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Activation of the CN Triple Bond of Substituted Benzonitriles in the Presence of $Ru_3(CO)_{12}$, Acetic Acid and Molecular Hydrogen. Crystal Structure of $(\mu\text{-}H)_2Ru_3(CO)_9(\mu_3\text{-}NCH_2C_6H_4OMe)$*

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Abstract

Reactions of $Ru_3(CO)_{12}$ with *p*-methoxybenzonitrile and *p*-nitrobenzonitrile have been studied in refluxing cyclohexane and the complexes formed were characterized by IR, ^1H NMR spectroscopy and mass spectrometry. In the presence of acetic acid and *p*-methoxybenzonitrile, $(\mu\text{-}H)Ru_3(CO)_{10}(\mu\text{-}NHCH_2C_6H_4OMe)$ is the main reaction product, whilst when acetic acid is replaced by H_2 at atmospheric pressure the main reaction products are $(\mu\text{-}H)Ru_3(CO)_{10}(\mu\text{-}NCHC_6H_4OMe)$ and $(\mu\text{-}H)_2Ru_3(CO)_9(\mu_3\text{-}NCH_2C_6H_4OMe)$. The crystal structure of $(\mu\text{-}H)_2Ru_3(CO)_9(\mu_3\text{-}NCH_2C_6H_4OMe)$ has been determined by X-ray diffraction methods. Crystals are triclinic, space group $P\bar{1}$, with $a = 11.255(6)$, $b = 12.205(8)$, $c = 8.831(6)$ Å, $\alpha = 108.98(2)$, $\beta = 99.43(2)$, $\gamma = 95.78(2)^\circ$, $V = 1116(1)$ Å^3, $Z = 2$. Full-matrix least-squares refinement (324 variables, 2938 observed reflections) converged to give R and R_w values of 0.0318 and 0.0435 respectively. The structure consists of an isosceles triangular cluster of Ru atoms (with the longer edges bridged by hydrides) bound to nine terminal carbonyls and triply bridged by the $NCH_2C_6H_4OMe$ group. Reaction of $Ru_3(CO)_{12}$ with *p*-nitrobenzonitrile and acetic acid only leads to decomposition. Addition of H_2 at atmospheric pressure to a cyclohexane solution of $Ru_3(CO)_{12}$ and *p*-nitrobenzonitrile leads to $(\mu\text{-}H)Ru_3(CO)_{10}(\mu\text{-}NCHC_6H_4NO_2)$ and $(\mu\text{-}H)_2Ru_3(CO)_9(\mu_3\text{-}NCH_2C_6H_4NO_2)$. In refluxing cyclohexane, $(\mu\text{-}H)Ru_3(CO)_{10}(\mu\text{-}NCHC_6H_4X)$ complexes (X = H, OMe, NO_2) are slowly converted into $(\mu\text{-}H)_2Ru_3(CO)_9(\mu_3\text{-}NCH_2C_6H_4X)$ (X = H, OMe, NO_2), and in n-octane at 100 °C, besides $(\mu\text{-}H)_2Ru_3(CO)_9(\mu_3\text{-}NCH_2C_6H_4X)$, minor amounts of $(\mu\text{-}H)Ru_3(CO)_{10}(\mu\text{-}NHCH_2C_6H_4X)$ are also formed. These results are discussed in terms of possible reaction pathways and of the role of acetic acid in the reaction of $Ru_3(CO)_{12}$ with benzonitrile and its substituted derivatives.

Introduction

Following the studies on the reactivity of ironcarbonyl compounds with organic nitriles [2–5], the clusters $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ are also prone to be activators of the CN triple bond of benzonitrile [6–9]. Complexes containing the benzonitrile ligand at different degrees of hydrogenation have been isolated and characterized. However the saturation of the CN triple bond with hydrogen bound to nitrogen on the ligand has been obtained only when acetic acid was present in the reaction [6–8]. Very recently the effect of some acids has been applied in the reaction of dimethylcyanamide with the formally electronically unsaturated $H_2Os_3(CO)_9L$ (L = CO, PEt_3) [10]. Previously the hydrogenation of the CN unit had been reported in the case of activated nitriles such as trifluoroacetonitrile, in the presence of the same cluster $H_2Os_3(CO)_{10}$ [11–13].

In this paper we describe the reactions of $Ru_3(CO)_{12}$ and benzonitriles substituted on the aromatic ring mainly with the aim of investigating the role of the acetic acid in the hydrogenation process of the CN unit.

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*Ref. 1.

0020-1693/86/$3.50

TABLE I. Spectroscopic Data of the Complexes Obtained from $Ru_3(CO)_{12}$, Benzonitrile and Its Substituted Derivatives

Complexes	IR data	^1H NMR data[b]		
	$\nu(CO)$ (cm^{-1})[a]	proton	τ	J (Hz)
$(\mu\text{-H})Ru_3(CO)_{10}(\mu\text{-NCHC}_6H_4X)$				
X = H **2a**	2101(mw), 2064(vs), 2054(vs),	CH	1.05(d)	1.5
	2024(vs) 2018(s), 2010(sh),	C_6H_5	2.35–2.65(m)	
	2006(ms), 1991(vw)	μ-H	23.28(d)	1.5
X = *p*-OCH_3 **2b**	2100(mw), 2063(vs), 2053(vs),	CH	1.15(d)	1.5
	2023(vs), 2017(s), 2009(m),	C_6H_4	2.34–2.97(m)	8.8
	2004(ms), 1989(vw)	OCH_3	6.13(s)	
		μ-H	23.28(d)	1.5
X = *p*-NO_2 **2c**	2104(mw), 2068(vs), 2058(vs),	CH	0.30(d)	1.4
	2029(vs), 2020(s), 2014(sh),	C_6H_4	1.60–2.19(m)	1.8
	2009(ms), 1995(vw)	μ-H	23.33(d)	1.4
$(\mu\text{-H})Ru_3(CO)_{10}(\mu\text{-NHCH}_2C_6H_4X)$				
X = H **3a**	2100(m), 2064(vs), 2049(vs),	C_6H_5	2.6–2.8(m)	
	2024(vs), 2009(s), 1999(s),	NH	4.95(br)	
	1992(m), 1980(m), 1965(w)	CH_2	6.18(d)	7.2
		μ-H	23.52(d)	1.6
X = *p*-OCH_3 **3b**	2099(mw), 2064(vs), 2049(vs),	C_6H_4	2.82–3.07(m)	8.8
	2024(vs), 2009(s), 1998(s)	NH	5.08(br)	
	1991(mw), 1980(mw), 1965(vw)	OCH_3	6.17(s)	
		CH_2	6.26(d)	7.2
		μ-H	23.55(d)	1.6
$(\mu\text{-H})_2Ru_3(CO)_9(\mu_3\text{-NCH}_2C_6H_4X)$				
X = *p*-OCH_3 **4b**	2109(mw), 2076(s), 2052(vs),	C_6H_4	2.78–3.09(m)	8.8
	2043(ms), 2037(mw), 2009(s),	CH_2	5.02(s)	
	1996(m), 1984(w)	OCH_3	6.20(s)	
		μ-H	27.17(s)	
X = *p*-NO_2 **4c**	2112(mw), 2078(s), 2054(vs),	C_6H_4	1.74–2.51(m)	8.7
	2047(ms), 2040(w), 2008(s),	CH_2	4.88(s)	
	1997(m), 1987(w)	μ-H	27.09(s)	

[a] Measured in n-hexane solution. [b] Measured in $CDCl_3$ solution.

Results and Discussion

Reactions of $Ru_3(CO)_{12}$ with p-Methoxybenzonitrile

In refluxing cyclohexane, *p*-methoxybenzonitrile (L) readily reacts with $Ru_3(CO)_{12}$ in the presence of acetic acid to give $H_4Ru_4(CO)_{12}$ (**1**) and a compound which is characterized by mass spectrometry as $Ru_3(CO)_{10}(L + 4H)$ (**3b**).

The ^1H NMR spectrum in deuterochloroform (Table I) shows a one proton hydride signal at τ 23.55 as a doublet ($J = 1.6$ Hz), a two proton doublet at τ 6.26 ($J = 7.2$ Hz) due to the benzylic CH_2 protons, a three proton singlet at τ 6.17 assigned to the OCH_3 protons, a broad signal at τ 5.08 due to NH (exchangeable with D_2O). The AA'BB' system at τ 2.82 and 3.07 (main $J = 8.8$ Hz) is due to the four benzene protons. The $\nu(CO)$ IR spectrum in n-hexane solution exhibits absorption bands in the terminal carbonyl groups region as shown in Table I. The electron impact mass spectrum displays the molecular ion at m/z 723 followed by the loss of ten CO groups. From these spectroscopic data it appears that *p*-methoxybenzonitrile, in complex **3b**, is coordinated to the Ru_3 cluster with complete hydrogenation of the CN bond. Comparison of IR and ^1H NMR data of **3b** with those found for $(\mu\text{-H})Ru_3(CO)_{10}(\mu\text{-NHCH}_2Ph)$ (**3a**) also reported in Table I, indicates that the structure of **3b** is similar to that of **3a**, which has been reported previously [6].

If the reaction of $Ru_3(CO)_{12}$ and *p*-methoxybenzonitrile in refluxing cyclohexane is carried out under a stream of molecular hydrogen and in the absence of acetic acid, **3b** is not found amongst the reaction products, but, in addition to $H_4Ru_4(CO)_{12}$, two different complexes, **2b** and **4b**, are isolated. The ^1H NMR spectrum of **2b**, in deuterochloroform, shows a one proton hydride signal at τ 23.28 (J = 1.5 Hz) as a doublet, a three proton singlet at τ 6.13 due to the OCH_3 protons, an AA'BB' system at τ 2.34 and 2.97 (main J = 8.8 Hz) due to the four benzene protons and a one proton doublet at τ 1.15 (J = 1.5 Hz) due to the =CH proton. These data together with the IR absorption bands in the CO groups region are reported in Table I. The electron impact mass spectrum displays the molecular ion at m/z 721 followed by the loss of ten carbonyl groups.

These findings indicate that **2b** can be formulated as $(\mu\text{-H})Ru_3(CO)_{10}(\mu\text{-NCHC}_6H_4OMe)$ showing a structure comparable to that of **2a**, which has been reported in a previous paper [7].

Compound **4b**, analyzed by ^1H NMR spectroscopy, shows a two proton hydride signal at τ 27.17 as a singlet, a three proton singlet at τ 6.20 due to the OCH_3 protons, a two proton singlet at τ 5.02 due to the benzylic CH_2 protons and an AA'BB' system at τ 2.78 and 3.09 (main J = 8.8 Hz) due to the four benzene protons. The ν(CO) IR and ^1H NMR data are reported in Table I. The electron impact mass spectrum of **4b** shows the molecular ion at m/z 695, followed by the loss of nine carbonyl groups.

On the basis of these results the molecular formula of **4b** is $Ru_3(CO)_9(L + 4H)$, where two of the added hydrogens are hydride ligands and two are bound to the carbon of the CN unit, whilst no hydrogen is bound to nitrogen. The structure of **4b** has been fully elucidated by a X-ray structural analysis (see below).

Reactions of $Ru_3(CO)_{12}$ with p-Nitrobenzonitrile

$Ru_3(CO)_{12}$ and *p*-nitrobenzonitrile (L') readily react under a stream of H_2 and in refluxing cyclohexane to give two complexes identified by mass spectrometry as $Ru_3(CO)_{10}(L' + 2H)$ (**2c**) and $Ru_3(CO)_9(L' + 4H)$ (**4c**) and the well-known $H_4Ru_4(CO)_{12}$ (**1**). The proton NMR spectrum of **2c** in deuterochloroform (Table I) shows a one proton doublet at τ 23.33 (J = 1.4 Hz) due to the hydride ligand, long range coupled with a one proton doublet at τ 0.30, which can be assigned to the =CH proton. The AA'BB' system at τ 1.60 and 2.19 (main J = 1.8) is due to the four benzene protons. From these data and from IR spectrum in the CO group region (Table I) the structure of **2c** should be similar to those of **2a** and **2b**. The proton NMR spectrum of **4c** displays a two protons hydride signal at τ 27.09 as a singlet, a two proton singlet at τ 4.88 due to the benzylic protons, an AA'BB' system at τ 1.74 and 2.51 (main J = 8.7 Hz) due to the four benzene protons. The spectroscopic data (Table I) indicate that **4c** is structurally analogous to **4b**.

The reaction of *p*-nitrobenzonitrile, $Ru_3(CO)_{12}$ and acetic acid in refluxing cyclohexane only leads to decomposition and no $(\mu\text{-H})Ru_3(CO)_{10}(\mu\text{-NHCH}_2\text{-C}_6H_4NO_2)$ is formed, contrary to what was observed with *p*-methoxybenzonitrile and benzonitrile [7].

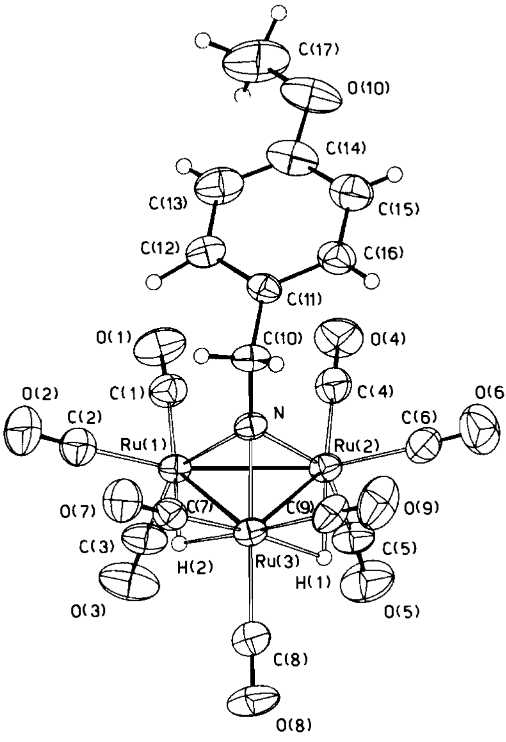


Fig. 1. View of the molecular structure of **4b** along with the atomic numbering system. The non-hydrogen atoms are represented by thermal ellipsoids at 40% probability levels.

X-ray Crystal Structure of $(\mu\text{-H})_2Ru_3(CO)_9(\mu_3\text{-NCH}_2C_6H_4OMe)$, 4b

An ORTEP [14] view of the molecule is shown in Fig. 1 with the atomic numbering scheme; selected bond distances and angles are given in Tables II and III respectively. The structure of **4b** consists of an isosceles triangle of Ru atoms (Ru–Ru bond distances: 2.676(2), 2.799(2) and 2.800(2) Å) with the two longer edges bridged by hydride ligands. The high e.s.d.s of the Ru–H bonds preclude any discussion on the asymmetry or not of these bridges. The two Ru_2H planes form dihedral angles of 136.9 and 127.1° with the Ru_3 plane. Three terminal carbonyl groups are coordinated to each metal atom.

The N atom from the $NCH_2C_6H_4OMe$ ligand almost symmetrically caps the metal triangle on the opposite side with respect to the hydride bridges and lies 1.280(5) Å out of this triangle (the Ru–N distances range from 2.030(5) to 2.056(5) Å).

TABLE II. Bond Distances (A) for $(\mu\text{-H})_2Ru_3(CO)_9(\mu_3\text{-}NCH_2C_6H_4OMe)$

Ru(1)–Ru(2)	2.676(2)	N–C(10)	1.464(8)
Ru(1)–Ru(3)	2.800(2)	C(10)–C(11)	1.491(10)
Ru(2)–Ru(3)	2.799(2)	C(11)–C(12)	1.378(11)
Ru(1)–N	2.046(6)	C(12)–C(13)	1.391(13)
Ru(2)–N	2.030(5)	C(13)–C(14)	1.369(15)
Ru(3)–N	2.056(5)	C(14)–C(15)	1.368(16)
Ru(1)–C(1)	1.891(8)	C(15)–C(16)	1.368(12)
Ru(1)–C(2)	1.921(9)	C(11)–C(16)	1.379(11)
Ru(1)–C(3)	1.908(8)	C(14)–O(10)	1.359(12)
Ru(2)–C(4)	1.891(8)	O(10)–C(17)	1.411(20)
Ru(2)–C(5)	1.915(7)	C(1)–O(1)	1.125(10)
Ru(2)–C(6)	1.935(9)	C(2)–O(2)	1.122(12)
Ru(3)–C(7)	1.917(8)	C(3)–O(3)	1.131(10)
Ru(3)–C(8)	1.925(7)	C(4)–O(4)	1.126(10)
Ru(3)–C(9)	1.918(9)	C(5)–O(5)	1.119(9)
Ru(1)–H(2)	1.75(8)	C(6)–O(6)	1.111(13)
Ru(3)–H(2)	1.65(9)	C(7)–O(7)	1.126(9)
Ru(2)–H(1)	1.87(9)	C(8)–O(8)	1.124(9)
Ru(3)–H(1)	1.85(9)	C(9)–O(9)	1.120(13)

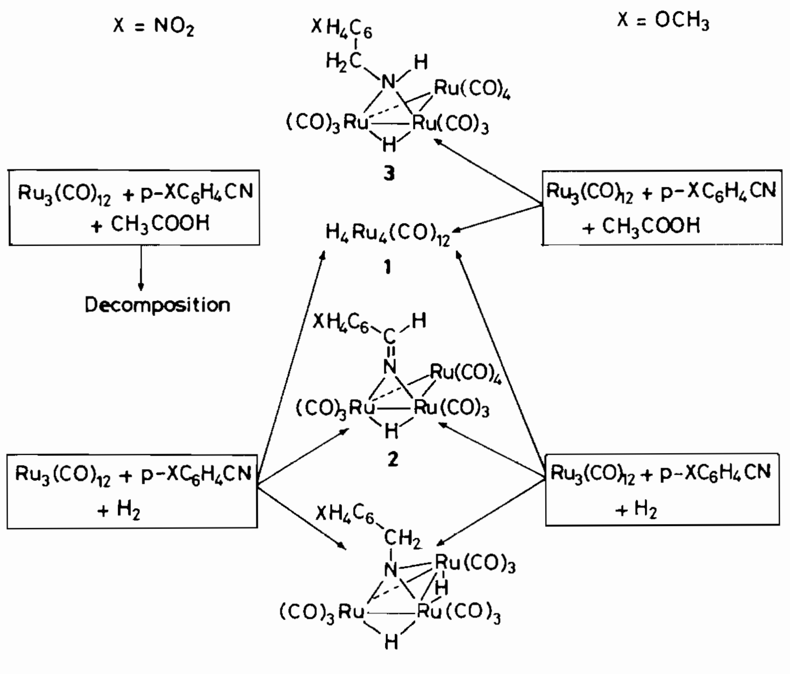
The structure of **4b** is closely comparable to those of $(\mu\text{-H})_2Os_3(CO)_9(\mu_3\text{-}NCH_2CF_3)$ [13] and $(\mu\text{-H})_2Ru_3(CO)_9(\mu_3\text{-}NPh)$ [15]. Also the main structural features show the same trend as **4b**. In the former the Os–Os bonds are 2.717(1), 2.856(1) and 2.863(1) Å and the Os–N bonds range from 2.056(12) to 2.119(13) Å, in the latter the Ru–Ru bonds are 2.680(1), 2.804(1) and 2.806(1) Å and the Ru–N bonds range from 2.059(4) to 2.074(4) Å.

TABLE III. Selected Bond Angles (°) for $(\mu\text{-H})_2Ru_3(CO)_9(\mu_3\text{-}NCH_2C_6H_4OMe)$

Ru(2)–Ru(1)–Ru(3)	61.4(1)	Ru(2)–Ru(3)–N	46.4(2)
Ru(1)–Ru(2)–Ru(3)	61.5(1)	C(1)–Ru(1)–C(2)	94.0(4)
Ru(1)–Ru(3)–Ru(2)	57.1(1)	C(1)–Ru(1)–C(3)	88.8(4)
Ru(2)–Ru(1)–C(1)	93.4(3)	C(2)–Ru(1)–C(3)	99.7(4)
Ru(2)–Ru(1)–C(2)	152.8(3)	C(4)–Ru(2)–C(5)	91.8(4)
Ru(2)–Ru(1)–C(3)	106.7(3)	C(4)–Ru(2)–C(6)	91.3(4)
Ru(2)–Ru(1)–N	48.7(2)	C(5)–Ru(2)–C(6)	99.9(4)
Ru(3)–Ru(1)–C(1)	148.9(3)	C(7)–Ru(3)–C(8)	93.7(3)
Ru(3)–Ru(1)–C(2)	101.3(3)	C(7)–Ru(3)–C(9)	95.1(4)
Ru(3)–Ru(1)–C(3)	114.6(3)	C(8)–Ru(3)–C(9)	92.8(4)
Ru(3)–Ru(1)–N	47.1(2)	Ru(1)–N–Ru(2)	82.1(2)
Ru(1)–Ru(2)–C(4)	94.4(3)	Ru(1)–N–Ru(3)	86.1(2)
Ru(1)–Ru(2)–C(5)	105.0(3)	Ru(2)–N–Ru(3)	86.5(2)
Ru(1)–Ru(2)–C(6)	154.3(3)	Ru(1)–N–C(10)	132.5(4)
Ru(1)–Ru(2)–N	49.2(2)	Ru(2)–N–C(10)	132.1(5)
Ru(3)–Ru(2)–C(4)	147.7(3)	Ru(3)–N–C(10)	121.7(5)
Ru(3)–Ru(2)–C(5)	114.1(3)	Ru(1)–C(1)–O(1)	175.0(7)
Ru(3)–Ru(2)–C(6)	102.3(2)	Ru(1)–C(2)–O(2)	177.8(8)
Ru(3)–Ru(2)–N	47.1(2)	Ru(1)–C(3)–O(3)	177.0(8)
Ru(1)–Ru(3)–C(7)	94.9(2)	Ru(2)–C(4)–O(4)	178.6(7)
Ru(1)–Ru(3)–C(8)	122.4(3)	Ru(2)–C(5)–O(5)	176.2(8)
Ru(1)–Ru(3)–C(9)	142.6(3)	Ru(2)–C(6)–O(6)	177.4(7)
Ru(1)–Ru(3)–N	46.8(2)	Ru(3)–C(7)–O(7)	176.3(7)
Ru(2)–Ru(3)–C(7)	142.1(2)	Ru(3)–C(8)–O(8)	178.8(7)
Ru(2)–Ru(3)–C(8)	122.1(2)	Ru(3)–C(9)–O(9)	178.2(8)
Ru(2)–Ru(3)–C(9)	95.0(3)	N–C(10)–C(11)	113.5(6)

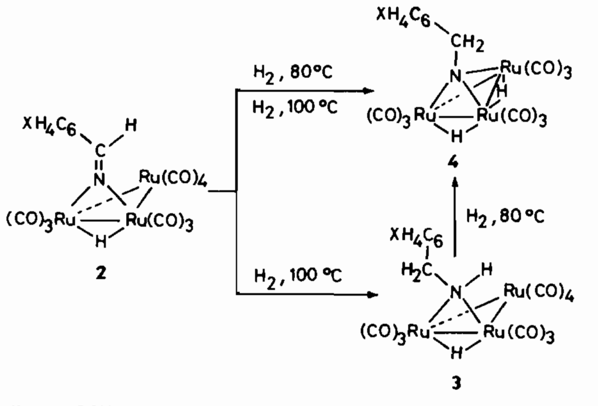
Reaction Sequences

As reported in Scheme 1 different reaction pathways prevail in the presence of molecular hydrogen or



Scheme 1.

acetic acid. Complexes **2** and **4** are formed under a stream of hydrogen with both *p*-methoxybenzonitrile and *p*-nitrobenzonitrile. Only compound **3b** is obtained from the reaction of $Ru_3(CO)_{12}$ and *p*-methoxybenzonitrile in the presence of acetic acid, whilst in the same conditions *p*-nitrobenzonitrile leads to decomposition and no complex **3c** is isolated.



Scheme 2

From Scheme 2 it appears that complexes **4** can be obtained by refluxing complexes **2** in cyclohexane under a stream of hydrogen. In the same experimental conditions complexes **4** are obtained also from complexes **3**. In n-octane at 100 °C under a stream of molecular hydrogen from complexes **2** a more efficient conversion of **2** into **4** takes place within shorter reaction times. However traces of complexes **3** are also detected at this higher temperature These results suggest that complexes **4** can be formed through two alternative and parallel pathways (Scheme 2).

The higher temperature required to give an efficient transformation of complexes **2** into **4**, as compared with the temperature used in the reaction of $Ru_3(CO)_{12}$ and benzonitrile under H_2, explains the fact that **4** may not be found amongst the products under the milder temperature and shorter reaction times.

The path leading to complexes **3** is highly favoured by the presence of acetic acid at the expense of the path leading to complexes **2** which is enhanced by molecular hydrogen.

A comparison of the results described above with those previously reported for the system $Ru_3(CO)_{12}$/benzonitrile/acetic acid [7], indicates that the formation of complexes **3** in the presence of acetic acid is significantly enhanced by an electron donor substituent on the phenyl of the nitrile such as the methoxy group in the *para* position. When the substituent is an electron withdrawing group, such as $-NO_2$ in the *para* position, only decomposition occurs and no complex **3c** is isolated, unlike what was observed with both benzonitrile and *p*-methoxybenzonitrile. These results strongly suggest that the role of acetic acid in these systems is mainly in relation to the activation of nitriles.

Experimental

Materials

All chemicals used were reagent grade. $Ru_3(CO)_{12}$ was prepared from $RuCl_3xH_2O$ (Johnson Matthey) according to the literature [16]. *p*-Methoxybenzonitrile and *p*-nitrobenzonitrile were from Jannsen, glacial acetic acid and Kieselgel 60PF (254-366) were from Merck. Solvents from Carlo Erba, were redistilled and dried over molecular sieves. Hydrogen and nitrogen, from SIAD, were dried before use.

Spectroscopic Characterization

Infrared spectra were recorded from n-hexane solutions on a Perkin-Elmer 580B spectrophotometer. Mass spectra were recorded on a double focusing Kratos MS 80 operating with direct inlet system at 70 eV. The ^1H NMR spectra were recorded from $CDCl_3$ solutions on a Varian XL200 spectrometer at 200057 MHz. A 5000 Hz sweep width was used with a digital resolution of 0.156 Hz/point. TMS was used as internal reference. The spectroscopic data of all the complexes isolated are reported in Table I.

Reaction of p-Methoxybenzonitrile with Glacial Acetic Acid and $Ru_3(CO)_{12}$

A solution containing 0.078 mmol $Ru_3(CO)_{12}$, 0.87 mmol glacial acetic acid and 0.48 mmol *p*-methoxybenzonitrile in 60 ml cyclohexane was saturated with nitrogen and then heated to reflux for 4 h. The solution was allowed to cool in a stream of nitrogen and the solvent was removed by evacuation. The residue was dissolved in a small volume of petroleum ether and separated by thin layer chromatography on 20 X 40 cm plates of Kieselgel 60 PF (254–366) using as eluent petroleum ether/diethyl ether (95/5). Two mobile yellow bands were resolved and were identified as unreacted $Ru_3(CO)_{12}$ with some $H_4Ru_4(CO)_{12}$ (**1**) and as $(\mu\text{-}H)Ru_3(CO)_{10}$-$(\mu\text{-}NHCH_2C_6H_4OMe)$ (**3b**) respectively. When necessary, this last compound was further purified by rechromatography on 20 X 40 cm plates of Kieselgel 60PF (254-366) using as eluent petroleum ether.

Reaction of p-Nitrobenzonitrile with Glacial Acetic Acid and $Ru_3(CO)_{12}$

The reaction of *p*-nitrobenzonitrile with glacial acetic acid and $Ru_3(CO)_{12}$ was carried out following the same procedure described above for *p*-methoxybenzontrile. The same relative amounts of the substituted benzonitrile to acetic acid and $Ru_3(CO)_{12}$

were used. Chromatography on Kieselgel 60PF (254-366) evidenced only the mobile yellow band, identified as unreacted $Ru_3(CO)_{12}$ with some $H_4Ru_4(CO)_{12}$ (**1**), and decomposition products which did not migrate from the origin.

Reaction of p-Methoxybenzonitrile with $Ru_3(CO)_{12}$ in the Presence of H_2 at Atmospheric Pressure

$Ru_3(CO)_{12}$ (0.87 mmol) was suspended in 60 ml cyclohexane and 0.48 mmol *p*-methoxybenzonitrile were added with stirring. Hydrogen was bubbled through the suspension for 15 min at room temperature and then heated to reflux for 4 h keeping a constant and slow flow of hydrogen through the solution. After cooling to room temperature, solvent was removed under vacuum and the residue taken up in a small volume of petroleum ether. Thin layer chromatrogaphy on 20 × 40 cm plates of Kieselgel 60PF (254-366) using petroleum ether/diethyl ether (95/5) as eluent gave three mobile yellow bands which were identified, in order of decreasing mobility, as a mixture of some unreacted $Ru_3(CO)_{12}$ and $H_4Ru_4(CO)_{12}$ (**1**), $(\mu\text{-H})Ru_3(CO)_{10}(\mu\text{-NCHC}_6H_4\text{-OMe})$ (**2b**) and $(\mu\text{-H})_2Ru_3(CO)_9(\mu_3\text{-NCH}_2C_6H_4OMe)$ (**4b**).

Reaction of p-Nitrobenzonitrile with $Ru_3(CO)_{12}$ in the Presence of H_2 at Atmospheric Pressure

The reaction of *p*-nitrobenzonitrile with $Ru_3(CO)_{12}$ and H_2 at atmospheric pressure was carried out as described above for *p*-methoxybenzonitrile using the same molar ratio of substituted benzonitrile to $Ru_3(CO)_{12}$. Chromatography on 20 × 40 cm thin layer plates of Kieselgel 60PF (254-366) (petroleum ether/diethyl ether 95/5) evidenced three yellow mobile bands identified, in order of decreasing mobility, as $H_4Ru_4(CO)_{12}$ (**1**) with some unreacted $Ru_3(CO)_{12}$, $(\mu\text{-H})Ru_3(CO)_{10}(\mu\text{-NCHC}_6H_4NO_2)$ (**2c**) and $(\mu\text{-H})_2Ru_3(CO)_9(\mu_3\text{-NCH}_2C_6H_4NO_2)$ (**4c**).

Reaction of $(\mu\text{-H})Ru_3(CO)_{10}(\mu\text{-NCHC}_6H_4X)$ (X = H, OMe, NO_2) with H_2 at Atmospheric Pressure

Approximately 30 mg of $(\mu\text{-H})Ru_3(CO)_{10}(\mu\text{-NCHC}_6H_4X)$ (**2**) (X = H, OMe, NO_2) were dissolved in 60 ml n-octane. The solution was saturated with hydrogen at room temperature and then heated at 100 °C for 4 h allowing a slow and constant flow of hydrogen through the solution. After cooling to room temperature, solvent was evaporated under reduced pressure and residue was taken up in a small volume of petroleum ether. Chromatography on Kieselgel 60PF (254-366) (eluent petroleum ether/diethyl ether 95/5) gave two yellow mobile bands identified as unaltered $(\mu\text{-H})Ru_3(CO)_{10}(\mu\text{-NCHC}_6H_4\text{-X})$ (**2**) and as $(\mu\text{-H})_2Ru_3(CO)_9(\mu_3\text{-NCH}_2C_6H_4X)$ (**4**). Minor amounts of $(\mu\text{-H})Ru_3(CO)_{10}(\mu\text{-NHCH}_2C_6H_4X)$ (**3**) and decomposition products, which remained at the origin, were also found.

TABLE IV. Experimental Data for the X-ray Diffraction Study on **4b**

$C_{17}H_{11}NO_{10}Ru_3$	
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	11.255(6)
b (Å)	12.205(8)
c (Å)	8.831(6)
α (°)	108.98(2)
β (°)	99.43(2)
γ (°)	95.78(2)
V (Å^3)	1116(1)
Z	2
$F(000)$	664
D (g cm^{-3})	2.061
M_r	692.48
Crystal dimensions (mm)	0.12 × 0.14 × 0.21
Linear absorption (cm^{-1})	20.17
Diffractometer	Siemens AED
Scan type	$\theta/2\theta$
Scan speed	3–12° θ/min
Scan width	$(\theta - 0.5)-[\theta + (0.5 + \Delta\theta)]$ $\{\Delta\theta = [(\lambda_{\alpha_2} - \lambda_{\alpha_1})/\lambda]\tan\theta\}$
Radiation	Nb-filtered Mo Kα (λ = 0.7107 Å)
2θ range (°)	6–52
Reflections measured	$\pm h, \pm k, l$
Standard reflections	1 measured every 50 reflections
Unique total data	4291
Unique observed data $[I > 2\sigma(I)]$	2938
No. of variables	324
R	0.0318
R_w	0.0435

X-ray Crystallographic Data Collection

A prismatic green–yellow crystal of **4b** was selected for the X-ray analysis. The crystallographic data are summarized in Table IV. Accurate unit-cell dimensions were determined by a least-squares fit of the θ values (in the range 10–16°) of 30 carefully centered reflections chosen from different regions of the reciprocal space. Intensity data were collected at room temperature, the individual reflection profiles having been analyzed following Lehmann and Larsen [17]. The structure amplitudes were obtained after usual Lorentz and polarization reduction* [18]. No absorption correction was carried out in view of the low absorbance of the sample [max(μR) = 0.20]. Only the observed reflections were used in the structure solution and refinement.

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*Data reduction, structure solution, and refinement were carried out on the CRAY X-MP(12 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Bologna and on the GOULD-SEL 32/77 computer of the Centro di Studi per la Strutturistica Diffrattometrica del C.N.R. Parma, using programs from ref. 18.

Structure Solution and Refinement

The structure was solved by using direct and Fourier methods and refined by full matrix least squares, first with isotropic and then with anisotropic thermal parameters for all non-hydrogen atoms. All the hydrogen atoms were clearly located in the final difference Fourier and refined isotropically. The function minimized during the refinement was $\Sigma w|\Delta F|^2$. The weighting scheme used in the last cycles of the refinement was $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$; at convergence the values for K and g were 0.5731 and 0.0045 respectively. The final R and R_w values were 0.0318 and 0.0435 ($R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$). The scattering factors were taken from ref. 19 with the exceptions of those of the hydrogen atoms which were taken from ref. 20. Corrections for the real and imaginary components of the anomalous dispersion were made for the non hydrogen atoms. Final atomic coordinates are listed in Table V.

TABLE V. Positional Parameters ($\times 10^4$) and Their Estimated Standard Deviations for the Non-hydrogen atoms of 4b

Atom	*x/a*	*y/b*	*z/c*
Ru1	7660(1)	1417(1)	5304(1)
Ru2	6416(1)	2351(1)	3315(1)
Ru3	8573(1)	1551(1)	2593(1)
O1	6456(6)	2463(5)	8131(7)
O2	9954(7)	1305(7)	7575(9)
O3	6124(6)	−937(5)	4701(9)
O4	5106(6)	3718(6)	5846(7)
O5	4159(6)	518(6)	1524(8)
O6	6126(7)	4099(6)	1536(9)
O7	11209(5)	1689(5)	4226(8)
O8	8554(5)	−612(5)	−372(7)
O9	9105(6)	3224(6)	795(8)
O10	6795(7)	7167(5)	9816(10)
N	8175(5)	2790(4)	4576(6)
C1	6895(7)	2114(6)	7052(9)
C2	9112(8)	1327(7)	6714(10)
C3	6712(7)	−61(7)	4965(10)
C4	5609(7)	3214(7)	4915(9)
C5	4966(7)	1223(7)	2197(9)
C6	6234(7)	3442(7)	2152(9)
C7	10244(7)	1626(6)	3571(9)
C8	8568(6)	180(7)	732(9)
C9	8926(7)	2600(7)	1453(9)
C10	8972(7)	3926(6)	5434(9)
C11	8426(6)	4775(5)	6648(8)
C12	8470(8)	4761(7)	8210(9)
C13	7932(9)	5549(8)	9307(11)
C14	7347(8)	6356(7)	8845(12)
C15	7336(8)	6401(8)	7315(12)
C16	7849(7)	5612(6)	6231(10)
C17	6699(19)	7088(15)	11352(18)

Supplementary Material

The found coordinates for the hydrogen atoms, the thermal parameters and a listing of observed and calculated structural factors are available from the authors on request.

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