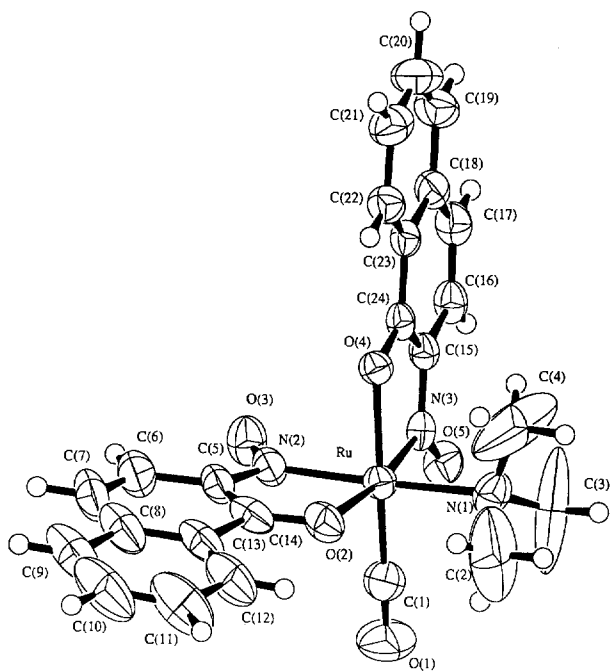


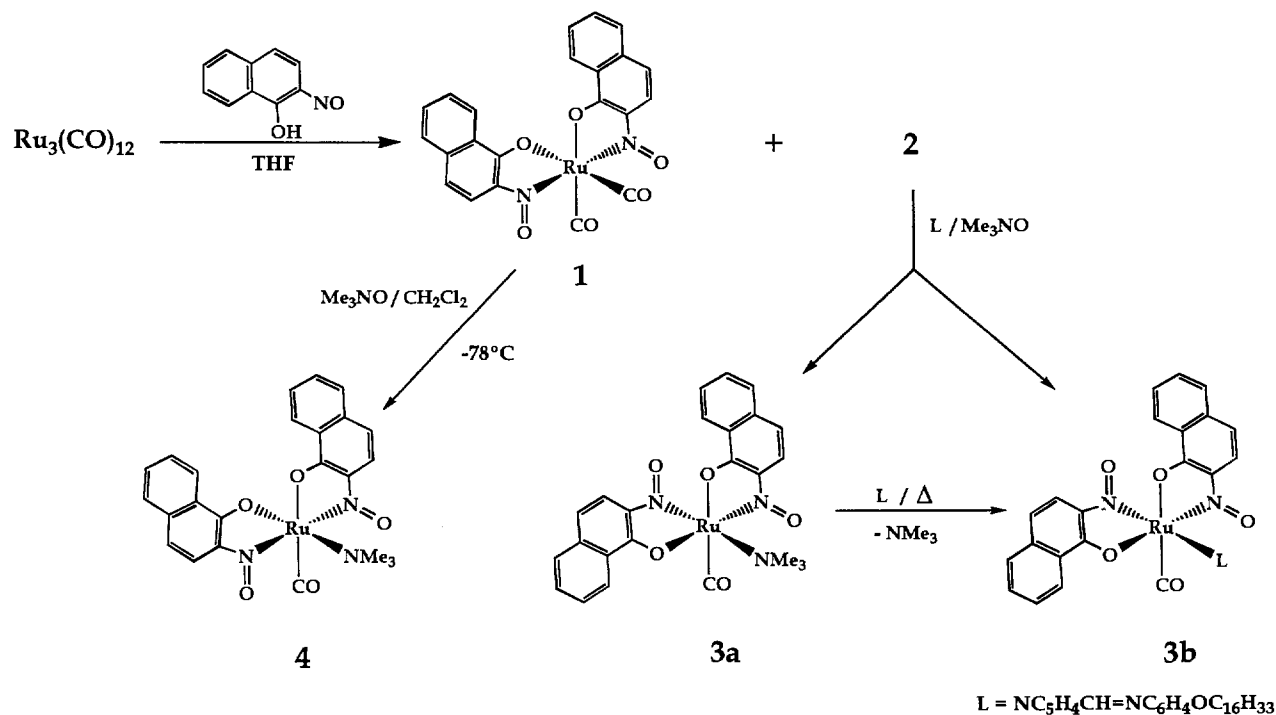
Fig. 2. Molecular structure of *cis*-[Ru(η^2 -OC₁₀H₆NO)₂(CO)(NMe₃)] **3a**, showing the atom-numbering scheme.

naphtholic oxygen atoms as well as the oxime nitrogen atoms of the two 2-nqo ligands are in a *cis* configuration as expected. The trimethylamine is located *trans* to the nitrosyl group with a bond distance [Ru–NMe₃] of 2.197(4) Å. The nitrosyl group *trans* to the naphtholic

Table 2
Selected bond lengths (Å) and angles (°) of complex **3a**

Ru–O(2)	2.095(3)	Ru–O(4)	2.087(3)
Ru–N(1)	2.197(4)	Ru–N(2)	2.024(4)
Ru–N(3)	1.965(3)	Ru–C(1)	1.858(5)
C(1)–O(1)	1.139(6)	N(2)–O(3)	1.248(4)
N(3)–O(5)	1.263(4)	O(2)–C(14)	1.272(6)
O(4)–C(24)	1.302(4)	C(5)–C(14)	1.408(7)
C(15)–C(24)	1.395(6)		
O(2)–Ru–O(4)	92.5(1)	O(4)–Ru–C(1)	174.1(2)
O(2)–Ru–N(3)	171.3(1)	N(1)–Ru–N(2)	170.1(1)
N(2)–Ru–N(3)	94.3(1)	N(2)–Ru–O(2)	79.8(1)
N(3)–Ru–O(4)	80.7(1)	Ru–N(2)–O(3)	126.0(3)
Ru–N(3)–O(5)	126.3(3)	C(1)–Ru–N(1)	92.8(2)

oxygen has a rather short bond distance [Ru–N(3) 1.965(3) Å] compared to the mean Ru–N distance of 2.065(1) Å in **1**. The reason for the shortening of Ru–N bond in **3a** is most probably due to the *trans*-influence of the electron-rich naphtholic moiety. The 2-nqo ligands are almost planar with maximum deviation of 0.19(1) and 0.15(1) Å while the dihedral angle between the planes of these two 2-nqo ligands is 82.0°. The similarity of the proton resonances due to the two 2-nqo ligands of **3a** and **3b** in the ¹H NMR spectra suggests that both N-donor ligand (Me₃N in **3a** and NC₅H₄CH=NC₆H₄OC₁₆H₃₃ in **3b**) are *trans* to the oxime. However, no mono-substituted products with the substituent *trans* to the naphtholic group were observed since the bond of carbonyl group *trans* to the naph-



Scheme 1.

tholic moiety is stronger than the carbonyl that is *trans* to the oxime in **2**.

The isolation of complex **3a** gave us some insight about its role during the substitution reaction. Further studies showed that **3a** is a reaction intermediate where the schiff base ligand displaces the labile trimethylamine at elevated temperature to give **3b** (Scheme 1). On the other hand, the carbonyl groups in complex **1** were also shown to be easily oxidised by trimethylamine-*N*-oxide, giving an intermediate complex **4** analogous to **3a**. Complex **4** is also stable enough for isolation in moderate yield by TLC. A perspective view of complex **4** is depicted in Fig. 3 while the selected bond parameters are listed in Table 3. The molecular geometry adopted by the two 2-nqo ligands around the ruthenium centre is identical to that in **1** except one of the CO is replaced by a trimethylamine moiety while both of them are also *cis* [C(1)–Ru–N(3) 92.4(3)°] to each other. The trimethylamine is located *trans* [N(3)–Ru–O(5) 172.3(2)°] to the naphtholic oxygen with a Ru–N(3) distance of 2.169(6) Å in **4** though the trimethylamine moiety in **3a** is preferentially coordinated *trans* to the oximic group. The mean Ru–O bonds is 2.085(5) Å while the Ru–N(1) bond [2.014(6) Å] is shorter than Ru–N(2) [2.060(6) Å]. The oxime nitrogen atoms are *trans* [N(1)–Ru–N(2) 168.6(2)°] to each other with mean N–O bond distance of 1.252(7) Å. Similar to **1** and **3a**, the two coordinated 2-nqo ligands in **4** are essentially planar with maximum deviation of 0.04 and 0.11 Å. The formation of **4** not only shows us that it is an intermediate in the substitution reaction involving trimethylamine-*N*-oxide, but it also proved that there was no rearrangement of the two

Table 3
Selected bond lengths (Å) and angles (°) of complex **4**

Ru–O(3)	2.090(5)	Ru–O(5)	2.080(5)
Ru–N(1)	2.014(6)	Ru–N(2)	2.060(6)
Ru–N(3)	2.169(6)	Ru–C(1)	1.838(9)
N(1)–O(2)	1.248(7)	N(2)–O(4)	1.255(7)
N(1)–C(2)	1.370(9)	N(2)–C(12)	1.362(9)
C(2)–C(11)	1.421(10)	C(12)–C(21)	1.419(10)
O(3)–C(11)	1.292(8)	O(5)–C(21)	1.289(8)
C(1)–O(1)	1.145(10)		
O(3)–Ru–O(5)	85.5(2)	N(3)–Ru–C(1)	92.4(3)
N(1)–Ru–O(3)	79.5(2)	N(2)–Ru–O(5)	79.3(2)
O(3)–Ru–C(1)	172.4(3)	N(1)–Ru–N(2)	168.6(2)
O(5)–Ru–N(3)	172.3(2)	Ru–N(1)–O(2)	126.1(5)
Ru–N(2)–O(4)	128.2(5)		

coordinated 2-nqo ligands that occurred during substitution. As a result, complex **2** should adopt the same molecular configuration as that of **3a**.

3. Conclusion

The reaction of [Ru₃(CO)₁₂] with 2-nitroso-1-naphthol gives only two thermodynamically stable products **1** and **2** in high yield. There is no evidence on the formation of *cis*-dicarbonyl isomer with *trans* naphtholic groups and the *trans*-dicarbonyl isomers. The carbonyl groups in both **1** and **2** can be oxidised by trimethylamine-*N*-oxide to give two intermediates **4** and **3a** respectively. The coordinated trimethylamine moiety is shown to be substitution labile and can be easily displaced by other nucleophiles, such as the N-donor ligands to form stable coordination complexes of Ru(II). Therefore, complexes **3a** and **4** are versatile molecular building blocks in coordination chemistry.

4. Experimental

All manipulations were carried out under an inert atmosphere of argon with standard Schlenk technique. However, the product-separation was achieved by preparative thin-layer chromatographic (TLC) plates which were prepared from silica (Merck Kieselgel 60 GF₂₅₄). Chemicals were purchased from a commercial source (Aldrich) and used as received, unless stated otherwise. Trimethylamine-*N*-oxide was dried by azeotropic distillation and sublimed prior to use. Solvents were dried according to standard methods. ¹H NMR spectra were obtained on a Bruker DPX-300 NMR spectrometer using deuterated solvents as lock and reference. Infrared spectra were recorded on a Bio-rad FTS-165 FT-IR spectrometer using 0.5 mm CaF₂ solution cells. Fast-atom bombardment (FAB)

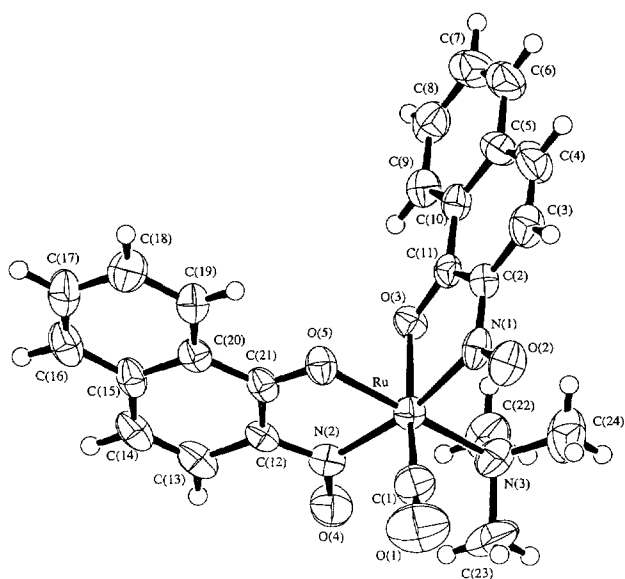


Fig. 3. Molecular structure of *trans*-[Ru(η²-OC₁₀H₆NO)₂(CO)(NMe₃)] **4**, showing the atom-numbering scheme.

mass spectra were recorded on a Finnigan MAT 95 mass spectrometer. Elemental analyses were performed by Butterworth Laboratories, UK.

4.1. Reaction of $[Ru_3(CO)_{12}]$ with 2-nitroso-1-naphthol

$[Ru_3(CO)_{12}]$ (639 mg, 1.0 mmol) and 2-nitroso-1-naphthol (346 mg, 2.0 mmol) were dissolved in 60 cm³ of THF. The dark red solution was allowed to reflux for 2 h. After cooling to room temperature, the solution was concentrated (~2 cm³) and *n*-hexane (20 cm³) was added to precipitate out most of the unreacted $[Ru_3(CO)_{12}]$ (50 mg). After filtering off the precipitate, the filtrate was dried in vacuo. The residue was then chromatographed on TLC using *n*-hexane/CH₂Cl₂ (1:1, v/v) mixture as eluent. Other than the traces of $[Ru_3(CO)_{12}]$, two red bands with $R_f \sim 0.4$ and 0.3 were obtained and characterised as *trans*- $[Ru(\eta^2-OC_{10}H_6NO)_2(CO)_2]$ **1** (416 mg, 30%) and *cis*- $[Ru(\eta^2-OC_{10}H_6NO)_2(CO)_2]$ **2** (416 mg, 30%) respectively based on $[Ru_3(CO)_{12}]$ consumed. Red rectangular crystals of **1**·THF were obtained by slow evaporation of a *n*-hexane/THF solution at room temperature.

Spectroscopic and analytical data for complex **1** (Found: C, 53.10; H, 2.35; N, 5.50%. C₂₂H₁₂N₂O₆Ru requires C, 52.70; H, 2.40; N, 5.60%). IR [*n*-hexane, $\nu(CO)$] 2079 vs and 2027 vs cm⁻¹. ¹H NMR(CD₂Cl₂): δ 8.21[d, $J_{HH} = 8.0$, 2H], 7.51[m, 4H], 7.29[m, 2H], 7.09[d, $J_{HH} = 9.8$, 2H], 6.83[d, $J_{HH} = 9.8$ Hz, 2H]. Fab mass spectrum: m/z 501 (calc. 501), M^+ .

Spectroscopic and analytical data for complex **2** (Found: C, 52.90; H, 2.35; N, 5.55%. C₂₂H₁₂N₂O₆Ru requires C, 52.70; H, 2.40; N, 5.60%). IR [*n*-hexane, $\nu(CO)$] 2078 vs and 2027 vs cm⁻¹. ¹H NMR(CD₂Cl₂): δ 8.66[d, $J_{HH} = 8.1$, 1H], 8.37[d, $J_{HH} = 8.1$, 1H], 7.79[t, $J_{HH} = 7.0$, 1H], 7.68[m, 4H], 7.47[m, 1H], 7.24[d, $J_{HH} = 9.8$, 1H], 7.16[d, $J_{HH} = 9.8$, 1H], 6.93[t, $J_{HH} = 10.3$ Hz, 2H]. Fab mass spectrum: m/z 501 (calc. 501), M^+ .

4.2. Reaction of **2** with $NC_5H_4CH=NC_6H_4OC_{16}H_{33}$

The solid of **2** (50 mg, 0.1 mmol) and the schiff base $NC_5H_4CH=NC_6H_4OC_{16}H_{33}$ (42 mg, 0.1 mmol) were dissolved in 40 cm³ of CH₂Cl₂ at room temperature. A CH₂Cl₂ solution (10 cm³) of Me₃NO (7.6 mg, 0.1 mmol) was added dropwise to this solution mixture and instantaneous colour change from dark red to dark purple was observed. After stirring for 1 h, the solvent was removed in vacuo and the residue was chromatographed by TLC using solution mixture of *n*-hexane/CH₂Cl₂ (2:1, v/v) as eluent to afford three bands. The first red band was characterised as unreacted **2** based on both R_f in spot TLC and IR spectroscopy. The second and third fractions were identified as *cis*- $[Ru(\eta^2-OC_{10}H_6NO)_2(CO)(NMe_3)]$ **3a** (5 mg, 10%) and

cis- $[Ru(\eta^2-OC_{10}H_6NO)_2(CO)(NC_5H_4CH=NC_6H_4OC_{16}H_{33})]$ **3b** (40 mg, 45%) respectively. Dark purple crystals of **3a** was obtained by diffusion of diethyl ether into a CH₂Cl₂ solution of **3a** at -20°C.

Spectroscopic and analytical data for complex **3a** (Found: C, 54.30; H, 4.00; N, 7.85%. C₂₄H₂₁N₃O₅Ru requires C, 54.10; H, 3.95; N, 7.90%). IR [CH₂Cl₂, $\nu(CO)$] 1984 vs cm⁻¹. ¹H NMR(CD₂Cl₂): δ 8.71[d, $J_{HH} = 8.0$, 1H], 8.43[d, $J_{HH} = 8.0$, 1H], 7.66[m, 5H], 7.39[m, 1H], 7.33[d, $J_{HH} = 9.5$, 1H], 7.06[d, $J_{HH} = 9.5$, 1H], 6.91[d, $J_{HH} = 9.5$, 1H], 6.85[t, $J_{HH} = 9.5$ Hz, 1H], 2.66[s, 9H]. Fab mass spectrum: m/z 532 (calc. 532), M^+ .

Spectroscopic and analytical data for complex **3b** (Found: C, 65.85; H, 6.10; N, 6.30%. C₄₉H₅₄N₄O₆Ru requires C, 65.70; H, 6.00; N, 6.25%). IR [CH₂Cl₂, $\nu(CO)$] 1980 vs cm⁻¹. ¹H NMR(CD₂Cl₂): δ 8.75[d, $J_{HH} = 5.3$, 2H], 8.64[d, $J_{HH} = 8.0$, 1H], 8.36[s, 1H], 8.29[d, $J_{HH} = 8.0$, 1H], 7.74[d, $J_{HH} = 5.3$, 2H], 7.60[m, 2H], 7.45[m, 3H], 7.23[m, 1H], 7.22[d, $J_{HH} = 9.5$, 1H], 7.21[d, $J_{HH} = 8.9$, 2H], 7.07[d, $J_{HH} = 9.5$, 1H], 6.84[d, $J_{HH} = 8.9$, 2H], 6.78[d, $J_{HH} = 9.5$, 1H], 6.74[d, $J_{HH} = 9.5$, 1H], 3.87[t, $J_{HH} = 6.6$, 2H], 1.68[qnt, $J_{HH} = 6.6$, 2H], 1.17[m, 26H], 0.78[t, $J_{HH} = 6.6$ Hz, 3H]. Fab mass spectrum: m/z 895 (calc. 895), M^+ .

4.3. Reaction of **1** with trimethylamine-*N*-oxide

To an orange-red solution of **1** (50 mg, 0.1 mmol) in CH₂Cl₂ (20 cm³) was added a solution of Me₃NO (8.25 mg, 0.11 mmol) of the same solvent (10 cm³) at -78°C. The resultant dark purple solution was stirred at -78°C for 15 min further after complete addition. The solution was then allowed to warm to room temperature and stirred for 1 h. The solvent was removed in vacuo and the residue was subjected to preparative TLC using a solution mixture of *n*-hexane/CH₂Cl₂ (1:2, v/v) as eluent. The first band contained majority of unreacted **1** (3 mg) and the second band was characterised as *trans*- $[Ru(\eta^2-OC_{10}H_6NO)_2(CO)(NMe_3)]$ **4** (18 mg), $R_f \sim 0.6$, ca. 34% yield. Dark purple rectangular crystals of **4** were grown by slow evaporation of a *n*-hexane/CH₂Cl₂ mixture at -20°C.

Spectroscopic and analytical data of complex **4** (Found: C, 54.20; H, 3.90; N, 8.00%. C₂₄H₂₁N₃O₅Ru requires C, 54.10; H, 3.95; N, 7.90%). IR [CH₂Cl₂, $\nu(CO)$] 1978 vs cm⁻¹. ¹H NMR(CD₂Cl₂): δ 8.44[d, $J_{HH} = 7.8$, 1H], 8.18[d, $J_{HH} = 7.8$, 1H], 7.60[m, 4H], 7.38[m, 4H], 6.93[dd, $J_{HH} = 9.5$, 3.2 Hz, 2H], 2.56[s, 9H]. Fab mass spectrum: m/z 532 (calc. 532), M^+ .

4.4. X-Ray crystal structure determination

Single crystals of **1**·THF, **3a** and **4**·0.5 CH₂Cl₂ for X-ray analyses were obtained as described above. A

Table 4
Summary of crystallographic parameters for complexes **1**, **3a** and **4**^a

Complex	1	3a	4
Formula	C ₂₂ H ₁₂ N ₂ O ₆ Ru · THF	C ₂₄ H ₂₁ N ₃ O ₅ Ru	C ₂₄ H ₂₁ N ₃ O ₅ Ru · 0.5CH ₂ Cl ₂
fw	573.52	532.52	574.98
Crystal color, habit	red, blocks	purple, blocks	purple, blocks
Crystal size (mm)	0.25 × 0.35 × 0.37	0.22 × 0.23 × 0.29	0.13 × 0.19 × 0.24
Crystal system	triclinic	monoclinic	monoclinic
Space group	P1 (No. 2)	P2 ₁ /c (No. 14)	P2 ₁ /n (No. 14)
a (Å)	10.306(2)	7.771(2)	8.418(2)
b (Å)	16.414(2)	7.917(1)	14.841(2)
c (Å)	7.684(2)	37.049(3)	19.570(2)
α (deg)	93.72(2)	90	90
β (deg)	109.66(2)	95.72(2)	102.15(2)
γ (deg)	106.42(1)	90	90
V (Å ³)	1155.5(5)	2268.1(6)	2390.3(7)
Z	2	4	4
D _{calc} (g cm ⁻³)	1.648	1.559	1.598
F(000)	580	1080	1164
μ(Mo K α)	7.30	7.32	8.09
Scan width (deg)	1.78 + 0.35 tan θ	0.73 + 0.35 tan θ	0.89 + 0.35 tan θ
Transmission factors	0.8564–1.0000	0.9654–1.0000	0.9662–1.0000
Reflections collected	3211	4151	4222
Unique reflections	3009	3839	3932
No. of reflections with I > 3σ(I)	1807	2685	2212
No. of variables	170	298	311
R ^b	0.072	0.034	0.043
R _w ^c	0.069	0.031	0.043
Goodness of fit	3.34	1.69	1.60
Largest Δ/σ	0.02	0.09	0.03
Residual electron density (e Å ⁻³)	1.15 to -1.20	0.45 to -0.46	0.82 to -1.29

^aDetail in common: Mo-K α radiation (λ = 0.71073 Å); T = 298 K; Diffractometer: Rigaku AFC7R; 2θ range of 4–45°; scan type ω-2θ; scan speed 16° min⁻¹.

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

^c $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2}$, where $w = \sigma^2(F_o)^{-1}$.

crystal of compound **3a** was mounted on top of a glass fiber using epoxy resin while crystals of complexes **1** · THF and **4** · 0.5 CH₂Cl₂ were sealed in Lindemann glass capillaries. Crystal intensity data were collected on a Rigaku-AFC7R diffractometer using graphite-monochromated Mo-K α radiation (λ = 0.71,073 Å) for unit-cell determination and data collection. Summary of the crystallographic data, structure solution and refinement are given in Table 4. Lorentz-polarisation and Ψ-scan absorption corrections [13] were applied to all the intensity data collected. The positions of ruthenium atoms were determined by direct methods (SIR92) [14]. The remaining non-hydrogen atoms were determined by subsequent Fourier and difference Fourier techniques. The structures were refined by full-matrix least-squares analysis on F until convergence is reached. The hydrogen atoms of the organic moieties were generated in their ideal positions (C–H, 0.95 Å). They are included in the structure factors calculations but were not refined. All calculations were performed on a Silicon-Graphics computer using the program package TEXSAN [15].

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References

- [1] J.A. Smieja, W.L. Gladfelter, *Inorg. Chem.* 25 (1986) 2667.
- [2] S. Bhaduri, K.S. Gopalkrishnan, G.M. Sheldrick, W. Clegg, D. Stalke, *J. Chem. Soc., Dalton Trans.* (1983) 2339.
- [3] S. Bhaduri, K.S. Gopalkrishnan, W. Clegg, P.G. Jones, G.M. Sheldrick, D. Stalke, *J. Chem. Soc., Dalton Trans.* (1984) 1765.
- [4] K.K.H. Lee, W.T. Wong, *J. Chem. Soc., Dalton Trans.* (1996) 3911.
- [5] B. Foretic, N. Burger, V. Hankonyi, *Polyhedron* 14 (1995) 605.
- [6] J. Korvenranta, H. Saarinen, *Acta Chem. Scand. A29* (1975) 861.
- [7] J. Charalambous, K. Henrick, Y. Musa, R.G. Rees, R.N. Whiteley, *Polyhedron* 6 (1987) 1509.

- [8] J. Charalambous, L.I.B. Haines, J.S. Morgan, D.S. Peat, M.J.M. Campbell, J. Bailey, *Polyhedron* 6 (1987) 1027.
- [9] A.J. Deeming, M.N. Meah, N.P. Randle, K.I. Hardcastle, *J. Chem. Soc., Dalton Trans.* (1989) 2211.
- [10] H. Saarinen, J. Korvenranta, *Acta Chem. Scand. A29* (1975) 409.
- [11] R.G. Buckley, J. Charalambous, M.J. Kensett, M. McPartlin, P. Mukerjee, E.G. Brain, J.M. Jenkins, *J. Chem. Soc., Perkin Trans.* (1983) 693.
- [12] J. Charalambous, W.C. Stoten, K. Henrick, *Polyhedron* 8 (1989) 103.
- [13] A.C.T. North, D.C. Phillips, F.S. Mathews, *Acta Crystallogr., Sect. A* 24 (1968) 351.
- [14] G. Cascarano, L. Favia, C. Giacovazzo, *SIR* 92, *J. Appl. Crystallogr.* 25 (1992) 310.
- [15] TEXSAN, Crystal Structure Analysis Package, Molecular Structure Corporation, 1985 and 1992.