Journal of Organometallic Chemistry, 294 (1985) 123–129
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

ortho-METALLATION REACTIONS OF VARIOUSLY SUBSTITUTED METHYLPYRIDINES, QUINOLINE, ISOQUINOLINE, DIAZINES AND 2,2′-BIPYRIDINE, WITH $[Ru_3(CO)_{10}(NCMe)_2]$

GARY A. FOULDS, BRIAN F.G. JOHNSON and JACK LEWIS
University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW (Great Britain)

(Received April 18th, 1985)

Summary

The *ortho*-metallated clusters $[HRu_3(CO)_{10}(L)]$ (L = 2-MeC_5H_3N, 3-MeC_5H_3N, 4-MeC_5H_3N, C_9H_6N and $C_4H_3N_2$) have been prepared by the reaction of $[Ru_3(CO)_{10}(NCMe)_2]$ with 2-, 3- and 4-methylpyridine, quinoline and isoquinoline, and 1,3- and 1,4-diazine, respectively. In the case of 3-methylpyridine, isoquinoline, and 1,3-diazine, isomers are obtained. 1,2-Diazine and 2,2′-bipyridine react with $[Ru_3(CO)_{10}(NCMe)_2]$ to give complexes of the type $[Ru_3(CO)_{10}L]$ (L = $C_4H_4N_2$ and $C_{10}H_8N_2$, respectively). Refluxing a toluene solution of $[Ru_3(CO)_{10}(C_{10}H_8N_2)]$ gives rise to the *ortho*-metallated complex $[HRu_3(CO)_9(C_{10}H_7N_2)]$.

Introduction

It has been shown in a recent review [1] that although many examples of cyclometallated complexes of osmium incorporating a heterocyclic donor exist [2,4], there are no known analogous ruthenium cluster compounds of this nature. This is probably due to the vigorous nature of the conditions used to date in the synthesis of these compounds.

However, with the recent synthesis of $[Ru_3(CO)_{10}(NCMe)_2]$ [5], a pathway for the synthesis of cyclometallated complexes of ruthenium cluster compounds with heterocyclic donor ligands, using mild conditions, has been established. In this paper we look at the reaction of $[Ru_3(CO)_{10}(NCMe)_2]$ with variously substituted methylpyridines, quinoline, iso-quinoline, various diazines, and 2,2′-bipyridine.

Results and discussion

Reaction of $[Ru_3(CO)_{10}(NCMe)_2]$ with 2-, 3- and 4-methylpyridine

The reaction of $[Ru_3(CO)_{10}(NCMe)_2]$ with the above substituted methylpyridines probably proceeds via the mechanism outlined for the analogous pyridine reaction

(Continued on p. 126)

0022-328X/85/$03.30

TABLE 1

SPECTROSCOPIC PROPERTIES

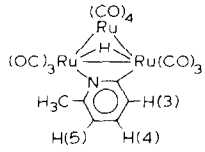
Compound	Infrared spectra [a] (ν(C–O)) (cm^{-1})	^1H NMR (τ) [b]		Molecular weight (mass spectrum) [c]
$[HRu_3(CO)_{10}(2\text{-}MeC_5H_3N)]$ (I)	2099(m), 2059(vs), 2049(vs), 2023(s), 2014(vs), 2008(s), 1997(s), 1983(w), 1971(w)	2.85(m)	H(4), H(5)	
		3.20(m)	H(3)	
		7.45(s)	CH_3	676
		24.06(s)	Ru–H	
$[HRu_3(CO)_{10}(3\text{-}MeC_5H_3N)]$ (II)	2098(m), 2059(vs), 2048(vs), 2022(s), 2013(vs), 2007(s), 1996(s), 1982(w)	2.11(s)	H(6)	
		2.80(m)	H(3), H(4)	
		7.78(s)	CH_3	676
		24.39(s)	Ru–H	
$[HRu_3(CO)_{10}(3\text{-}MeC_5H_3N)]$ (III)	2098(m), 2059(vs), 2048(vs), 2022(s), 2009(sh, s), 1995(s), 1981(w)	2.12(d)	H(6)	
		2.82(d)	H(4)	
		3.27(dd)	H(5)	676
		7.56(s)	CH_3	
		24.28(s)	Ru–H	
$[HRu_3(CO)_{10}(4\text{-}MeC_5H_3N)]$ (IV)	2099(m), 2060(vs), 2049(vs), 2023(s) 2014(vs), 2008(s), 1997(s), 1983(w)	1.14(d)	H(6)	
		1.74(m)	H(3)	
		2.33(dd)	H(s)	676
		7.76(s)	CH_3	
		24.41(s)	Ru–H	
$[HRu_3(CO)_{10}(C_9H_6N)]$ (V)	2099(m), 2059(vs), 2050(vs), 2024(s), 2016(vs), 2009(s), 1998(s), 1984(w)	1.90	H(3), H(4)	
		to	H(6), H(7)	
		2.60(m)	H(8), H(9)	712
		23.96(s)	Ru–H	
$[HRu_3(CO)_{10}(C_9H_6N)]$ (VI)	2099(m), 2060(vs), 2050(vs), 2024(s), 2016(vs), 2010(s), 1998(s), 1982(w)	1.66(m)	H(4), H(5)	
		2.23(m)	H(6), H(7)	712
		2.13(d)	H(10)	
		2.75(d)	H(9)	
		24.02(s)	Ru–H	

$[HRu_3(CO)_{10}(C_9H_6N)]$ (VII)	2098(m), 2060(vs), 2050(vs), 2023(s), 2614(vs), 2008(sh, s), 1998(s), 1983(w)	1.18(s)	H(10)	
		2.26(m) to 2.36	H(3), H(5) H(6), H(7) H(8)	712
		24.33(s)	Ru–H	
$[HRu_3(CO)_{10}(C_4H_3N_2)]$ (VIII)	2102(m), 2064(vs), 2054(vs), 2018(s), 2017(vs), 2010(sh), 2003(s), 1988(w), 1955(w)	1.56(d)	H(6)	
		1.98(s)	H(3)	
		2.04(d)	H(5)	663
		24.48(s)	Ru–H	
$[HRu_3(CO)_{10}(C_4H_3N_2)]$ (IX)	2102(m), 2065(vs), 2054(vs), 2028(s), 2016(vs), 2003(s), 1989(w), 1956(w)	1.53(s)	H(6)	
		2.06(d)	H(4)	663
		2.43(d)	H(3)	
		24.57(s)	Ru–H	
$[HRu_3(CO)_{10}(C_4H_3N_2)]$ (X)	2101(m), 2065(vs), 2051(vs), 2027(s), 2012(s), 2005(s), 1992(w)	1.62(dd)	H(6)	
		1.98(dd)	H(4)	
		3.19(dd)	H(5)	663
		24.53(s)	Ru–H	
$[Ru_3(CO)_{10}(C_4H_4N_2)]$ (XI)	2082(sh, m), 2056(s), 2032(s), 2017(vs), 2001(vs), 1975(s, vb), 1815(m, br) [d]	1.43(t) 1.58(t)	H(3), H(4)	
		2.54(t) 2.72(t)	H(5), H(6)	
$[Ru_3(CO)_{10}(C_{10}H_8N_2)]$ (XIII)	2074(s), 2030(vs), 1995(sh, vs), 1990(vs), 1975(sh, s), 1964(m) [e]	0.05(d)	H(2), H(11)	
		1.72(d)	H(5), H(8)	
		1.93(dt)	H(4), H(9)	
		2.26(dt)	H(3), H(10)	
$[HRu_3(CO)_9(C_{10}H_7N_2)]$ (XIV)	2079(m), 2066(vw), 2052(w), 2037(m), 2014(s), 2008(m), 1994(m), 1985(m), 1980(m), 1969(m), 1956(m)	1.05(d)	H(2)	
		1.92(d)	H(5)	
		2.04(dt)	H(4)	
		2.50(m)	H(3), H(8), H(9), H(10)	
		29.98(s)	Ru–H	

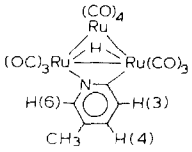
[a] In cyclohexane unless otherwise stated. [b] In CD_2Cl_2 unless otherwise stated. [c] Based on ^{101}Ru. [d] Run in CH_2Cl_2. [e] Run in THF.

referred to in earlier work [5]. In all cases *ortho*-metallation occurs, and in the case of 3-methylpyridine, the possibility of isomers exists.

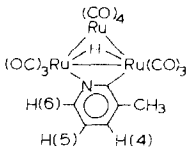
2-Methylpyridine and 4-methylpyridine react with $[Ru_3(CO)_{10}(NCMe)_2]$ to form $[HRu_3(CO)_{10}(2\text{-}MeC_5H_3N)]$ (I) and $[HRu_3(CO)_{10}(4\text{-}MeC_5H_3N)]$ (IV), respectively (see Fig. 1). 3-Methylpyridine reacts to form two isomers of $[HRu_3(CO)_{10}(3\text{-}MeC_5H_3N]$ viz. II and III in Fig. 1. These isomers are easily characterised on the



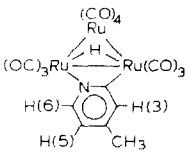
(I)



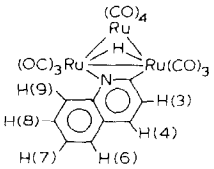
(II)



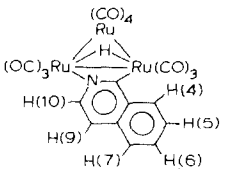
(III)



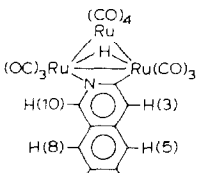
(IV)



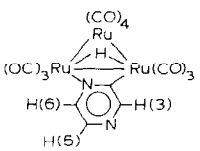
(V)



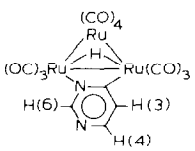
(VI)



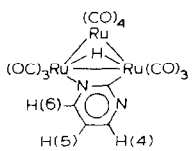
(VII)



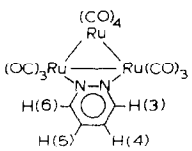
(VIII)



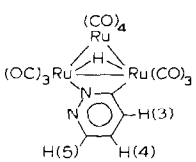
(IX)



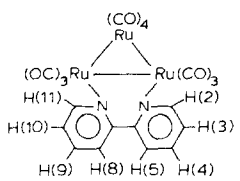
(X)



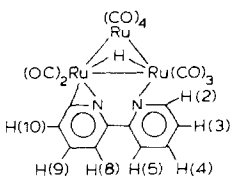
(XI)



(XII)



(XIII)



(XIV)

basis of their ^1H NMR spectra, since proton H(6) is "isolated" by the methyl group in II, but not in III, and thus exhibits coupling in the latter case. It is worth noting that isomer II is formed in far greater yield than isomer III, (45 and 15%, respectively). This is probably due to the more favourable steric arrangement in II where the methyl group is pointed well away from the ruthenium triangle. The spectral data for I, II, III and IV are listed in Table 1.

Reaction of $[Ru_3(CO)_{10}(NCMe)_2]$ with quinoline and isoquinoline

The reaction of quinoline with $[Ru_3(CO)_{10}(NCMe)_2]$ is analagous to that of

2-methylpyridine with $[Ru_3(CO)_{10}(NCMe)_2]$, since in both cases there is a unique proton in the *ortho* position. As a result quinoline reacts to form $[HRu_3(CO)_{10}(C_9H_6N]$ (V) in Fig. 1, which is easily identifiable by the absence of a proton in the *ortho* position in the ^1H NMR.

Isoquinoline reacts with $[Ru_3(CO)_{10}(NCMe)_2]$ in the same way as 3-methylpyridine does, since both are asymmetrical ligands with two protons in different *ortho* positions. Consequently, two isomers of $[HRu_3(CO)_{10}(C_9H_6N)]$, VI and VII, respectively, are formed as shown in Fig. 1. The two isomers are distinguished on the basis of their ^1H NMR spectra, since isomer VII has H(10) as an "isolated" proton, occurring as a singlet, whereas in isomer VI H(10) is not "isolated" and exhibits the corresponding coupling. Once again, the more sterically favourable isomer, VII, is formed in greater abundance than the less favourable isomer, VI, with the respective yields being 40 and 25%. The spectral data for V, VI and VII are listed in Table 1.

Reaction of $[Ru_3(CO)_{10}(NCMe)_2]$ with 1,2-, 1,3- and 1,4-diazine

The number of possible modes of coordination is increased in the case of the various diazines, by the presence of a second nitrogen atom in the ring.

Pyrazine (1,4-diazine), being a symmetrical ligand with all protons in the *ortho* position being equivalent, reacts with $[Ru_3(CO)_{10}(NCMe)_2]$ to form a single compound $[HRu_3(CO)_{10}(C_4H_3N_2)]$ (VIII). The position of metallation is easily identified from the ^1H NMR spectrum.

Pyrimidine (1,3-diazine), although being a symmetrical ligand, has one unique proton in an *ortho* position, as well as two other equivalent *ortho* protons. As a result, when treated with $[Ru_3(CO)_{10}(NCMe)_2]$, pyrimidine gives two isomeric forms of $[HRu_3(CO)_{10}(C_4H_3N_2)]$, IX and X, respectively. The isomers are distinguished on the basis of their ^1H NMR spectra, with proton H(6) observed as a singlet for isomer IX, but as a doublet of doublets for isomer X. Structure IX is slightly more favoured than structure X as indicated by the relative yields (40 and 30%, respectively).

Pyridazine (1,2-diazine) reacts instantaneously with $[Ru_3(CO)_{10}(NCMe)_2]$ to give a non-metallated compound, structure XI in Fig. 1, previously identified by Cotton et al. [6]. The mode of coordination, via the two nitrogen atoms, is easily verified by the absence of a hydride signal in the ^1H NMR spectrum. Attempts to form the *ortho*-metallated compound (structure XII in Fig. 1), using the method employed by Deeming et al. [3] in making the corresponding osmium analogue, were unsuccessful.

Reaction of $[Ru_3(CO)_{10}(NCMe)_2]$ with 2,2'-bipyridine

2,2'-Bipyridine reacts instantaneously with $[Ru_3(CO)_{10}(NCMe)_2]$ to give $[Ru_3(CO)_{10}(C_{10}H_8N_2)]$ (XIII) in good yield. The complex was characterised on the basis of its spectral data, and in particular the ^1H NMR spectrum which does not contain a hydride signal. Under electron impact the complex undergoes decomposition and no parent ion was observed. However the complex does give satisfactory analytical data.

Refluxing $[Ru_3(CO)_{10}(C_{10}H_8N_2)]$ in toluene for fifteen minutes yields the *ortho*-metallated complex, $[HRu_3(CO)_9(C_{10}H_7N_2)]$ (XIV) (see Fig. 1), easily characterised by its ^1H NMR spectrum (see Table 1) which contains a hydride signal, and indicates that the symmetry of the bipyridyl has been destroyed. Under electron impact this complex undergoes decomposition and no parent ion was observed, but

the spectral data show good agreement with those for the analogous osmium compound [3].

Experimental

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

$[Ru_3(CO)_{10}(NCMe)_2]$ was prepared by the method of Foulds, Johnson and Lewis [5] and stored as a solid in a freezer.

Reactions of $[Ru_3(CO)_{10}(NCMe)_2]$

(a) With 2-methylpyridine. A solution of $[Ru_3(CO)_{10}(NCMe)_2]$ (50 mg) in tetrahydrofuran (5 ml) is stirred with an excess of 2-methylpyridine for a few minutes at room temperature under nitrogen during which the colour of the solution changes from yellow to red-orange, indicating that reaction has taken place. The solution is chromatographed using acetone/cyclohexane (40/60) as eluent. The major product is $[HRu_3(CO)_{10}(2\text{-}MeC_5H_3N)]$ (I) (ca. 65%), isolated as a yellow-green crystalline solid, with $[Ru_3(CO)_{12}]$ and decomposition products constituting the remainder. Recrystallisation of I is achieved with an acetone/water mixture. Microanalysis. Found: C, 28.71; H, 1.39; N, 2.01. $C_{16}H_7NO_{10}Ru_3$ calcd.: C, 28.40; H, 1.04; N, 2.07%).

(b) With 3-methylpyridine. The procedure is similar to that described in (a), with the exception that n-pentane is used as eluent for the TLC. Three bands move significantly, the first being $[Ru_3(CO)_{12}]$ (ca. 5%), the second being $[HRu_3(CO)_{10}(3\text{-}MeC_5H_3N)]$ (isomer A) (II) (ca. 45%), followed by $[HRu_3(CO)_{10}(3\text{-}Me\text{-}C_5H_3N)]$ (isomer B) (III) (ca. 15%), with decomposition products constituting the remainder. Recrystallisation of II and III is achieved with an acetone/water mixture, with both being isolated as yellow-green crystals. Microanalysis. Isomer A (II). Found: C, 28.25; H, 1.01; N, 2.04.

Isomer B (III). Found: C, 28.14; H, 1.02; N, 2.07. $C_{16}H_7NO_{10}Ru_3$ calcd.: C, 28.40; H, 1.04; N, 2.07%).

(c) With 4-methylpyridine. The reaction is carried out in an analogous manner to that described in (a). The major product is $[HRu_3(CO)_{10}(4\text{-}MeC_5H_3N)]$ (IV) (ca. 55%) isolated as a yellow-green solid and recrystallised as before. Microanalysis. Found: C, 29.20; H, 1.41; N, 1.93. $C_{16}H_7NO_{10}Ru_3$ calcd.: C, 28.40; H, 1.04; N, 2.07%).

(d) With quinoline. The reaction is carried out as described in (a). The major product is $[HRu_3(CO)_{10}(C_9H_6N)]$ (V) (ca. 50%) isolated as a yellow-green solid and recrystallised as before. Microanalysis. Found: C, 32.61; H, 1.73; N, 1.92. $C_{19}H_7NO_{10}Ru_3$ calcd.: C, 32.02; H, 0.98; N, 1.97%).

(e) With isoquinoline. The reaction procedure is similar to that described in (a), except that n-pentane is used as eluant for the TLC. Three bands move, the first being $[Ru_3(CO)_{12}]$ (ca. 5%), the second being $[HRu_3(CO)_{10}(C_9H_6N)]$ (isomer A)(VI) (ca. 25%), followed by $[HRu_3(CO)_{10}(C_9H_6N)]$ (isomer B)(VIII) (ca. 40%), with decomposition products constituting the remainder. Recrystallisation of VI and VII is achieved with an acetone/water mixture, with both being isolated as yellow-green solids. Microanalysis. Isomer A (VI). Found: C, 33.13; H, 1.30; N, 1.83.

Isomer B (VII). Found: C, 32.86; H, 1.26; N, 1.95. $C_{19}H_7NO_{10}Ru_3$ calcd.: C, 32.02; H, 0.98; N, 1.97%).

(f) With pyrazine (1,4-diazine). The reaction is carried out as in (a), using acetone/cyclohexane (20/80) as eluent for TLC. The major product is $[HRu_3(CO)_{10}(C_4H_3N_2)]$ (VIII) (ca. 70%), with decomposition products constituting the rest. VIII is isolated as a yellow solid which decomposes on standing to a hexane-insoluble dark orange solid, which was not characterised. Microanalysis. Found: C, 25.51; H, 1.06; N, 4.82. $C_{14}H_4N_2O_{10}Ru_3$ calcd.: C, 25.34; H, 0.60; N, 4.22%).

(g) With pyrimidine (1,3-diazine). The reaction is carried out as in (a), using acetone/cyclohexane (20/80) as eluent for TLC. Three bands move significantly, the first being $[Ru_3(CO)_{12}]$ (ca. 5%), the second being $[HRu_3(CO)_{10}(C_4H_3N_2)]$ (isomer A) (IX) (ca. 40%), followed by $[HRu_3(CO)_{10}(C_4H_3N_2)]$ (isomer B) (X) (ca. 30%), with the remainder being decomposition products. Recrystallisation of IX and X is achieved in an acetone/water mixture, with both being isolated as yellow-green solids. Microanalysis. Isomer A (IX). Found: C, 25.61; H, 1.06; N, 4.86.

Isomer B (X). Found: C, 25.57; H, 1.03; N, 4.85. $C_{14}H_4N_2O_{10}Ru_3$ calcd.: C, 25.34; H, 0.60; N, 4.22%).

(h) With pyridazine (1,2-diazine). An excess of pyridazine (1 drop) is added to a solution of $[Ru_3(CO)_{10}(NCMe)_2]$ (50 mg) dissolved in THF (ca. 5 ml). Reaction is instantaneous with the solution changing from yellow to dark maroon. TLC, using acetone/cyclohexane (50/50) as eluent yields $[Ru_3(CO)_{10}(C_4H_3N_2)]$ (XI) (ca. 70%) as the major product, with decomposition products constituting the remainder.

(i) With 2,2'-bipyridine. The reaction procedure is similar to that described in (h), with the solution changing from yellow to dark red. TLC, using the conditions described in (h), yields one major product, $[Ru_3(CO)_{10}(C_{10}H_8N_2)]$ (XIII) (ca. 70%), isolated as a maroon-violet solid, which was recrystallised from dichloromethane and cyclohexane. Decomposition products constitute the remainder. Microanalysis. Found: C, 33.29; H, 1.77; N, 3.68. $C_{20}H_8N_2O_{10}Ru_3$ calcd.: C, 32.48; H, 1.08; N, 3.79%).

30 mg of $[Ru_3(CO)_{10}(C_{10}H_8N_2)]$ was dissolved in toluene (ca. 30 ml) and refluxed for 10–15 min. During this time the colour of the solution changes from maroon-violet to red. The solvent was removed and the residue redissolved in acetone, before being chromatographed. TLC, with acetone/cyclohexane (30/70) as eluent yielded three bands that moved appreciably. These corresponded to $[Ru_3(CO)_{12}]$ (ca. 5%), $[HRu_3(CO)_9(C_{10}H_7N_2)]$ (XIV) (ca. 30%), and unreacted $[Ru_3(CO)_{10}(C_{10}H_8N_2)]$ (ca. 35%). The remainder was composed of decomposition products (ca. 30%). $[HRu_3(CO)_9(C_{10}H_7N_2)]$ (XIV), isolated as a red solid, was recrystallised from cyclohexane. Microanalysis. Found: C, 31.99; H, 1.04; N, 3.76. $C_{19}H_8N_2O_9Ru_3$ calcd.: C, 32.07; H, 1.13; N, 3.94%).

Acknowledgement

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

References

1 E.C. Constable, Polyhedron, 3 (1984) 1037–1057.
2 C.C. Yin and A.J. Deeming, J. Chem. Soc. Dalton, (1975) 2091.
3 A.J. Deeming, R. Peters, M.B. Hursthouse, J.D. Julius Backer-Dirks, J. Chem. Soc. Dalton, (1982) 787.
4 J. Shapley, D. Samkoff, C. Bueno and M.R. Churchill, Inorg. Chem., 21 (1982) 634.
5 G.A. Foulds, B.F.G. Johnson and J. Lewis, J. Organomet. Chem., in press.
6 F.A. Cotton and B.E. Hanson, Inorg. Chem., 16 (1977) 11.