PREPARATION AND COMPARISON STUDY OF SOME NEW BIS (ARYLIMIDO) TRIRUTHENIUM COMPLEXES

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Abstract

A comparison study was made for the reaction of triruthenium carbonyl Ru₃(CO)₁₂ with azoaranc ArN-NAr. This reaction was monitored in two kinds of solvents, toluene and n-octane, which yielded new triruthenium carbonyl complex, Ru₃(μ₃-NAr)₃(CO)₉. The reactions of azoaranc ArN-NAr with Ru₃(CO)₁₂ formed the following trinuclear compound of Ru₃(μ₂-NAr)₃(CO)₆ (Ar=C₆H₄Br-4) in low yield. In addition, to new isomers species of mononuclear cyclometalated of Ru₃(BrC₆H₄1,1',2,2',3,3',4,4'-N-C₆H₄Br-4)₂(CO)₆ in different percentages. The mechanism of the reaction demonstrates that the formation of trinuclear bis arylimido complexes and cyclometalated was the result of cleavage of nitrogen-nitrogen bond. Monitoring this gave evidence that the reaction is preceded faster in presence of n-octane and slowly in presence of toluene solvent. The proposed structure of bis-aryl imido triruthenium complex was based on the results of instrumental analysis.

Introduction

There has been an extensive interest in the chemistry of the ruthenium carbonyl complexes. So far extensive interest has been done on the reaction of Ru₃(CO)₁₂ with azoarancs. Spectroscopic studies were carried out to elucidate the reaction mechanism by forming different products of triruthenium and cyclometalated complexes. According to the literature review, the first cluster complexes of ruthenium triad containing the M₂N₂ skeletal framework was reported by Sappar and Milieu [1] who showed the reaction between Ru₃(CO)₁₂ and nitrobenzene yielding Ru₃(CO)₉(μ₃-CO)₂ and Ru₃(CO)₉(μ₂-NPh)₂. Park showed similar complexes, formed in the reactions of Ru₃(CO)₁₂ with nitroaranc [2].

More investigations of characterization of the complexes Ru₃(μ₃-NPh) (μ₃-NCO) (CO)₉ [3] and Ru₃(μ₃-NPh)₃(CO)₆ [4], have been determined by means of x-ray diffraction studies. The reactions between azoarancene and Ru₃(CO)₁₂ were examined several years later showed that the major product was found to be trinuclear bis (aryl imido) cluster structure that was confirmed both spectroscopically and x-ray structure studies [5-7].

Bruce and Humphry [8] found that the reactions of ArN=NAr with Ru₃(CO)₁₂ produced both Ru₃(μ₂-NAr)(μ₂-NAr')(CO)(Ar=Ph, Ar'=Ph, C₆H₄Me₂, C₆H₄CF₃, C₆H₄H₂-C₆H₄Me₂, Ar=Ar'=C₆H₄Me-3) in moderate yields, Ar=Ar'=Ph or C₆H₄Me-3, and the mononuclear cyclometalated Ru₃(C₆H₄-5-R, C₆H₄-5-H, C₆H₄-5-C₆H₅) in low yield. Some of the reports explained the nitrogen-nitrogen double bond cleavage of azoarancene by triruthenium pentacarbonyl complex (CF₆Ru₃(m-C₆H₄-H)₃(C₆H₄-p-C₆H₅)) [7]. The reactions of transition metal clusters have been a subject of many studies. These promote understanding, the reactivity of unsaturated organic compounds containing olefinic or acetylenic centers towards metal carbonyl. Hence, the interest of this work was based on the preparation of triruthenium carbonyl cluster to make comparison study by using two different solvent in order to isolate a new bis (aryl imido) cluster complexes which might be conceivably act as a good reagent for successful
coupling reaction. On the other hand, bis (phenyliminido) triruthenium cluster product can displace bimetallic phosphine[8, 9].

Experimental section

General conditions

All the reactions were carried out under nitrogen and no special precautions were taken to exclude air during work up, since most complexes proved stable in air as solids and for short time depended on the kind of solvent in the solution. Reactions and solvent solvents were dried and distilled. Column chromatography was performed using Merck silica gel 60 of particle size 0.040-0.063 mm (230-400 mesh ASTM) and petroleum ether boiling range 60-80°C.

Instrumentation

Infrared spectra were recorded as dichloromethane solutions using a Perkin-Elmer system 2000 FT-IR.

^1^H NMR spectra were recorded using a Varian Gemini -300 FT NMR spectrometer and referenced to residual chloroform (7.25 ppm). An electron impact (EI) mass spectra (unit resolution and high resolution) was used. Secondary ion mass spectrometry (SIMS) were recorded using a VG ZAB 2SEQ instrument (30 kV Cs⁺ ions, current 1 µA, accelerating potential 8 kV, 3-nitrobenzyl alcohol matrix, solutions in CH₂Cl₂). Fast atom bombardment (FAB) mass spectra were obtained on a VG ZAB 2HF instrument equipped with a FAB source. Argon was used as the exciting gas, with source pressures typically 10⁻⁸ mbar; the FAB gun voltage was 7.5 kV, current 1 µA. The ion accelerating potential was 8 kV. The matrix was 3-nitrobenzyl alcohol at the Research School of Chemistry, Australian National University or Department of Chemistry, University of Western Australia. The complexes were made up as ca. 0.5 M solutions in acetone or dichloromethane: a drop up. All MS were calculated with the m/z value based on ³⁷Br, ¹⁰⁹Ru or ¹⁰⁵Ru.

Starting materials

Ru₂(CO)₁₂ was prepared using a new modified method from the literature [10, 11]. Ru₂(CO)₁₂ purchased from chemicals, was used without further purification. Other chemicals, lauric acid, bismuth powder a mangano dioxinate (infrared) with high purification were used as starting materials to synthesise compounds according to the literature procedures [12, 13].

Reactions between Ru₂(CO)₁₂ and 4,4'-dibromoazobenzene using :

1- n-octane (solvent)

A mixture Ru₂(CO)₁₂(500 mg, 0.78 mmol) and 4,4'-dibromoazobenzene (530 mg, 1.56 mmol) was heated at reflux in (80 ml ) n-octane and the reaction was monitored by (IR) spectroscopy to be completed after (8 hr). The reaction mixture was taken to dryness in vacuum. The residue was dissolved in CH₂Cl₂ (3ml) and then transferred to the top of a silica column. The column was first eluted with light petroleum. The solvent was removed from the eluate using a rotary evaporator, allowing trace amounts of an unidentified yellow powder. Increasing the polarity to light petroleum / dichloromethane (9:1) fractions were collected & solvent was removed from the second eluent affording an orange crystal, which was recrystallised by dichloromethane / methanol, to give a yield (89.6 mg, 0.10 mmole, 13%). This was identified as Ru₂[(L-NC₆H₄-Br)₂ CO] mp = 158°C.

The third eluent was obtained by increasing the polarity to light petroleum / dichloromethane (8:2). After removing the solvent, orange crystals were obtained. They were recrystallised by dichloromethane/methanol to give a yield of (25 mg, 0.02 mmole, 3.8%), which was identified as Ru₂[(L-NC₆H₄-Br)₂(CO)] mp=190°C. The fourth compound was eluted by dichloromethane.

After removing solvent a brownish powder was obtained, which was recrystallised by
(dichloromethane/ methanol) to give a yield of 
(520mg, 0.62mmole, 79.6%) which was identified 
as another isomer of orthometallated complex mp = 190 °C.

2-Toluene (solvent)
As in (1) above, the mixture was heated at 
reflux toluene (50mL), for (36h). The reaction was 
monitored by (IR) spectroscopy. The first 
compound was eluted with light petroleum 
affording trace amounts of an unidentified yellow 
powder. By increasing the polarity to light 
petroleum/dichloromethane (9:1), the second 
compound afforded orange crystal, which was 
recrystallised by dichloromethane/methanol to give 
a low yield (62mg, 0.07mmole, 9%). This was 
identified as

Ru2(1py- NC6H4-(Aryl))2, mp = 158 °C. The third 
compound and after removal of solvent, orange 
crystals were obtained, then recrystallised by 
(dichloromethane/methanol) giving (9 mg, 
0.01mmole, 1.3%). This was identified as

RuBr2(C6H4-NC6H4-(Aryl)-4), (CO)2, mp=190 °C. The 
fourth compound was eluted by dichloromethane 
methanol, affording a brownish powder, which was 
recrystallised by dichloromethane/methanol, 
yielding (446mg, 0.53mmole, 68.3%). This was 
identified as another isomer of orthometallated 
complex mp= 190 °C.

Mechanistic aspects and comparison study of the 
reaction of 1 with 4, 4'-dihomoazulene in 
presence of two different solvent

This study explains the comparison of some 
new bis (Aryl imido) triruthenium complexes that 
have the M3N3 skeleton. The mechanism of this 
reaction revealed that the formation of these 
complexes from azoarene required N=N cleavage 
occurred at same stage of the reaction. First step of 
the transformation-involved coordination of the 
azoarene to the cluster by the nitrogen atoms, 
perhaps giving an intermediate in which one of the 
M-M bonds is bridged by the azoarene such as E 
(scheme 1). Sippage of the azoarene and further 
interaction with the third metal atom resulted in 
N=N bond cleavage together with electron 
rearrangement following capping leading to opening 
of the M3 triangle.

Result and discussion
Nitrogen-Nitrogen double bond cleavage of 
azoarene by triruthenium carbonyl. The reaction of 
(1) with (2) in presence of toluene solvent 
proceeded much slower (36h) at 110 °C, while the 
reaction was faster and completed within 8h at 
elevated temperature at 127 °C in the presence of 
n-octane solvent, to yield both (3) and (4a+4b) in a 
different percentage yield, as shown in equation - 1. 
The reactions could be attributed to the nitrogen 
double bond cleavage [8].
Plausible mechanism for the reaction of 1 with azoarene

(A) - 2CO → (B) + Rearrangement

ArN-NAr +

(C) 

- M(CO)₃, M=Ru (scheme I)
The eventual cleavage of the N-N bond was consistent with the formation of the α-semidihydrate derivatives such as (C). An alternative reaction can take place when one nitrogen is coordinated to one metal atom, namely the well-known cycloaddition reaction [8].

**Comparison study**

The reactions between azulene and Ru$_2$(CO)$_{12}$ were carried out in two different kinds of solvents (toluene and n-octane). Monitoring the reaction by spectroscopic techniques was very helpful for elucidating the reaction mechanism. In case of the toluene solvent in comparison with the n-octane (table1), the reaction was obtained between Ru$_2$(CO)$_{12}$ and azulene in refluxing toluene solvent (36 hr); to afford orange Ru$_2$(μ-Br$_2$)(CO)$_{12}$, in 9% yield, associated with a smaller amount of the yellow monocyclic cycloaddition complex, Ru$_2$(Br$_2$C$_4$H$_3$N=NC,HBr-4)$_2$(CO)$_{12}$. In addition, another isomer of brown monocyclic cycloaddition complex was afforded. A slightly higher yield 12.8% of the same above reaction occurred when the reaction carried out by n-octane solvent [6]. Similarly, Ru$_2$(CO)$_{12}$ afforded orange Ru$_2$(μ-Br$_2$)(CO)$_{12}$, but in a better yield 20% accompanied by a smaller amount (3.8%) of the monocyclic cycloaddition complex, and a (brownish powder, 4% as). Up to our knowledge, this is the first study that included a preparation of bisaryl (imido complexes containing bromide. The identity of this reaction was monitored by IR ν(CO) spectra. In case of using toluene solvent, the reaction proceeded to end slowly after refluxing for 36 hours in comparison with the same reaction by using n-octane solvent, which proceeded faster after 8 hours. This reaction was examined several times using different types of column chromatography florosil and silica, showed that there was no effect on the separated complexes by using both silica or florosil column chromatography.
Table 1: Reaction conditions of Ru₅(CO)₁₂ and azalenes in presence of toluene and n-octane solvents (under nitrogen)

| Ru₅(CO)₁₂ Amount (Mgole) | ArN=NC Ar Amount (mole) | Solvent (ml) | Reaction (°C, h) | Separation technique | Products | Yield%
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<td>500mg</td>
<td>p-Br</td>
<td>n-octane</td>
<td>(80)</td>
<td>Column</td>
<td>Ru₅(η₂-NAr)₄(CO)₆ (2a)</td>
<td>13</td>
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<td></td>
<td>Ru₅Br₄(η₂-NAr)₄(CO)₆ (2b)</td>
<td>3.8</td>
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<td></td>
<td>Ru₅(CO)₂ (2c)</td>
<td>1.5</td>
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<tr>
<td>500mg</td>
<td>p-Br</td>
<td>Toluene</td>
<td>(60)</td>
<td>Column</td>
<td>Ru₅(η₂-NAr)₄(CO)₆ (2a)</td>
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<td></td>
<td>Ru₅Br₄(η₂-NAr)₄(CO)₆ (2b)</td>
<td>75.6</td>
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<td>Ru₅(CO)₂ (2c)</td>
<td>68.3</td>
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The identity of trinuclear complex was established by IR, 'H NMR, MS (secondary ion, CI⁺) and ESI mass spectra. Trinuclear complex showed in both solvents similar characterization properties. IR ν(CO) of the product (3) Fig (1) in cyclohexane showed several bands at the range of (2096-1980) cm⁻¹ indicating carbonyl groups [12].

Figure 1: FT-IR of [Ru₅ (η₂-NC₆H₄Br₂)(CO)₆]

On the other hand, 'H NMR of (CDCl₃) ppm spectrum contains doublet at 6.6-7.2 (d, 8H, (C₆H₄Br)₂)2. Fig (2).

Figure 2: 'H NMR spectrum of [Ru₅(η₂-NC₆H₄Br₂)(CO)₆]

The fast atom bombardment (FAB) mass of product (3) contains ions [M-3CO⁻] (m/z) 895, 675; [M-CO⁻]⁺ (100), 839 [M-2CO⁻]⁺, (76); 811 [M-3CO⁻]⁺, (100), 783 [M-4CO⁻]⁺, (55); (11); 727, [M-5CO⁻]⁺, (57); 699[M-7CO⁻]⁺. According to these parameters, the trinuclear complexes have the trinuclear bis (aryl-imido) cluster structure and this strongly confirmed by an
x-ray structure study [13, 14]. Meanwhile, the other products of cyclometallation were confirmed by x-ray diffraction study [15, 16], which clearly demonstrated the structure identity of the cyclometallated complexes consisted of two different isomers.

Conclusion
1. The cleavage of the nitrogen-nitrogen double bond of the azoarene was achieved by using triruthenium carbonyl.
2. Monitoring the reaction using two different solvents (toluene and n-octane) by spectroscopic techniques showed that the reaction proceeded very slowly (36hr) in toluene at 110 °C, while the reaction proceeded faster (8hr) in n-octane solvent at 127 °C.
3. The percentage yield of triruthenium complexes products did not depend on the kind of solvents, but depend on the time of the reaction refluxing and reaction temperature.
4. There was no effect of column chromatography (florisil or silica) on the resulted products.

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References

