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

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Abstract

A comparison study was made for the reaction of triruthenium carbonyl Ru$_3$ (CO)$_{12}$ with azoarene ArN-NAr. This reaction was monitered in two kinds of solvents, toluene and n-octane ,which yielded new triruthenium carbonyl complex, Ru$_3$ (μ_3- NAr)$_2$(CO)$_9$. The reactions of azoarenes ArN-NAr with Ru$_3$(CO)$_{12}$ formed the following trinuclear compound of Ru$_3$(μ_3-NAr)$_2$(CO)$_9$, (Ar=C$_6$H$_4$Br-4) in low yield. In addition, to new isomers species of mononuclear cyclometallated of Ru(BrC$_6$H$_3$N=NC$_6$H$_4$Br-4)$_2$ (CO)$_2$ in different percentages. The mechanism of the reaction demonstrates that the formation of trinuclear bis arylimido complexes and orthometallated 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 Ru$_3$(CO)$_{12}$ with azoarenes. Spectroscopic studies were carried out to elucidate the reaction mechanism by forming different products of triruthenium and cyclometallated complexes. According to the literature review the first cluster complexes of ruthenium triad containing the M$_3$N$_2$ skeletal framework was reported by Sappa and Milone [1] who showed the reaction between Ru$_3$(CO)$_{12}$ and nitrobenzene yielding Ru$_3$(CO)$_{10}$(μ_2-CO)$_2$ and Ru$_3$ (CO)$_9$(μ_3-Nph)$_2$. Paik showed similar complexes, formed in the reactions of Ru$_3$(CO)$_{12}$ with nitroarenes [2].

More investigations of characterization of the complexes Ru$_3$ (μ_3Nph) (μ_3- CO)(CO)$_9$ [3] and Ru$_3$((μ_3-Nph)$_2$ (CO)$_9$ [4], have been determined by means of x-ray diffraction studies. The reactions between azobenzene and Ru$_3$ (CO)$_{12}$ were examined several years later showed that the major product was found to be trinuclear bis (arylimido) cluster structure, that was confirmed by both spectroscopically and x-ray structure studies [5-7].

Bruce and Humphery, found that the reactions of ArN=NAr` with Ru$_3$(CO)$_{12}$ produced both Ru$_3$($\mu_3$-NAr)($\mu_3$-NAr`)(CO)(Ar=Ph,Ar`=Ph, C$_6$H$_4$Me-3,C$_6$H$_4$CF-3,C$_6$H$_4$F-4 Ar=Ar`=C$_6$H$_4$Me-3) in moderate yields; Ar=Ar`=Ph or C$_6$H$_4$Me-3, and the mononuclear cyclometallated Ru(C$_6$H$_3$RN=NC$_6$H$_4$R-3)$_2$(CO)$_2$ (R=H or Me ) in low yield. Some of the reports explained the nitrogen-nitrogen double bond cleavage of azobenzene by triruthenium pentahydrido complex (CP`Ru)$_3$(μ_3-H)$_2$(μ-H)$_3$ (Cp`=η^5-C5Me$_5$)[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 reactant for successful

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coupling reaction. On the other hand, bis (phenylimido) triruthenium cluster product can displace by mono or bidentate phosphines [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. n-octane and toluene solvents were dried and distilled. Column chromatography was preformed 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 2000FT-IR.

^1H NMR spectra were recorded using a varian Gemini –300 FT NMR spectrometer and referenced to residual chloroform (7.52 ppm). An electron impact (EI) mass spectra (unit resolution and high resolution) was used. Secondary ion mass spectra spectrometry (SI MS) were recorded using a VGZAB 2SEQ instrument (30kV Cs^+ ions, current 1 m A, accelerating potential 8 KV, 3- nitro benzyl alcohol matrix, solutions in CH_2Cl_2). 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^{-5} mbar; the FAB gun voltage was 7.5 KV, current 1 mA. 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 tip. All MS were calculated with the m/z value based on ^{79}Br, ^{102}Ru or $^{303}Ru_3$.

Starting materials

$Ru_3(CO)_{12}$ was prepared using a new modified method from the literature [10,11]. $Ru_3(CO)_{12}$ purchased stem chemicals, was used without further purification. Other chemicals amines, bismuth powder a manganese dioxide (Aldrich) with high purification were used as starting materials to synthesize azoarenes according to the literature procedures [12, 13].

Reactions between $Ru_3(CO)_{12}$ and 4,4'-dibromoazobenzene using :

1- n-octane (solvent)

A mixture $Ru_3(CO)_{12}$(500 mg , 0.78 mmol) and **4,4'-** dibromo azobenzene (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 CH_2Cl_2 (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 eluant using a rotary evaporater, affording 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 low yield (89.6 mg, 0.10mmole, 13%). This was identified as $Ru_3(\mu_3\text{-}NC_6H_4\text{-}Br)_2$, mp = 158 C°. The third eluant 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, 0.02mmole, 3.8%), which was identified as $Ru(BrC_6H_4N{-}NC_6H_3Br\text{-}4)_2(CO)_2$, 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°.

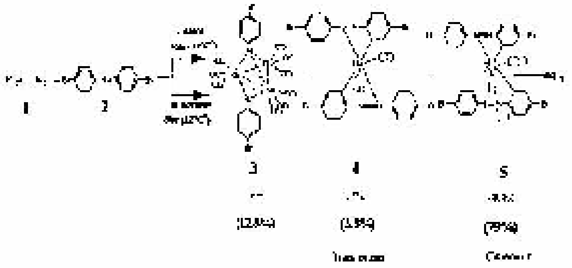
2-Toluene (solvent)

As in **(1)** above, the mixture was heated at reflux toluene (80ml), 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

Ru_3 (μ_3- NC_6H_4-Br)$_2$, 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 $Ru(BrC_6H_4N{=}NC_6H_4Br\text{-}4)_2\ (CO)_2$,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°.

Result and discussion

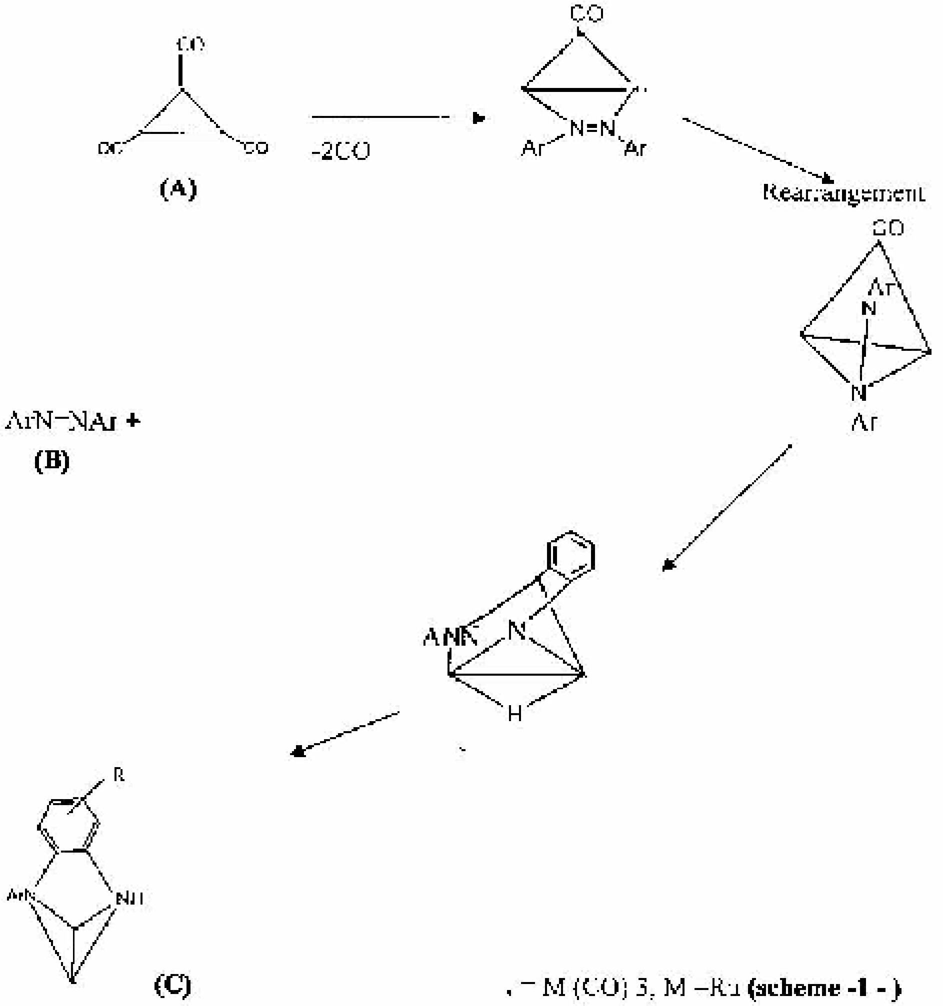
Nitrogen-Nitrogen double bond cleavage of azoarene by triruthenium carbonyl. The reaction of (1) with (2) in presence of toluene solvent was proceeded much slower (36hr) at 110 C°, while the reaction was faster and completed within 8h at elevated temperature at 127 C° in the presence of n-octane solvent, 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].



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

This study explains the comparison of some new bis (Aryl imide) triruthenium complexes that have the M_3N_2 skeleton. The mechanism of this reaction revealed that the formation of these complexes from azoarenes required N=N cleavage occurred at some 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 B (scheme 1). Slippage 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 M_3 triangle.

Plausible mechanism for the reaction of 1 with azoarene



, = M (CO) 3, M =Ru **(scheme -1 -)**

The eventual cleavage of the N-N bond was consistent with the formation of the o-semidine derivatives such as **(C)**. An alternative reaction can take place when one nitrogen is coordinated to one metal atom, namely the well – known cyclometallation reaction [8].

Comparison study

The reactions between azoarene and $Ru_3(CO)_{12}$ 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 $Ru_3(CO)_{12}$ and azoarene in refluxing toluene solvent (36 hr), to afford orange $Ru_3(\mu_3NAr)_2(CO)_9$ in 9% yield, associated with a smaller amount of the yellow mononuclear cyclometallated complex , $Ru(BrC_6H_4N{=}NC_6H_3Br\text{-}4)_2(CO)_2$. In addition, another isomer of brown mononuclear cyclometallated 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, $Ru_3(CO)_{12}$ afforded orange $Ru_3(\mu_3\text{-}NAr)_2(CO)_9$, but in a better yield 20% accompanied by a smaller amount (3.8%) of the mononuclear cyclometallated complex, and a (brownish powder 490mg). Up to our knowledge, this the first study that included a preparation of bis aryl (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 hour 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 florisil and silica, showed that there was no effect on the separated complexes by using both silica or florisil column chromatography

Table-1: Reactions conditions of Ru$_3$ (CO)$_{12}$ and azoarenes in presence of toluene and n- octane solvents (under nitrogen)

Ru$_3$(CO)$_{12}$ Amount (mmole)	ArN=NAr Ar	Ar	Amount (mmole)	Solvent (ml)	Condition (C°, h)	Separation technique	Products	Yield %
500mg	p-Br	p-Br	550 mg	n-octane (80)	(127°,8h)	Column	Ru$_3$(μ$_3$-NAr)$_2$(CO)$_9$ (2a)	13
							Ru(BrC$_6$H$_3$N=NC$_6$H$_4$Br-4) (CO)$_2$ (3b) Trans	5.8
							Ru(BrC$_6$H$_3$N=NC$_6$H$_4$Br-4) (CO)$_2$ (4c)cis	79.6
500mg	p-Br	p-Br	550mg	Toluene (80)	(110°,36h)	Column	Ru$_3$(μ$_3$-NAr)$_2$(CO)$_9$(2a)	9
							Ru(BrC$_6$H$_3$N=NC$_6$H$_4$Br-4) (CO)$_2$ (3b) Trans	1.5
							Ru(BrC$_6$H$_3$N=NC$_6$H$_4$Br-4) (CO)$_2$ (4c)cis	68.3

The identity of triruthenium complex was established by IR, ^{1}HNMR, MS (secondaryion,Cs$^+$) and FAB mass spectra. Triruthenium 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].

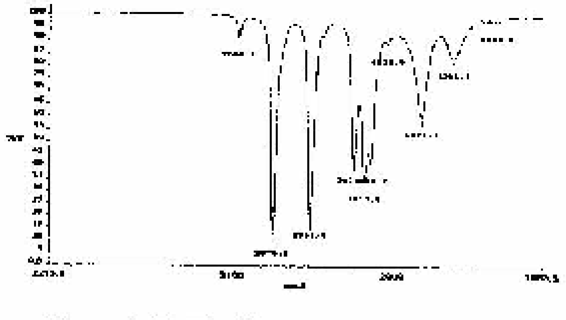


Figure-1: Ft-IR of [Ru$_3$ (μ$_3$-NC$_6$H$_4$Br)$_2$(CO)$_9$]

On the other hand ^{1}HNMR δ (CDCl$_3$) (ppm) spectrum contains doublet at 6.6-7.2 (d , 8H, (C$_2$H$_4$Br)2. Fig (2).

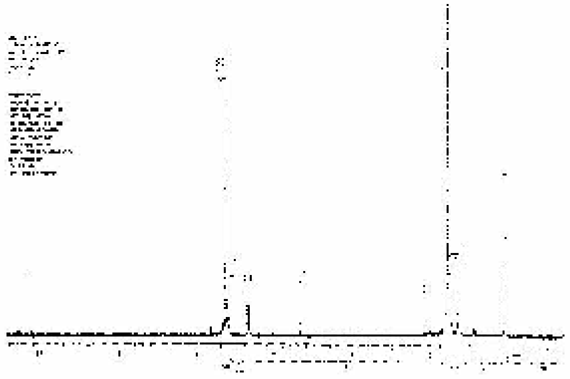


Figure-2 : ^{1}HNMR spectrum of [Ru$_3$(μ$_3$NC$_6$H$_4$Br)$_2$(CO)$_9$

The fast atom bombardment (FAB) mass of product(3) contains ions [M-nCO]$^+$ (n=0-7)[M$^+$] 895, (63); 867, [M-CO]$^+$, (100); 839 [M-2CO]$^+$, (76);811 [M-3CO]$^+$, (100); 783 [M-4CO]$^+$, (55); (11); 727, [M-6CO]$^+$, (57); 699[M-7CO]$^+$. According to these parameters, the trinuclear complexes have the trinuclear bis (arylimido) cluster structure and this strongly confirmed by an x-ray structure study [13,14]. Meanwhile, the other products of cyclometallated 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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