Journal of Organometallic Chemistry, 296 (1985) 147-153
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

THE PREPARATION, CHARACTERIZATION AND SOME REACTIONS OF $[Ru_3(CO)_{11}(NCMe)]$ AND $[Ru_3(CO)_{10}(NCMe)_2]$ *

G.A. FOULDS, B.F.G. JOHNSON and J. LEWIS

University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW (Great Britain)

(Received March 29th, 1985)

Summary

The clusters $[Ru_3(CO)_{11}(NCMe)]$ and $[Ru_3(CO)_{10}(NCMe)_2]$ have been prepared from the reaction of $[Ru_3(CO)_{12}]$ with NMe_3O in the presence of CH_3CN. Thus, these new clusters have been shown to be convenient precursors in the preparation of other Ru_3 cluster species. $[Ru_3(CO)_{11}(NCMe)]$ reacts with ligands L (L = $P(OMe)_3$ and PPh_3) to form $[Ru_3(CO)_{11}L]$ derivatives, while $[Ru_3(CO)_{10}(NCMe)_2]$ reacts to form $[Ru_3(CO)_{10}L_2]$ derivatives. Both clusters react with CH_3CH_2SH, $HC{\equiv}CPh$, $PhC{\equiv}CPh$ and C_5H_5N to form $[HRu_3(CO)_{10}(SCH_2CH_3)]$, $[HRu_3(CO)_9(C_2Ph)]$, $[Ru_3(CO)_8(C_2Ph_2)_2]$ and $[HRu_3(CO)_{10}(C_5H_4N)]$, respectively.

Introduction

Part of our strategy in studying controlled synthetic methods in osmium carbonyl cluster chemistry has been the preparation of stable intermediates that allow displacement of ligand groups under relatively mild conditions, thus avoiding extreme thermal conditions normally required for direct substitution of the carbonyl groups. Initially, we employed the cyclohexadiene complex $[Os_3(CO)_{10}(C_6H_8)]$ [1] in such a role and we were able to illustrate the preparation of a range of decacarbonyl derivatives by displacement of the cyclohexadiene group, in high yields. However the more ready preparation of the acetonitrile complexes $[Os_3(CO)_{11}(NCMe)]$, $[Os_3(CO)_{10}(NCMe)_2]$ [2] by amine oxide oxidation of the carbonyl groups in acetonitrile has superceded the cyclohexadiene complex as a preparative reagent.

Recently, we have been able to extend the synthetic procedure to Os_4 [3], Os_5 [4], Os_6 [5], carbonyl cluster systems. Our attempts to extend this reaction procedure to ruthenium clusters were initially unsuccessful. However, we here report the preparation of the mono- and bis-acetonitrile complexes of ruthenium dodecacarbonyl and illustrate some of the synthetic potential of these complexes.

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* This paper is dedicated to Professor Lamberto Malatesta in recognition of his contributions to synthetic organometallic chemistry.

0022-328X/85/$03.30

TABLE 1

SPECTROSCOPIC PROPERTIES OF [(Ru$_3$(CO)$_{11}$(NCMe)], [Ru$_3$(CO)$_{10}$(NCMe)$_2$], AND DERIVATIVES

Compound	Infrared spectra [a], ν(C–O) (cm^{-1})	^{1}H NMR (τ) [b]	Molecular weight (mass spectrum) [c]
[Ru$_3$(CO)$_{11}$(NCMe)]	2098(w), 2045(s), 2037(s), 2021(m), 2001(s) 1994(s), 1972(vw)	7.53 (s, 3H) [d]	
[Ru$_3$(CO)$_{11}${P(OCH$_3$)$_3$}]	2102(m), 2062(vw), 2047(vs), 2034(s), 2017(vs), 1998(s), 1991(s), 1980(m)	6.25 (d, 9H) (J(P–H) 12.1 Hz)	735
[Ru$_3$(CO)$_{11}$(PPh$_3$)]	2097(m), 2046(vs), 2031(s), 2024(s), 2015(vs), 2001(w), 1986(w)	2.45 (m, 15H)	
[Ru$_3$(CO)$_{10}$(NCMe)$_2$]	2086(w), 2055(sh), 2018(vs), 1999(s), 1987(sh), 1954(m), 1819(mw) [e]	7.37 (s, 6H) [f]	
[Ru$_3$(CO)$_{10}${P(OCH$_3$)$_3$}$_2$]	2083(w), 2048(w), 2029(s), 2004(vs), 1982(m), 1960(sh)	6.28 (d, 18 H) (J(P–H) 12.1 Hz)	831
[Ru$_3$(CO)$_{10}$(PPh$_3$)$_2$]	2077(m), 2060(w), 2047(w), 2030(sh), 2019(vs), 1996(vs), 1978(s), 1956(s)	2.50 (m, 30H)	
[HRu$_3$(CO)$_{10}$(SCH$_2$CH$_3$)]	2104(w), 2081(w), 2063(s), 2053(s), 2024(vs), 2007(s), 1998(m) [d]	7.80 (q, 2H) 8.65 (t, 3H) 25.40 (s, 1H)	645
[HRu$_3$(CO)$_{10}$(C$_5$H$_4$N)]	2099(m), 2061(vs), 2050(vs), 2024(s), 2015(vs), 2008(sh), 1999(s), 1984(w)	1.87 (dd, 1H) 2.52 (m, 2H) 3.17 (td, 1H) 24.37 (d, 1H)	662
[HRu$_3$(CO)$_9$(CCPh)]	2097(m), 2062(vs), 2053(vs), 2031(vs), 2013(s), 1998(m)	2.60 (m, 5H) 30.50 (s, 1H)	657
[Ru$_3$(CO)$_8$(C$_2$Ph$_2$)$_2$]	2080(s), 2049(vs), 2027(vs), 2007(w), 1995(m) 1966(m)	2.71 (m, 20H)	

[a] In cyclohexane unless otherwise stated. [b] In CD$_2$Cl$_2$ unless otherwise stated. [c] Based on ^{101}Ru. [d] Run in CDCl$_3$. [e] Run in THF. [f] Run in THF-d_8.

Results and discussion

Preparation and characterisation of [Ru$_3$(CO)$_{11}$(NCMe)] (1)

[Ru$_3$(CO)$_{12}$] in dichloromethane reacts with trimethylamine oxide in dichloromethane in the presence of CH$_3$CN as the temperature of the reaction mixture is allowed to slowly warm from −78°C to ambient temperature (ca. 20°C). The reaction is easily monitored by a change in colour of the solution from light orange to dark orange, after which the complex [Ru$_3$(CO)$_{11}$(NCMe)] may be isolated as dark orange crystals by means of TLC. Owing to the relative instability of the complex, it should be used immediately, or stored under nitrogen in the freezer.

The IR and ^{1}H NMR spectra are shown in Table 1. The IR spectrum (ν(C–O) region) closely resembles that of the analogous osmium compound [2], while the ^{1}H NMR spectrum (ca. 25°C) shows one signal at τ 7.53(s) corresponding to protons of the coordinated NCMe ligand. Under electron impact the complex undergoes decomposition, with some [Ru$_3$(CO)$_{12}$] being formed. However, the complex does give satisfactory analytical data as shown in the Experimental section.

Preparation and characterisation of [Ru$_3$(CO)$_{10}$(NCMe)$_2$] (2)

[Ru$_3$(CO)$_{10}$(NCMe)$_2$] may be prepared from [Ru$_3$(CO)$_{11}$(NCMe)] or directly from [Ru$_3$(CO)$_{12}$]. In both cases, the starting material reacts with a slight excess (stoichiometric) of trimethylamine oxide in the presence of CH$_3$CN as the temperature of the reaction mixture is allowed to slowly warm from −78°C to ambient temperature (ca. 20°C). The reaction is easily monitored by following the change in colour of the solution from dark orange and light orange respectively to light yellow. [Ru$_3$(CO)$_{10}$(NCMe)$_2$] may be isolated as light yellow crystals, which due to its relative instability should be used immediately or stored under nitrogen in the freezer.

The IR and ^{1}H NMR data are listed in Table 1. The IR spectrum (ν(C–O) region) (run in acetonitrile due to the instability of [Ru$_3$(CO)$_{10}$(NCMe)$_2$] in other pure solvents) closely resembles that of the osmium analogue [6], while the ^{1}H NMR spectrum (ca. 25°C) shows one signal at τ 7.37(s) corresponding to protons of the coordinated NCMe ligands.

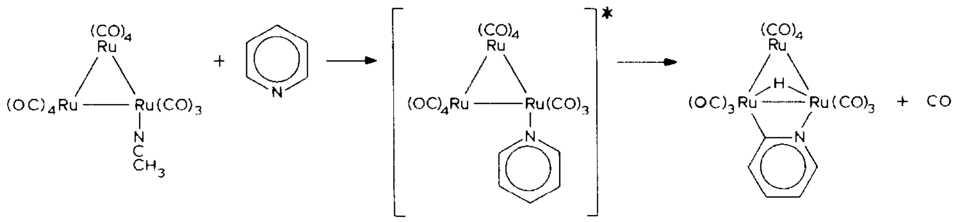
Under election impact the complex undergoes decomposition with some [Ru$_3$(CO)$_{12}$] being formed. However, the complex does give satisfactory analytical data as shown in the Experimental Section.

Reaction of 1 and 2 with other donor ligands

Treatment of **1** with P(OMe)$_3$ and PPh$_3$ resulted in the formation of known compounds [Ru$_3$(CO)$_{11}$P(OMe)$_3$] and [Ru$_3$(CO)$_{11}$PPh$_3$] [7] in good yield, with very little of the disubstituted compounds [Ru$_3$(CO)$_{10}$L$_2$] being formed. Similarly, treatment of **2** with P(OMe)$_3$ and PPh$_3$ resulted in the formation of the known compounds [Ru$_3$(CO)$_{10}$\{P(OMe)$_2$\}$_2$] and [Ru$_3$(CO)$_{10}$(PPh$_3$)$_2$] [7] in good yield, with very little formation of the tri-substituted compounds [Ru$_3$(CO)$_9$L$_3$]. Thus, this method shows distinct advantages over some of the thermal reactions of [Ru$_3$(CO)$_{12}$] with PPh$_3$ or P(OMe)$_3$, where the tri-substituted compounds form the predominant products. The spectroscopic properties of the mono- and di-substituted compounds are listed in Table 1.

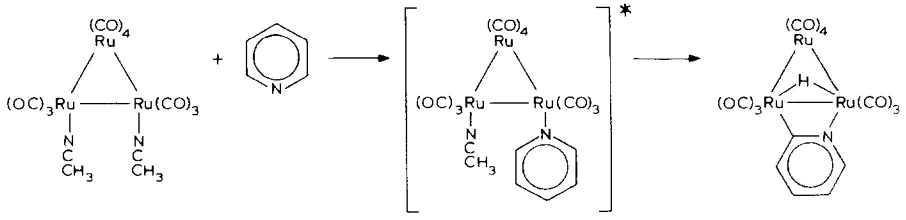
Treatment of both **1** and **2** with CH$_3$CH$_2$SH and PhC≡CH at room temperature resulted in the known compounds [$HRu_3(CO)_{10}(SCH_2CH_3)$] [8] and [$HRu_3(CO)_9$-(CCPh)] [9] being formed in good yields (ca. 90%). These compounds have previously been synthesised using forcing conditions resulting in low yields, thus emphasising the advantages offered by this milder synthetic route. The spectroscopic properties of the above compounds are shown in Table 1.

Pyridine reacts with both **1** and **2** at room temperature to form the new compound [$HRu_3(CO)_{10}(C_5H_4N)$], with the yield being greater in the latter case. The reaction with **1** probably proceeds via the mechanism suggested for the analogous osmium compound [2,10], with the exception that owing to the greater reactivity of ruthenium, the intermediate [$Ru_3(CO)_{11}py$], is not isolated. Thus, we have:



where the CO liberated during the reaction can react with unreacted [$Ru_3(CO)_{11}(NCMe)$] to form [$Ru_3(CO)_{12}$].

The reaction of **2** with pyridine probably proceeds via the following mechanism:



which would explain the higher yield and lack of generation of [$Ru_3(CO)_{12}$]. The complex [$HRu_3(CO)_{10}(C_5H_4N)$] was characterised on the basis of its spectral data (see Table 1) in conjunction with its analogous osmium compound [10].

Excess diphenylacetylene reacts with both **1** and **2** at room temperature to selectively form the violet-red isomer of [$Ru_3(CO)_8(C_2Ph_2)_2$], which contains only terminal carbonyl groups, as found by Cetini et al. [11], in quantitative yield. No bright orange isomer of [$Ru_3(CO)_8(C_2Ph_2)_2$], which contains bridging carbonyl groups, was found, probably due to the mild conditions employed. (The orange isomer can be made by refluxing the violet-red isomer in petroleum and gasoline [11].) Thus this milder synthetic route facilitates both excellent yield and selectivity as opposed to the aggressive conditions used by Cetini et al. [11] where after the refluxing for 15 h in benzene, nine products were obtained.

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* Not observed.

Experimental

Preparation of $[Ru_3(CO)_{11}(NCMe)]$ *(1)*

100 mg of $[Ru_3(CO)_{12}]$ is dissolved in 150 ml of CH_2Cl_2. 5 ml of CH_3CN is added and the reaction flask is placed in a dry ice/acetone bath (-78°C). 14 mg of $(CH_3)_3NO$, dissolved in 5 ml of CH_2Cl_2, is added over a period of 5 min with constant stirring. After all the amine oxide has been added, the dry ice/acetone bath is removed, and the reaction mixture is allowed to slowly warm to ambient temperature. This is accompanied by a change in colour of the solution from light orange to dark orange. The solution is immediately chromatographed using CH_2Cl_2/cyclohexane/CH_3CN (35/60/5) as eluant. Three bands are observed, corresponding to unreached $[Ru_3(CO)_{12}]$ (ca. 15%), $[Ru_3(CO)_{11}(NCMe)]$ (ca. 70%) and $[Ru_3(CO)_{10}(NCMe)_2]$ (ca. 15%) respectively. The dark orange compound $[Ru_3(CO)_{11}(NCMe)]$ is removed from the silica using CH_3CN as solvent.The solvent is then removed until precipitation just begins, upon which it is placed in the freezer to facilitate further precipitation. The orange crystals were then filtered and dried under vacuum over silica gel. (Found: C, 23.99; H, 0.71; N, 1.98. $[Ru_3(CO)_{11}(NCMe)]$ calcd.: C, 23.92; H, 0.46; N, 2.15%). Yield: 58 mg (Note $[Ru_3(CO)_{11}(NCMe)]$ decomposes and should be used immediately or stored in the freezer under nitrogen.)

Preparation of $[Ru_3(CO)_{10}(NCMe)_2]$ *(2)*

100 mg of $[Ru_3(CO)_{12}]$ is dissolved in 150 ml of CH_2Cl_2. 10 ml of CH_3CN is added and the reaction flask is placed in a dry ice/acetone bath (-78°C). 30 mg of $(CH_3)_3NO$, dissolved in 5 ml of CH_3CN, is added over a period of 5 minutes with constant stirring. After all the amine oxide has been added, the dry ice/acetone bath is removed, and the reaction mixture is allowed to slowly warm to ambient temperature. This is accompanied by a change in colour of the solution from orange to bright yellow. The solution is immediately chromatographed using the same conditions as for **1**. Two bands are observed, corresponding to $[Ru_3(CO)_{11}(NCMe)]$ (ca. 15%) and $[Ru_3(CO)_{10}(NCMe)_2]$ (ca. 85%), respectively. The bright yellow $[Ru_3(CO)_{10}(NCMe)_2]$ is removed from the silica using CH_3CN as solvent. The solvent is removed until precipitation starts to commence, upon which it is placed in the freezer to facilitate further precipitation. The yellow crystals are filtered, washed with diethyl ether and dried under vacuum over silica gel. (Found: C, 24.60; H, 0.94; N, 4.14. $[Ru_3(CO)_{10}(NCMe)_2]$ calcd.: C, 25.26; H, 0.90; N, 4.21%. Yield: 65 mg (Note $[Ru_3(CO)_{10}(NCMe)_2]$ decomposes and should be used immediately or stored in the freezer under nitrogen).

Reactions of 1 and 2 with $P(OMe)_3$

An excess of $P(OMe)_3$ (1 drop) is added to a cool solution of **1** (30 mg in 3 ml of CH_2Cl_2 at -78°C) with stirring. The solution is stirred for 15 seconds before being chromatographed. TLC yields one major product, $[Ru_3(CO)_{11}P(OMe)_3]$ (ca. 80%), isolated as an orange powder, with $[Ru_3(CO)_{10}P(OMe)_{3\ 2}]$ (ca. 20%), isolated as a slightly darker orange powder being a second product. Eluant used is CH_2Cl_2/cyclohexane (40/60).

Reaction of $P(OMe)_3$ with **2** is achieved by adding an excess of $P(OMe)_3$ (1 drop) to a cool solution of **2** (30 mg in 3 ml of CH_2Cl_2/CH_3CN (50/50) at about -40°C) with stirring. The solution is stirred for 15 seconds before being chromatographed.

TLC yields one major product, $[Ru_3(CO)_{10}(P(OMe)_3)_2]$ (ca. 95% isolated as a dark orange powder, with a trace amount of $[Ru_3(CO)_9\{P(OMe)_3\}_3]$ (ca. 5%) as a second product.

*Reactions of **1** and **2** with PPh_3*

An excess of PPh_3 (15 mg) is added to a cool solution of **1** (30 mg in 3 ml of CH_2Cl_2 at −78°C) with stirring. The solution is stirred until it darkens (~ 1 minute), before being chromatographed. The major product is $[Ru_3(CO)_{11}PPh_3]$ (ca. 90%), isolated as an orange powder, with a small amount of $[Ru_3(CO)_{10}(PPh_3)_2]$ (ca. 10%), isolated as a red solid, formed as a second product. Eluant used is CH_2Cl_2/cyclohexane (40/60).

Similarly, an excess of PPh_3 (30 mg) is added to a cool solution of **2** (30 mg in 3 ml of CH_2Cl_2/CH_3CN (50/50) at about −40°C) with stirring. The solution is stirred until it darkens (~ 30 seconds), before being chromatographed. Eluting with CH_2Cl_2/cyclohexane (40/60) yields one major product, $[Ru_3(CO)_{10}(PPh_3)_2]$ (ca. 90%), isolated as a red solid, with a small amount of violet-red $[Ru_3(CO)_9(PPh_3)_3]$ formed as a secondary product.

*Reactions of **1** and **2** with CH_3CH_2SH*

An excess (1 drop) of CH_3CH_2SH is added to a solution of **1** (30 mg in 5 ml of CH_3CN) at room temperature with stirring. After about one minute the reaction mixture darkens, indicating that reaction has taken place. Chromatography yields one major product, $[HRu_3(CO)_{10}(SCH_2CH_3)]$ (ca. 70%), isolated as an orange solid, as well as some decomposition products (ca. 30%). Eluant used is CH_2Cl_2/cyclohexane (50/50).

Reaction of **2** with CH_3CH_2SH carried out as above is instantaneous yielding the same product viz. $[HRu_3(CO)_{10}(SCH_2CH_3)]$.

*Reaction of **1** and **2** with HC≡CPh*

An excess (1 drop) of HC≡CPh is added to a solution of **1** (30 mg in 5 ml of CH_3CN) at room temperature with stirring. After a couple of minutes the solution darkens indicating that reaction had taken place. Chromatography, using CH_2Cl_2/cyclohexane (30/70) as eluant, yields one product, $[HRu_3(CO)_9(CCPh)]$ (ca. 95%) isolated as red-orange powder.

Reaction of **2** with HC≡CPh carried out as above is instantaneous yielding the same product viz. $[HRu_3(CO)_9(CCPh)]$ in quantitative yield.

*Reaction of **1** and **2** with pyridine*

30 mg of **1** dissolved in 5 ml of CH_2Cl_2 is stirred in the presence of excess pyridine (3 drops) at room temperature for about 5 min. The solution is chromatographed using an eluant of acetone/cyclohexane (40/60). Two bands move significantly, the first being $[Ru_3(CO)_{12}]$ (ca. 40%), followed by $[HRu_3(CO)_{10}(C_5H_4N)]$ (ca. 30%), which was isolated as a yellow-green crystalline solid. Some decomposition products (ca. 30%) remain on the baseline.

30 mg of **2** dissolved in 5 ml of CH_2Cl_2/CH_3CN (80/20) is stirred in the presence of excess pyridine (3–4 drops) at room temperature for 5 min. The solution is chromatographed using the same conditions as above. The major product is $[HRu_3(CO)_{10}(C_5H_4N)]$ (ca. 70%), isolated as a yellow-green solid. Some decomposi-

tion products (ca. 30%) remain on the baseline. Microanalysis. Found: C, 27.80; H, 0.60; N, 1.90. $[HRu_3(CO)_{10}(C_5H_4N)]$ calcd.: C, 27.20; H. 0.76; N, 2.11%.

*Reaction of **1** and **2** with PhC≡CPh*

A two fold excess of PhC≡CPh is added to a solution of **1** (30 mg in CH_2Cl_2) at room temperature with constant stirring. The solution is stirred for a few minutes during which it changes from orange to dark red. Chromatography, using CH_2Cl_2/cyclohexane (30/70), yields one major product, $[Ru_3(CO)_8(C_2Ph_2)]$ (ca. 90%), isolated as a red-violet solid, as well as an unidentified red-brown secondary product (ca. 10%).

Reaction of **2** with PhC≡CPh, carried out under conditions similar to those outlined above, yielded the same products in similar yields.

*Further reaction of **1** with $(CH_3)_3NO$ in CH_3CN*

Complex **1** (50 mg) is dissolved in 100 ml of CH_2Cl_2/CH_3CN (80/20) and placed in a dry ice/acetone bath. 10 mg of $(CH_3)_3NO$, dissolved in 5 ml of CH_3CN is added over a period of 5 min with constant stirring. After all the amine oxide has been added, the dry ice-acetone bath is removed, and the reaction mixture is allowed to slowly warm to ambient temperature. This is accompanied by a change in colour of the solution from dark orange to light yellow. The solution is filtered through a short silica column which in turn is washed with a small amount of CH_3CN. Removal of solvent gave a quantitative yield of $[Ru_3(CO)_{10}(NCMe)_{10}]$.

Acknowledgement

We wish to thank the C.S.I.R. for financial support (to G.A.F.).

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