Synthesis, Crystal Structure of Ruthenium 1,2-Naphthoquinone-1-oxime Complex and Its Mediated C—C Coupling Reactions of Terminal Alkynes

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Substituted decarbonylation reaction of ruthenium 1,2-naphthoquinone-1-oxime (1-nqo) complex, *cis*-,*cis*-[Ru {η^2-N(O)$C_{10}H_6O$}$_2$(CO)$_2$] (1), with acetonitrile gave *cis*-,*cis*-[Ru {η^2-N(O)$C_{10}H_6O$}$_2$(CO)(NCMe)] (2). Complex 2 was fully characterized by ^{1}H NMR, FAB MS, IR spectra and single crystal X-ray analysis. Complex 2 maintains the coordination structure of 1 with the two naphthoquinonic oxygen atoms, as well as the two oximato nitrogen atoms located *cis* to each other, showing that there is no ligand rearrangement of the 1-nqo ligands during the substitution reaction. The carbonyl group originally *trans* to the naphthoquinonic oxygen in one 1-nqo ligand is left in its original position [O(5)-Ru-C(1), 174.0(6)°], while the other one originally *trans* to the oximato group of the other 1-nqo ligand is substituted by NCMe [N(1)-Ru-N(3), 170.6(6)°]. This shows that the carbonyl *trans* to oximato group is more labile than the one *trans* to naphthoquinonic O atom towards substitution. This is probably due to the comparatively stronger π back bonding from ruthenium metal to the carbonyl group *trans* to naphthoquinonic O atom, than the one *trans* to oximato group, resulting in the comparatively weaker Ru—CO bond for the latter and consequently easier replacement of this carbonyl. Selected coupling of phenylacetylene mediated by 2 gave a single *trans*-dimerization product 3, while 2 mediated coupling reaction of methyl propiolate produced three products: one *trans*-dimerization product 4 and two cyclotrimeric products 5 and 6.

Keywords ruthenium, 1,2-naphthoquinone-1-oxime, crystal structure

Introduction

Recently, we have reported the coordination chemistry of 1,2-naphthoquinone-mono-oxime (nqoH) towards platinum group metals including ruthenium and rhodium.[1-8] The reactions of nqoH with ruthenium carbonyl [$Ru_3(CO)_{12}$] lead to five isomers of mononuclear ruthenium carbonyl complexes of 1,2-naphthoquinone- monooxime.[1-3] The presence of the liable carbonyl ligands offers the opportunity to introduce a variety of ligands with specific functional groups into the molecule.[3] By this strategy, metal-containing polymers, supramolecular species and long alkyl chain containing molecules are synthesized.[4,5,7,8]

Organic syntheses mediated by transition metal complexes have become increasingly important since the catalytic activity can be modified by associating suitable ligands with the metal center and so a cleaner and more efficient route is possible. Catalysts based on ruthenium complexes have provided efficient routes including a wide range of coupling reactions with chem-, regio- or stereo-selectivity under mild conditions.[9-16] Each of the five isomers of our ruthenium nqo complexes has two nqo ligands in the molecule with specific spatial orientation. We are interested in organic reactions mediated by these complexes. To make it easier for the complex to mediate organic reaction, a more liable ligand, acetonitrile was introduced into the coordination sphere of the *cis*-NO,*cis*-O isomer of ruthenium 1,2-naphthoquinone-1-oxime (1-nqo) complex, *cis*-,*cis*-[Ru {η^2-N(O)$C_{10}H_6O$}$_2$(CO)$_2$] (1), through substituted decarbonylation reaction. Herein, the substitution reaction result was demostrated and carbon—carbon bond formation reactions of terminal alkynes were mediated by the product **2**.

Experimental

Chemical and equipment

cis-,*cis*-[Ru {η^2-N(O)$C_{10}H_6O$}$_2$(CO)$_2$] (1) was synthesized according to our previously reported procedure.[1] Trimethylamine *N*-oxide (Me_3NO, Aldrich) was dried by azeotropic distillation in benzene and sublimed prior to use. Other chemicals were purchased from commercial sources and used as received. Preparative thin-layer chromatographic (TLC) plates were prepared from silica. Infrared spectrum was recorded on a Bio-Rad FTS-7

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IR spectrometer using 0.5 mm of CaF_2 solution cells. ^1H NMR spectra were obtained on a Bruker DPX-300 NMR spectrometer using deuteriated dicholomethane as the lock and reference. Fast atom bombardment (FAB) mass spectrum was recorded on a Finnigan MAT 95 mass spectrometer. GC-MS measurement was done on an HP5890 series II GC equipped with Ultra II capillary column, using HP 5970 MSD as detector.

Synthesis of cis-,cis-[Ru{η^2-N(O)$C_{10}H_6O$}$_2$(CO)(NCMe)] (**2**)

Solid sample of *cis,cis*-[Ru{η^2-N(O)$C_{10}H_6O$}$_2$-(CO)$_2$] (**1**, 50 mg, 0.1 mmol) was dissolved in the solvent mixture of CH_2Cl_2 (40 cm^3) and MeCN (5 cm^3). A CH_2Cl_2 solution (10 cm^3) of Me_3NO (7.5 mg, 0.1 mmol) was added dropwise at room temperature and an instantaneous colour change occurred from orange to dark red. After stirring for 1 h, the solvent was removed *in vacuo* and the residue was subjected to TLC using CH_2Cl_2 as the eluent to afford the complex *cis,cis*-[Ru{η^2-N(O)$C_{10}H_6O$}$_2$-(CO)(NCMe)] (**2**) in 94% yield. Reddish brown; ^1H NMR δ: 9.15 (d, J = 8.5 Hz, 1H), 8.95 (d, J = 8.5 Hz, 1H), 7.79—7.75 (m, 2H), 7.69—7.62 (m, 3H), 7.54—7.50 (m, 1H), 7.44—7.39 (m, 2H), 7.14 (d, J = 9.4 Hz, 1H), 7.01 (d, J = 9.4 Hz, 1H), 2.36 (s, 3H); IR (CH_2Cl_2) ν (CO): 1991 cm^{-1}; FAB MS m/z: 514 (M^+) Anal. calcd for $C_{23}H_{15}N_3O_5Ru$: C 53.69, H 2.94, N 8.17; found C 54.50, H 3.21, N 8.64. Reddish brown crystals of **2** were obtained by slow evaporation of *n*-hexane-CH_2Cl_2 solution at −20 ℃.

C—C *coupling reaction of terminal alkynes mediated by* **2**

Catalytic amount of **2** (30 mg, 0.06 mmol) was added to the benzene solution of terminal alkyne (3 mmol, phenylacetylene or methyl propiolate) and then refluxed. The catalytic reactions were routinely monitored by HP 5890 series II GC equipped with Ultra II capillary column, using FID (flame ionization detector) as the detector. After the reaction, the complexes were isolated from the reaction mixture through column chromatography, using *n*-hexane/CH_2Cl_2 (5/2, V/V) as eluent. Two complexes as **1** and its isomer, *trans-,cis*-[Ru{η^2-N(O)$C_{10}H_6O$}$_2$(CO)$_2$][1] (identified through X-ray diffraction measurement for **1** and IR, spot TLC for both) were isolated through further TLC separation [*n*-hexane/CH_2Cl_2 (2/1, V/V) as eluent]. The organic products were characterized by GC-MS and ^1H NMR spectroscopy. Based on routine GC measurement, GC-MS and ^1H NMR spectra, single *trans*-dimerization product **3** was obtained from the reaction mixture containing phenylacetylene. 60% yield; ^1H NMR δ: 8.11—6.82 (m, 10H), 7.05 (d, J = 16.2 Hz, 1H), 6.30 (d, J = 16.2 Hz, 1H); GC-MS m/z: 204, 126, 101, 76. Through routine GC measurement of the reaction mixture of methyl propiolate combined with GC-MS and ^1H NMR measurements, three products were detected as *trans*-dimerization product **4** and trimeric products **5** and **6**.

4: 14 % yield; ^1H NMR δ: 6.46 (d, J = 16.2 Hz, 1H), 6.03 (d, J = 16.2 Hz, 1H), 3.25 (s, 3H), 3.23 (s, 3H); GC-MS m/z: 168, 137, 109, 77.

5: 23% yield; ^1H NMR δ: 8.41 (s, 1H), 8.19 (d, J = 8.1 Hz, 1H), 7.75 (d, J = 8.1 Hz, 1H), 3.94 (s, 3H), 3.92(s, 6H); GC-MS m/z: 252, 221, 193, 162, 103,75.

6: 31% yield; ^1H NMR δ: 8.81 (s, 3H), 3.99 (s, 9H); GC-MS m/z: 252, 221, 193, 162, 103, 75.

Crystallography

A reddish brown crystal of **2** was sealed in Lindemann glass capillary. Crystal intensity data were collected on an MAR research image-plate scanner using graphite-monochromated Mo Kα radiation (λ = 0.071069 nm) for unit-cell determination and data collection. The structure was solved by direct methods (SHELXS 86)[17] and expanded using Fourier techniques. The structure was refined by full-matrix least-squares analysis on F, with all non-hydrogen atoms refined anisotropically until convergence was reached. The hydrogen atoms of the organic moieties were generated in their ideal positions (C—H, 0.095 nm). They were included in the structure factor calculations on a Silicon-Graphics computer using the program package teXsan.[18]

Results and discussion

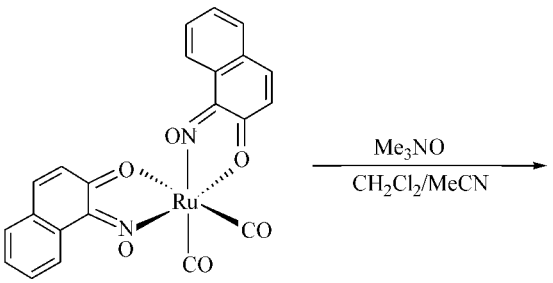
Synthesis of complex cis-,cis-[Ru{η^2-N(O)$C_{10}H_6O$}$_2$-(CO)(NCMe)] (**2**)

The reaction of *cis-,cis*-[Ru{η^2-N(O)$C_{10}H_6O$}$_2$-(CO)$_2$] (**1**) with equivalent of Me_3NO in a solvent mixture of CH_2Cl_2 and MeCN at room temperature affords a single product [Ru{η^2-N(O)$C_{10}H_6O$}$_2$(CO)(NCMe)] (**2**) in high yield (Scheme 1). This is a little different from our previous report about the decarbonylation substitution reactions in which there was also a NMe_3 substituted product detected. It may be due to the comparative large amount of the starting material, MeCN. Complex **2** was fully characterized by IR, ^1H NMR and FAB MS spectra. The ^1H NMR spectrum of **2** shows definite signals for the two 1-nqo ligands and a methyl signal at δ 2.63 due to the coordinated MeCN. **2** shows a sharp single carbonyl stretching at 1991 cm^{-1} characteristic to a mono-carbonyl complex. The MS spectrum of **2** exhibits a molecular peak at 514 amu.

In order to elucidate the molecular structure of complex **2**, X-ray analysis was carried out on prisms of **2**, grown from a mixture of *n*-hexane and dichloromethane at −20 ℃. The unit cell of **2** includes one CH_2Cl_2 molecule as solvent of crystallization. Summaries of the crystallographic data, structure solution and refinement are given in Table 1. Selected bond parameters of complex **2** are giv-

en in Table 2, while nonhydrogen atomic coordinates and equivalent temperature factors are in Table 3. The molecular structure of complex **2** is given in Fig. 1. The ruthenium center is slightly distorted from perfect octahedron. The two 1-nqo ligands chelate to the ruthenium center, adopting a *cis*-configuration in which both oximes and naphthoquinonic oxygen atoms located *cis* to each other. The similar ligand arrangement of the two 1-nqo moieties in **1** and **2** indicates that there is no ligand rearrangement

Scheme 1 Formation of acetonitrile-substitution complex [Ru {η^2-N(O)$C_{10}H_6$O}$_2$(CO)(NCMe)] (**2**)



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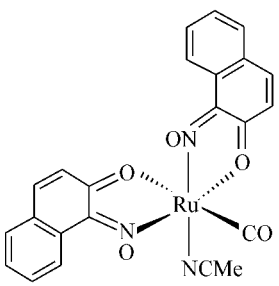

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Table 1 Crystal data and data collection parameters for complex **2**·CH_2Cl_2

Empirical formula	$C_{24}H_{17}Cl_2N_3O_5Ru$
M_r	599.39
Crystal color, habit	Red, block
Crystal dimension (mm^3)	$0.19\times0.20\times0.22$
Crystal system	Triclinic
Space group	$P\bar{1}$ (# 2)
a (nm)	0.7285(1)
b (nm)	1.2783(1)
c (nm)	1.4666(1)
α (°)	111.34(2)
β (°)	97.28(2)
γ (°)	99.11(2)
V (nm^3)	1.2306(4)
Z	2
D_c ($g\cdot cm^{-3}$)	1.618
μ(Mo Kα) (cm^{-1})	8.94
Reflections collected	4677
Unique reflections	2897
Observed reflectons [$I>3.00\sigma(I)$]	1570
R	0.073
R'	0.085
Goodness of fit, S	1.91

Table 2 Selected bond lengths (nm) and bond angles (°) for complex **2**

Ru—O(3)	0.209(1)	Ru—N(1)	0.202(1)
Ru—O(5)	0.206(10)	Ru—N(2)	0.202(1)
Ru—N(3)	0.210(2)	Ru—C(1)	0.186(2)
O(2)—N(1)	0.127(2)	O(4)—N(2)	0.127(1)
N(3)—C(22)	0.108(2)	C(22)—C(23)	0.147(3)
O(1)—C(1)	0.115(2)		
O(3)-Ru-N(1)	79.2(5)	O(3)-Ru-O(5)	91.6(4)
O(3)-Ru-N(2)	170.2(5)	O(3)-Ru-N(3)	93.6(5)
O(3)-Ru-C(1)	94.3(6)	N(1)-Ru-O(5)	85.9(4)
N(1)-Ru-N(2)	95.1(5)	N(1)-Ru-N(3)	170.6(6)
N(1)-Ru-C(1)	94.4(5)	O(5)-Ru-N(2)	80.0(5)
O(5)-Ru-N(3)	88.3(5)	O(5)-Ru-C(1)	174.0(6)
N(2)-Ru-N(3)	91.1(5)	N(2)-Ru-C(1)	94.1(6)
N(3)-Ru-C(1)	92.1(6)		

Table 3 Nonhydrogen atomic coordinates and equivalent temperature factors ($nm^2\times10^2$) for complex **2**

Atom	x	y	z	B_{eq}
Ru	0.301(2)	0.751(1)	0.312(1)	4.7(4)
O(1)	0.711(2)	0.870(1)	0.3531(9)	7.1(4)
O(2)	0.392(1)	0.527(1)	0.2823(8)	4.8(3)
O(3)	0.242(1)	0.735(1)	0.1630(8)	4.5(3)
O(4)	0.479(2)	0.784(1)	0.5114(9)	7.0(3)
O(5)	0.027(1)	0.669(9)	0.3013(8)	4.5(3)
N(1)	0.344(2)	0.592(1)	0.240(1)	3.8(3)
N(2)	0.325(2)	0.742(1)	0.447(9)	3.9(3)
N(3)	0.218(2)	0.909(1)	0.367(1)	5.0(4)
C(1)	0.554(2)	0.825(1)	0.334(1)	4.4(4)
C(2)	0.248(2)	0.636(1)	0.103(1)	3.9(4)
C(3)	0.209(2)	0.611(2)	−0.001(2)	4.8(5)
C(4)	0.208(2)	0.505(2)	−0.066(1)	4.8(5)
C(5)	0.258(2)	0.415(2)	−0.036(1)	4.6(5)
C(6)	0.254(2)	0.307(2)	−0.108(1)	5.7(5)
C(7)	0.297(3)	0.222(2)	−0.078(2)	6.6(6)
C(8)	0.338(2)	0.242(2)	0.023(2)	6.0(6)
C(9)	0.340(2)	0.350(2)	0.096(1)	5.1(5)
C(10)	0.301(2)	0.436(1)	0.069(1)	4.4(4)
C(11)	0.297(2)	0.551(1)	0.137(1)	4.0(4)
C(12)	0.166(2)	0.696(1)	0.467(1)	4.2(4)
C(13)	0.140(2)	0.686(1)	0.560(1)	4.9(5)
C(14)	0.279(3)	0.723(2)	0.646(1)	6.2(5)
C(15)	0.240(3)	0.710(2)	0.732(2)	7.9(7)
C(16)	0.061(4)	0.664(2)	0.737(2)	7.3(7)
C(17)	−0.084(3)	0.627(2)	0.655(2)	6.8(6)
C(18)	−0.045(2)	0.636(1)	0.563(1)	5.1(5)
C(19)	−0.195(2)	0.599(1)	0.481(1)	5.1(5)
C(20)	−0.171(2)	0.607(1)	0.396(1)	4.9(5)
C(21)	0.004(2)	0.655(1)	0.384(1)	4.6(5)
C(22)	0.159(2)	0.985(2)	0.381(2)	5.9(6)
C(23)	0.079(3)	1.088(2)	0.407(2)	8.0(6)

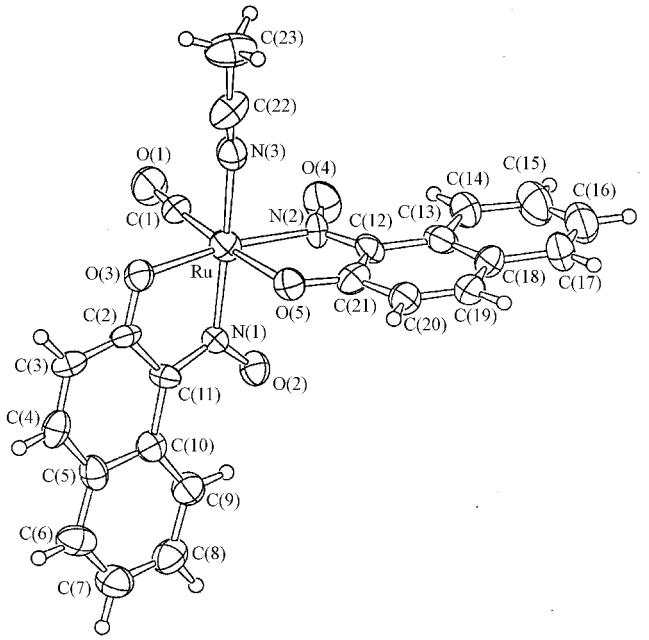


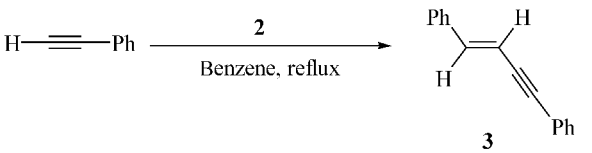
Fig. 1 Molecular structure of [Ru {η^2-N(O)$C_{10}H_6O$}$_2$(CO)(NCMe)] (**2**)

happening during the reaction. The carbonyl group originally *trans* to the naphthoquinonic oxygen in one 1-nqo ligand is left in its original position [O(5)-Ru-C(1), 174.0(6)°], while the other one originally *trans* to the oximato group of the other nqo ligand, as expected, is substituted by NCMe [N(1)-Ru-N(3), 170.6(6)°]. This shows that the carbonyl *trans* to oximato group is more labile than the one *trans* to naphthoquinonic O atom towards substitution. This is probably due to the comparatively stronger π back bonding from ruthenium metal to the carbonyl group *trans* to naphthoquinonic O atom, than the one *trans* to oximato group, resulting in the comparatively weaker Ru—CO bond for the latter and consequently easier replacement of this carbonyl. The configuration of **2** is very similar to our early reported *cis*-NO, *cis*-O isomer of ruthenium 1-nqo complexes with one pyridyl or phosphorus donor ligand coordinating to the metal center.[3-5]

Complex **2** *mediated carbon—carbon coupling reactions of terminal alkynes*

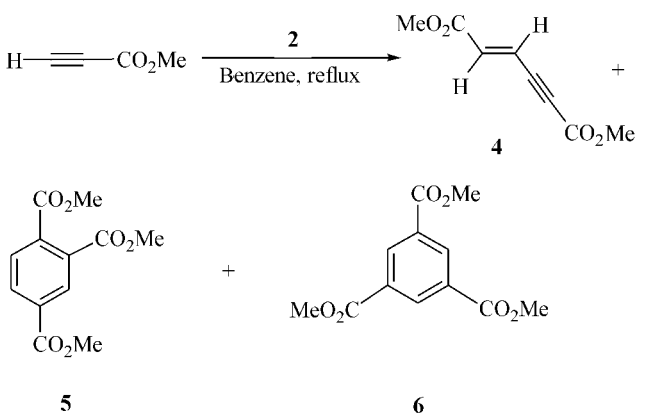
Transition metal mediated C—C coupling reaction of terminal alkyne is of considerable current interest as it can lead to a wide variety of organic enyne and oligoacetylene products that are useful synthetic precursors for organic conducting polymers. C—C coupling reactions of phenylacetylene and methyl propiolate in the presence of catalytic amount of **2** were investigated respectively. Single *trans*-dimerization product **3** was detected in the reaction of phenylacetylene through GC and ^{1}H NMR measurement (Scheme 2). The GC-MS spectrum of this product shows the molecular ion peak at 204 for the dimerization product and daughter peaks attributed to [M^+ – Ph], [M^+ – C≡CPh], and *etc*. ^{1}H NMR spectrum of **3** indicates that the stereochemistry of the product is *E*. The presence of the single product means that complex **2** has high selectivity towards coupling reaction of phenylacetylene. Usually, a mixture of several coupling isomers is obtained in the catalytic coupling reaction of phenylacetylene[10-12] and the isomer distribution is much influenced by the ligand environment of the metal catalyst.[11] The high selectivity in our reaction may be due to the specific spatial orientation of the two 1-nqo ligands.

Scheme 2 Polymerization of phenylacetylene



Three products are detected in the coupling reaction of methyl propiolate as *trans*-dimerization produt **4** and trimerization produts **5** and **6** through GC monitor and ^{1}H NMR measurements (Scheme 3). The GC-MS spectrum corresponding to **4** shows a comparatively weak molecular ion peak at 168, a strong daughter peak due to [M^+ – OMe] and other daughter peaks for [M^+ – COOMe], [M^+ – OMe – COOMe], *etc*. ^{1}H NMR spectrum of **4** shows doublet signals with J = 16.2 Hz for vinyl protons, indicating that the stereochemistry of **4** is *E*. Both the spectra of **5** and **6** show a weak molecular ion peak at 252 corresponding to trimeric product, a strong daughter peak due to [M^+ – OMe] and other daughter peaks for [M^+ – COOMe], [M^+ – OMe – COOMe], [M^+ – OMe – 2COOMe], [M^+ – 3COOMe], *etc*. ^{1}H NMR spectra of **4** and **5** show typical 1,2,4- and 1,2,3-substituted phenyl ring, respectively. Similar cyclotrimerization products were also investigated in phosphinenickel carbonyl complexes catalyzed polymerization reaction of ethyl propiolate.[13]

Scheme 3 Polymerization of methyl propiolate



A coordinatively unsaturated alkyne complex may be involved in the polymerization procedure. The attack of a second alkyne molecule followed by a selective coupling step gives the dimerization product. In our previous work,

the transfer of complex **1** to its *trans*-NO, *cis*-O isomer in the presence of acid was observed.[1] A penta-coordinated transition state was supposed to form by the cleavage of ruthenium-oxime bond *trans* to the naphthoquionic oxygen atom in the other 1-nqo ligand.[1] The presence of the liable ligand NCMe located aside this oxime in **2** offers the opportunity for the two coordinated alkyne molecules to couple with each other. For smaller alkynes (methyl propiolate), the insertion of another alkyne before elimination would produce trimeric products. This proposal is in accord with other works.[10-12] No **2** is detected through spot TLC check after the reaction. In stead, both the dicarbonyl complex **1** and its *trans*-NO, *cis*-O isomer are isolated in the reaction mixture (based on the results of X-ray diffraction measurement for **1** and IR, spot TLC for both). This proves the cleavage of Ru-oxime bond during the reaction.

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