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REACTIONS BETWEEN 8-QUINOLINOL (AND RELATED LIGANDS) AND TRIRUTHENIUM DODECACARBONYL; X-RAY CRYSTAL STRUCTURE DETERMINATION OF $Ru_3(CO)_8(C_9H_6NO)_2$

J.A. VAN DOORN and P.W.N.M. VAN LEEUWEN

Koninklijke/Shell-Laboratorium, Amsterdam, (Shell Research B.V.), Badhuisweg 3, Amsterdam (The Netherlands)

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Summary

8-Quinolinol reacts with $Ru_3(CO)_{12}$ to give $Ru_3(CO)_8(C_9H_6NO)_2$ and $Ru(CO)_2(C_9H_6NO)_2$. A single-crystal X-ray study of the cluster compound shows that the three ruthenium atoms define an isosceles triangle, with two distances of 2.77 Å and one of 3.04 Å. Since both metalated oxygens act as three-electron donors (Ru—O distances 2.12 and 2.18 Å), the cluster is a fifty-electron species with a formal zero bond order for the elongated Ru—Ru bond. Four other hydroxyhydrocarbylpyridine compounds also give complexes of composition $Ru_3(CO)_8(L)_2$ which probably have analogous structures.

Introduction

Many metal carbonyl cluster compounds have been prepared and their structures determined. Triangular metal carbonyls of osmium and ruthenium have been treated with aromatic amines [1,2], N- and C-metalation often being observed. Triosmium clusters containing phenoxy [3] and methoxy [4] ligands have also been studied in detail. These clusters maintain a structure based on an equilateral triangle of metals and only rarely is an isosceles triangle formed, with either one shorter bond as for $H_2Os_3(CO)_{10}$ [5] or one longer bond as for $(OCH_3)_2Os_3(CO)_{10}$ [6] and $Ru_3(CO)_{10}(NO)_2$ [7].

We report below on the preparation and structure of trinuclear ruthenium clusters and mononuclear ruthenium compounds with 8-quinolinol and related ligands. With these ligands only O-metalation takes place. The composition of the cluster compounds $Ru_3(CO)_8$(oxyalkylpyridine)$_2$ gives no information about the type of cluster that is formed, since the number of valence electrons depends on the mode of coordination. The crystal structure of one such a complex, that with 8-quinolinol as the ligand, has been determined.

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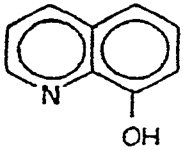
Results and discussion

Complexes formed between 8-quinolinol and $Ru_3(CO)_{12}$

Two complexes were obtained from the reaction of 8-quinolinol with $Ru_3(CO)_{12}$.



8—QUINOLINOL

The main product, with composition $Ru_3(CO)_8(C_9H_6NO)_2$, was obtained in 76% yield, while a second product, identified as $Ru(CO)_2(C_9H_6NO)_2$, was formed in 6% yield based on $Ru_3(CO)_{12}$. The latter compound was produced in 24% yield when $H_4Ru_4(CO)_{12}$ was used as the starting material.

Structure of $Ru_3(CO)_8(C_9H_6NO)_2$

This compound is a triruthenium cluster, as is apparent from the mass spectral data. The infrared spectrum in chloroform contains a number of bands in the 2072—1930 cm^{-1} region, indicating the presence of several types of terminal carbonyl ligands. The ^1H NMR spectrum in acetone-d_6 (Table 1) shows only one type of quinolin-8-oxy ligand, which implies that the two ligands occupy (within NMR limits) equivalent sites on the cluster. No hydroxyl or hydride hydrogens are detected. Moreover, the IR spectrum of $Ru_3(CO)_8(C_9H_6NO)_2$ prepared from O-deuterated 8-quinolinol is identical with that of the complex from the protium analogue.

Although the eighteen-electron rule has less general validity in cluster chemistry than in the chemistry of mononuclear species [6], triangular cluster compounds with very few exceptions [8] contain forty-eight valence electrons. With 46 electrons as in $H_2Os_3(CO)_{10}$ [5,6] one bond is shorter (formally being a double bond), and with 50 electrons one bond is elongated and has a formal bond order of zero [6,7], as is the case for $(OCH_3)_2Os(CO)_{10}$ and $Ru_3(CO)_{10}(NO)_2$. The present compound $Ru_3(CO)_8(C_9H_6NO)_2$ contains either 46 valence electrons (Ia), with both oxygen atoms acting as one-electron ligands, or 50 valence electrons (Ib), with the oxygen atoms acting as three-electron donors. If these were two different oxygens, a one-electron donor and a three-electron donor, an equilateral triangular cluster with 48 electrons might be obtained (Ic), but this does not seem likely. For simplicity, for each electronic configuration only one structural isomer is depicted. Isomer Ia would be of particular interest because of the reactions which could be expected to take place at the unsaturated double bond of the cluster.

We were unable to establish the structure of $Ru_3(CO)_8(C_9H_6NO)_2$ from the data presented above, so we undertook a single-crystal X-ray analysis, the result of which is shown in Fig. 1. Some selected bond distances and bond angles are given in Tables 2 and 3. The two ligands are bonded to only two ruthenium

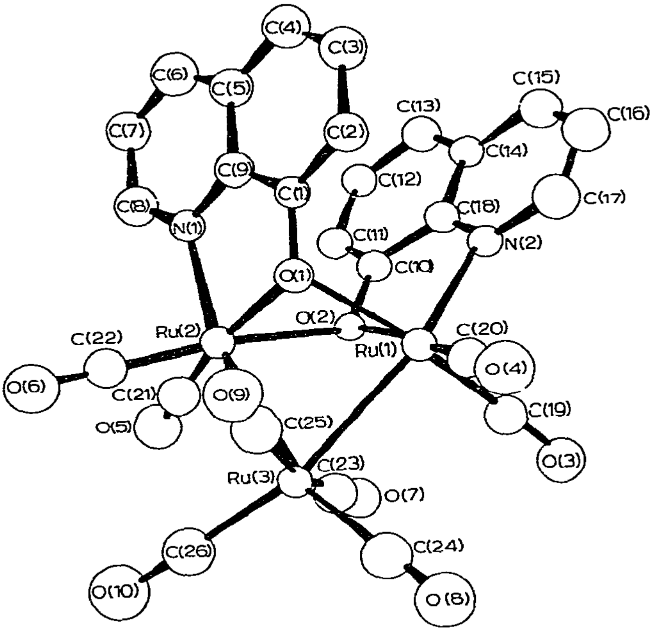
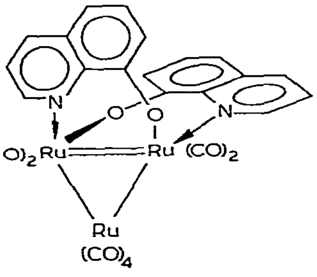
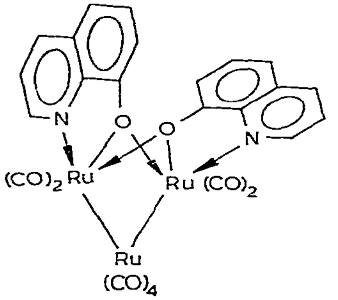


Fig. 1. The molecular structure of $Ru_3(CO)_8(C_9H_6NO)_2$ and the atom numbering scheme.

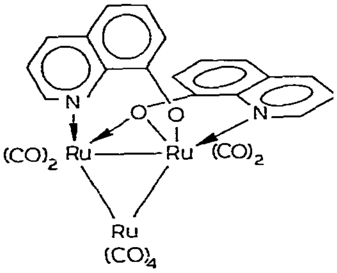
atoms. The data show that the three ruthenium atoms form an isosceles triangle with two Ru—Ru distances of 2.77 Å and one of 3.04 Å. The Ru—Ru distance in $Ru_3(CO)_{12}$ amounts to 2.85 Å [9].



(Ia)



(Ib)



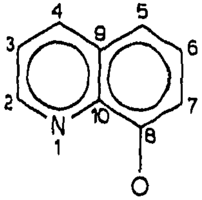
(Ic)

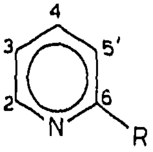
The distances between ruthenium (1) and oxygens (1) and (2) (derived from 8-quinolinol) (2.19 and 2.12 Å) are very similar and so are the Ru(2)—O(1) and Ru(2)—O(2) distances (2.13 and 2.18 Å). This nearly symmetric bonding indicates that the oxygens act as three-electron donors, which in terms of the noble gas formalism means that there will be no Ru(1)—Ru(2) bond, as is shown in Ib. The elongated Ru(1)—Ru(2) bond distance of 3.04 Å may well be a result of this. The structure found is very similar to that of nitrosyl compound $Ru_3(CO)_{10}(NO)_2$ [7] and the osmium cluster $(OCH_3)_2Os_3(CO)_{10}$ [6]. In the former compound the Ru—Ru distances are 2.86, 2.87 and 3.15 Å and slightly longer

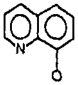
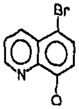
(Continued on p. 304)

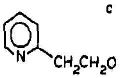
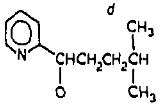
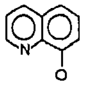
TABLE 1

90 MHz ^1H NMR SPECTRAL DATA FOR THE CLUSTER COMPLEXES $Ru_3(CO)_8L_2$ AND MONOMERIC SPECIES $Ru(CO)_2L_2$





Cluster, L =	Chemical shifts (δ, ppm) of hydrogens at positions [a]					
	2	3	4	5′	5/7	6
	9.06(d1, d5)	7.48(d5, d8)	8.08(d1, d8)	—	~6.8	~6.8
	9.20(d1, d5)	7.69(d5, d8.5)	8.33(d1.5, d8.5)	—	6.70(d8.5)	7.20(d8.5)

 [c]		8.99(d5, d1.5, d1)	7.52(d7.5, d5, d1)	7.92(d7.5, d1.5)	7.41(d7.5 + uc)	—	—
 [d]		8.92(d5)	7.56("t"8)	7.89("t"8)	7.02(d8)	—	—
Monomer, L = 	Ia	9.03(d5, d1) 7.4(d5, d1)	7.67(d8, d5) 7.28(d8, d5)	8.52(d8, d1) 8.37(d8, d1)		7.1/7.1 6.7(d8, d1)/7.1	7.39(t8) ~7.4
	Ib,c	8.99(d5, d1)	7.61(d8.5, d5)	8.49(d8.5, d1.5)		6.73(d7.5, d2)/7.07(d7.5, d2)	7.41(t7.5)

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[a] Coupling constants, in Hz, given in parentheses, d = doublet, t = triplet, "t" = three lines, expected two (overlapping) doublets, uc = unresolved coupling. Measured in perdeuterioacetone at 27°C. [b] CH_2 hydrogens gave rise to two signals: at δ 5.06 ppm (d18 Hz) and δ 4.23 ppm (d18 Hz). [c] CH_2CH_2 hydrogens gave rise to two sets of signals, a multiplet at δ 4.08 ppm corresponding to one hydrogen and a multiplet at ca. δ 3.0 ppm corresponding to three hydrogens. [d] $^{11}CH^{12}CH_2{}^{13}CH_2{}^{14}CH(^{15}CH_3)(^{16}CH_3)$ unit gave rise to signals at: δ 3.89 ppm (multiplet) assigned to H at ^{11}C, δ 1.5 ppm (multiplet) assigned to $^{12}CH_2{}^{13}CH_2{}^{14}CH$ unit, two doublets (6 Hz) at δ 0.89 ppm and δ 0.84 ppm assigned to the two methyl groups $^{15}CH_3$ and $^{16}CH_3$.

TABLE 2

TABLE OF SELECTED BOND DISTANCES FOR $Ru_3(CO)_8$(QUINOLIN-8-OXY)$_2$, Ib [a]

Atom 1	Atom 2	Distance (Å)	Atom 1	Atom 2	Distance (Å)
Ru(1)	Ru(2)	3.039(1)	C(1)	O(1)	1.359(5)
Ru(1)	Ru(3)	2.774(1)	C(1)	C(9)	1.411(6)
Ru(2)	Ru(3)	2.773(1)	N(1)	C(9)	1.376(6)
Ru(1)	C(19)	1.817(5)	C(10)	O(2)	1.353(5)
Ru(1)	C(20)	1.820(5)	C(10)	C(18)	1.431(6)
Ru(2)	C(21)	1.819(5)	N(2)	C(18)	1.361(5)
Ru(2)	C(22)	1.818(5)	O(3)	C(19)	1.159(6)
Ru(3)	C(23)	1.928(5)	O(4)	C(20)	1.175(7)
Ru(3)	C(24)	1.895(6)	O(5)	C(21)	1.161(6)
Ru(3)	C(25)	1.924(5)	O(6)	C(22)	1.173(6)
Ru(3)	C(26)	1.899(6)	O(7)	C(23)	1.133(6)
Ru(1)	O(1)	2.188(3)	O(8)	C(24)	1.152(7)
Ru(1)	O(2)	2.117(3)	O(9)	C(25)	1.146(6)
Ru(1)	N(2)	2.157(3)	O(10)	C(26)	1.176(8)
Ru(2)	O(1)	2.126(3)			
Ru(2)	O(2)	2.183(3)			
Ru(2)	N(1)	2.142(3)			

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

than in the present compound. The mode of bonding of 8-quinolinol is reminiscent of that in a 2-naphthoxy complex of osmium [10]. The Ru(3)—C and C—O distances in the carbonyl ligands are not significantly different from those in $Ru_3(CO)_{10}(NO)_2$ or $Ru_3(CO)_{12}$. The Ru(1, 2)—C distances are slightly shorter (1.82 vs ~1.90 Å). The Ru—O—Ru bond angles are 89.6 and 89.9°, slightly smaller than the Os—O—Os bond angles (95°) in $Os_3(CO)_{10}(OCH_3)_2$.

TABLE 3

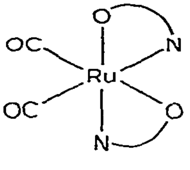
TABLE OF SELECTED BOND ANGLES OF $Ru_3(CO)_8$(QUINOLIN-8-OXY)$_2$, Ib [a]

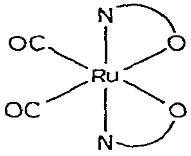
Atom 1	Atom 2	Atom 3	Angle (°)	Atom 1	Atom 2	Atom 3	Angle (°)
Ru(2)	Ru(1)	Ru(3)	56.77(1)	Ru(1)	Ru(3)	C(25)	83.8(2)
Ru(2)	Ru(1)	O(1)	44.40(8)	Ru(1)	Ru(3)	C(26)	163.4(2)
Ru(2)	Ru(1)	O(2)	45.91(7)	Ru(2)	Ru(3)	C(23)	82.6(2)
Ru(2)	Ru(1)	N(2)	108.28(9)	Ru(2)	Ru(3)	C(24)	162.1(2)
Ru(2)	Ru(1)	C(19)	128.2(2)	Ru(2)	Ru(3)	C(25)	83.3(2)
Ru(2)	Ru(1)	C(20)	126.4(2)	Ru(2)	Ru(1)	C(26)	97.1(2)
Ru(3)	Ru(1)	O(1)	82.82(8)	Ru(1)	O(2)	Ru(2)	89.9(1)
Ru(3)	Ru(1)	O(2)	85.93(7)	Ru(1)	O(2)	C(10)	113.8(2)
Ru(3)	Ru(1)	N(2)	163.54(9)	Ru(1)	N(2)	C(18)	112.6(3)
Ru(3)	Ru(1)	C(19)	89.2(1)	O(2)	C(10)	C(18)	118.0(3)
Ru(3)	Ru(1)	C(20)	90.9(2)	N(2)	C(18)	C(10)	117.2(4)
O(1)	Ru(1)	O(2)	76.6(1)	C(23)	Ru(3)	C(24)	97.0(2)
O(1)	Ru(1)	N(2)	90.2(1)	C(23)	Ru(3)	C(25)	163.0(2)
C(19)	Ru(1)	C(20)	87.2(2)	C(23)	Ru(3)	C(26)	94.1(2)
Ru(1)	Ru(2)	Ru(3)	56.78(1)	C(24)	Ru(3)	C(25)	93.5(2)
Ru(1)	Ru(3)	Ru(2)	66.44(1)	C(24)	Ru(3)	C(26)	100.7(3)
Ru(1)	Ru(3)	C(23)	81.9(2)	C(25)	Ru(3)	C(26)	97.0(2)
Ru(1)	Ru(3)	C(24)	95.8(2)				

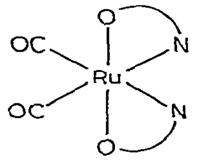
[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

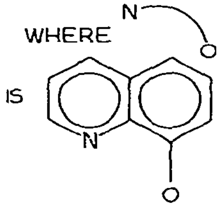
Identification of $Ru(CO)_2(C_9H_6NO)_2$

According to its mass spectrum, the second compound, shown by analysis to have the composition $Ru(CO)_2(C_9H_6NO)_2$, is a monomeric species. The infrared spectrum of the complex in acetone featured two strong carbonyl absorptions at 2055 and 1980 cm^{-1}, indicative of two *cis* carbonyl ligands. Both the ^1H and ^{13}C NMR spectra showed the presence of two non-equivalent quinolin-8-oxy ligands and two non-equivalent carbonyl ligands. Of the three possible *cis*-carbonyl isomers this complex must be IIa.


(IIa)


(IIb)


(IIc)



A detailed analysis of the NMR spectra (Experimental, Table 1) of the compound $Ru(CO)_2(C_9H_6NO)_2$ with structure IIa showed an anomalous chemical shift for both the C and the H atom in the 2-position of one ligand with respect to the free ligand, the other ligand in IIa and the coordinated ligand in the cluster. The upfield shift (1.5 ppm is for ^1H in the 2-position, 4 ppm for ^{13}C in the 2-position) can be explained by a shielding effect caused by the pyridine ring of the second ligand, which is in close proximity to the 2-position, as is shown schematically in Fig. 2. A similar effect was recently observed in a complex of rhodium in which a quinoline hydrogen in the 3-position was shielded by a nearby phenyl ring of triphenylphosphine [11].

When IIa was heated at 170°C a new isomer giving the same mass spectrum

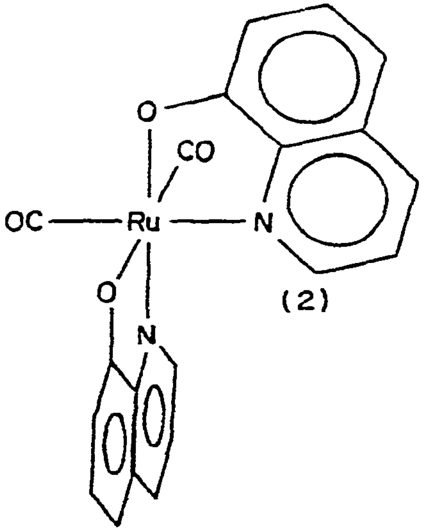
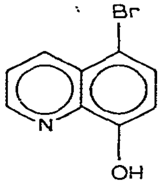


Fig. 2. Schematic structure for IIa showing the close proximity of position 2 of the quinolin-8-oxy ligand in the plane of the paper to the pyridine ring of the other ligand.

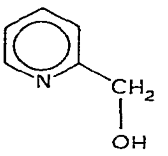
and elemental analysis as IIa was formed. This isomer was also obtained from cluster Ib with concomitant formation of metal. This new isomer also showed two carbonyl stretching frequencies (at 2055 and 1980 cm^{-1}), indicative of a *cis* dicarbonyl complex. The ^{13}C and ^{1}H NMR spectra (Experimental, Table 1) revealed the presence of only one type of quinolin-8-oxy ligand, and two equivalent carbons of the carbon monoxide ligands. Hence, the structure of this thermodynamically favoured isomer is either IIb or IIc, and we cannot at present distinguish between these possibilities.

Complexes $Ru_3(CO)_8(\widehat{NO})_2$ with related ligands

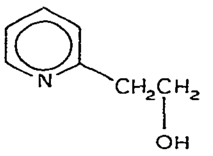
Cluster compounds similar to Ia have been prepared from four other ligands (III—VI). The 1 H NMR data are shown in Table 1.



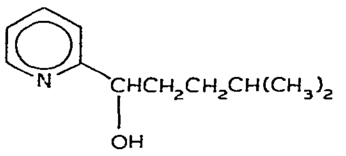
(III)



(IV)



(V)



(VI)

The reaction of $Ru_3(CO)_{12}$ with 5-bromoquinolin-8-ol afforded a mixture of monomeric species and a trimeric cluster. These structures are probably related to IIa, b, c and Ib, respectively. The mixture of monomers was not separated.

The yields of $Ru_3(CO)_8(\widehat{NO})_2$ where $\widehat{NO}$ represents oxy derivatives IV, V and VI were 80, 53 and 69%, respectively. Only in the case of VI was a small amount of another, possibly monomeric, ruthenium complex detected. No X-ray structure determinations have been performed on these compounds, but on the basis of their ^{1}H NMR, IR and elemental analyses their structures are concluded to be analogous to Ib. The triruthenium complex of VI, especially made because of its higher solubility, shows a ^{13}C spectrum which fully supports this conclusion.

The reactions of $Ru_3(CO)_{12}$ with several other compounds with one nitrogen and one oxygen donor ligand have been screened. We could not isolate complexes from α-picolinic acid, *N,N*-dimethylethanolamine and *N,N*-dimethylaminomethyl-2-hydroxybenzene. No reaction took place with 8-isopropylquinoline and 8-methylquinoline, showing that metalation at carbon is more difficult than that at oxygen. The negative result with *N,N*-dimethylethanolamine indicates that the presence of a pyridine nitrogen is necessary for the formation of $Ru_3(CO)_8(\widehat{NO})$.

Experimental

X-ray structure determination

Suitable crystals were obtained by slow evaporation of an acetone solution of the complex. The single-crystal X-ray structure determination of $Ru_3(CO)_8(C_9H_6NO)_2$ was carried out by the Molecular Structure Corporation, P.O. Box DF, College Station, Texas 77840, on an Enraf-Nonius CAD4 diffractometer using Mo-K irradiation at 23 ± 1°C. The crystal was triclinic with space group $P1$ or $P\bar{1}$. Cell constants were obtained by computer-centering of 25 reflections, followed by least-squares refinement of the settling angles. The following value were obtained:

a = 10.734(2) Å α = 99.97(2)°
b = 13.668(6) Å β = 108.56(2)°
c = 9.984(3) Å γ = 80.22(2)°
V = 1357.3(10) Å^3
λ = 0.7107 Å

There were two molecules per unit cell. 4771 independent reflections were collected and the structure was solved using the Patterson method. The Patterson map showed the positions of the three ruthenium atoms. Least-squares refinement of the atoms resulted in agreement factors of R_1 = 0.24 and R_2 = 0.34.

Materials

The ligands were obtained commercially and generally used without further purification. The metal carbonyl clusters were purchased from Strem Chemicals.

Reaction between $Ru_3(CO)_{12}$ and 8-quinolinol

A solution of 5.0 g (7.82 mmol) $Ru_3(CO)_{12}$ and 7.0 g (48.3 mmol) 8-quinolinol in 1200 ml dry THF was refluxed overnight under argon. The solvent was evaporated in vacuum and the residue was thoroughly washed with ether to remove the excess of 8-quinolinol. The resulting mixture of complexes Ib and IIa was separated by washing with methanol (ca. 50 ml). Brilliant yellow crystals of pure Ib (4.886 g; 5.98 mmol; 76.5%) were left on the filter.

Elemental analysis: found: C, 38.0; H, 1.7; N, 3.4; Ru, 35.5. $C_{26}H_{12}N_2O_{10}Ru_3$ calcd.: C, 38.2; H, 1.5; N, 3.4; Ru, 37.1%. IR ($CHCl_3$), CO frequencies, 2072, 2015, 2000, 1980, 1968(sh), and 1930 cm^{-1}; all medium to strong absorptions.

Greenish yellow crystals of pure IIa (1.126 g; 1.38 mmol; 6% on Ru) were obtained from the filtrate after evaporation of the solvent.

Elemental analysis: found: C, 53.1; H, 3.0; N, 6.1. $C_{20}H_{12}N_2O_4Ru$ calcd.: C, 53.7; H, 3.1; N, 6.3%. IR (acetone), CO frequencies, 2055 and 1980 cm^{-1}. ^{13}C NMR (ppm, $CDCl_3$). Carbonyl ligands, δ = 196.0 and 194.7; C(2), δ = 149.8 and 143.2; C(3), δ = 122.0 and 120.8; C(4), δ = 138.8 and 138.8; C(5), δ = 116.5 and 116.1; C(6), δ = 132.2 and 130.3; C(7), δ = 111.7 and 111.4; C(8), δ = 168.6 and 167.1; C(9), δ = 130.6 and 130.6; C(10), δ = 144.8 and 142.8 ppm. For numbering systems see Table 1.

The reaction can also be successfully performed in heptane.

Reaction between $H_4Ru_4(CO)_{12}$ and 8-quinolinol

A solution of 0.707 g (0.95 mmol) $H_4Ru_4(CO)_{12}$ and 1.0 g (6.9 mmol) 8-quinolinol in 50 ml dry THF was refluxed in argon. Work-up and separation as above afforded 0.299 g (0.37 mmol 39%) of complex Ib and 0.403 g (0.91 mmol; 24% on Ru) of complex (IIa).

Preparation of complex $Ru(CO)_2$(quinolinol-8-oxy)$_2$, isomers IIb and IIc

(1) By pyrolysis of cluster compound. A solution of 100 mg of Ib in 25 ml dry diglyme was heated for 16 h at 175°C under argon. After cooling the precipitated metal was filtered off and the solvent was evaporated off, leaving a mixture of starting material and complex IIb or IIc.

(2) By isomerization of IIa. A solution of 0.089 g (0.20 mmol) of isomer IIa in 20 ml dry diglyme was heated for 16 h at 175°C under argon. The solvent was removed in vacuum and the residue washed with ether. Yield: 0.068 g (0.15 mmol; 76%) of yellow crystals of isomer IIb or IIc.

Elemental analysis: found: C, 52.4; H, 3.0; N, 6.0. $C_{20}H_{12}N_2O_4Ru$ calcd.: C, 53.7; H, 3.1; N, 6.3%. IR (acetone), CO frequencies, 2055 and 1980 cm^{-1}. ^{13}C NMR (ppm, $CDCl_3$), carbonyl ligands, $\delta = 198.4$; C(2), $\delta = 149.9$; C(3), $\delta = 121.6$; C(4), $\delta = 138.7$; C(5), $\delta = 116.0$; C(6), $\delta = 130.9$; C(7), $\delta = 111.7$; C(8), $\delta = 170.6$; C(9), $\delta = 130.9$ and C(10), $\delta = 150.0$ ppm.

Reaction between $Ru_3(CO)_{12}$ and 5-bromo-8-quinolinol

A mixture of 0.639 g (1.0 mmol) $Ru_3(CO)_{12}$ and 0.6 g (2.7 mmol) of 5-bromo-8-quinolinol and 125 ml dry THF was refluxed overnight under argon. The solvent was evaporated in vacuo and the residue thoroughly washed with ether. Washing with methanol left 0.608 g (0.62 mmol, 62%) of brilliant yellow crystals of the cluster compound $Ru_3(CO)_8(C_9H_5BrNO)_2$.

Elemental analysis: found: C, 32.9; H, 1.2; N, 3.4; Br, 16.1. $C_{26}H_{10}Br_2N_2O_{10}Ru_3$ calcd.: C, 32.0; H, 1.0; N, 2.9; Br, 16.4%. Evaporation of the methanol left 0.239 g of a mixture of the cluster compound and three others (according to ^1H NMR) which may be analogous to IIa and IIb and/or isomers of the cluster complex. (They were formed in the ratio of 1 : 1.5 : 1 : 0.5). No attempts were made to separate these complexes.

Reaction between $Ru_3(CO)_{12}$ and pyridine ligands

(a) Ligands IV and V. A mixture of 0.639 g (1.0 mmol) $Ru_3(CO)_{12}$, 0.218 g IV (2.0 mmol) and 125 ml of dry THF was refluxed overnight. Evaporation of the solvent and washing with ether left 0.598 g (0.8 mmol; 80%) of pale brown crystals. No other complexes could be detected in the filtrate.

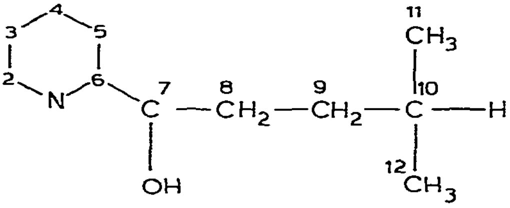
Elemental analysis: found: C, 32.6; H, 1.85; N, 3.7. $Ru_3(CO)_8(C_6H_6NO)_2$ calcd.: C, 32.2; H, 1.7; N, 3.8%. IR ($CHCl_3$), CO frequencies, 2080, 2000 (broad band), and 1920 cm^{-1}. Similarly ligand V yielded 53% of the cluster compound. Elemental analysis: found: C, 35.2; H, 2.5; N, 3.9. $C_{22}H_{16}N_2O_{10}Ru_3$ calcd.: C, 34.2; H, 2.2; N, 3.6%.

(b) Ligand VI. Reaction of 0.500 g (0.78 mmol) $Ru_3(CO)_{12}$ and 0.7 g VI in 100 ml THF as described above, with subsequent evaporation of the solvent gave an oil, which on trituration with a pentane/ether mixture (90/10) yielded 0.475 g of yellow crystals. NMR showed the existence of another complex as an impurity.

^{13}C NMR (ppm, $CDCl_3$), carbonyls, $\delta = 206.1$, 204.5, 203.8 and 194.2; C(2), $\delta = 150.6$; C(3), $\delta = 123.3$; C(4), $\delta = 136.9$; C(5), $\delta = 120.5$; C(6), $\delta = 171.2$; C(7), $\delta = 86.8$; C(8), $\delta = 38.6$; C(9), $\delta = 35.4$; C(10), $\delta = 27.9$; C(11)/C(12), $\delta = 22.6$ and 22.1 ppm.

^{13}C NMR (ppm, $CDCl_3$), of the free ligand: C(2), $\delta = 147.7$ (d176, d8, d4);

C(3), δ = 121.8 (d163, t6); C(4), δ = 136.2 (d162, d6); C(5), δ = 120.2 (d164, d6); C(6), δ = 163.0 (m); C(7), δ = 73.7 (d143); C(8), δ = 36.4; C(9), δ = 34.6; C(10), δ = 28.0; C(11)/C(12), δ = 22.9 and 22.6 ppm.



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