Ruthenium carbonyl carboxylates with nitrogen-containing ligands: II. Synthesis and characterization of mononuclear compounds *

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Abstract

Several mononuclear acetatoruthenium(II) carbonyls containing bipyridine or phenanthroline ligands, of general formula $[Ru(CO)_2(MeCOO)_2(N\text{-}N)]$, have been synthesized and spectroscopically characterized. The *cis,cis,cis*, octahedral structure of these compounds has been assigned on the basis of spectroscopic data.

Key words: Ruthenium; Carbonyls; Nuclear magnetic resonance; Carboxylate

1. Introduction

In order to provide ruthenium catalyst precursors for hydrogenation and carbonylation with no phosphine ligands and appropriate solubility we have recently synthesized [1] and characterized cationic binuclear acetatoruthenium carbonyls containing nitrogen ligands such as 1,10-phenanthroline (phen), 2,2′-bipyridine (bpy) and their dimethylsubstituted derivatives [2,9-dimethyl-1,10-phenanthroline (2,9-dmphen), 4,7-dimethyl-1,10-phenanthroline (4,7-dmphen), 5,6-dimethyl-1,10-phenanthroline (5,6-dmphen), 4,4′-dimethyl-2,2′-bipyridine (4,4′-dmbpy)]. In this paper we report the synthesis of mononuclear ruthenium(II) compounds containing these ligands, and their spectroscopic characterization. The synthesis of *cis,trans,cis*-$[Ru(CO)_2(MeCOO)_2(N\text{-}N)]$ [N-N: bpy or phen] has been described [3] starting from $[Ru(CO)_2(N\text{-}N)Cl_2]$ and silver acetate.

2. Results and discussion

2.1. Synthesis of complexes

The syntheses of $[Ru(CO)_2(MeCOO)_2(N\text{-}N)]$ were performed following the procedure suggested by Bianchi *et al.* [2] for the phosphine-substituted derivatives (Scheme 1).

The nitrogen base was added in 1/1.15 = Ru/base molar ratio to an acetic acid suspension of $[\{Ru_2(CO)_4(MeCOO)_2\}_n]$ (**7**). After heating at reflux temperature for 60 h, acetic acid was distilled off under reduced pressure and the residue dissolved in methanol. By cooling the solution at −5°C, the expected compound was recovered in crystalline form. The analytical data are reported in Table 1.

The Ru^{II} compounds obtained differ from the disubstituted mononuclear phosphine complexes [2] obtained by a similar procedure because the nitrogen-containing ligands, due to their structure, occupy two *cis* positions.

2.2. IR data

The IR spectra of **1**, **3–6** (Table 2), in the range between 2200 and 1500 cm^{-1}, show two strong absorptions which may be attributed to the stretching of the terminal carbonyl groups, and one band which may be attributed to the asymmetric stretching of the coordinated acetato groups.

The IR spectrum of **2** (Table 2) differs from those of the other compounds reported because of the bathochromic shift of the two absorptions, in the carbonyl stretching region.

The same IR absorptions have been reported for

* For part I see ref. 1.

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$$1/n[\{Ru_2(CO)_4(MeCOO)_2\}_n] + 2N\text{-}N + 2MeCOOH \xrightarrow{\Delta} 2[Ru(CO)_2(MeCOO)_2(N\text{-}N)] + H_2$$

N-N=phen (**1**), 2,9-dmphen (**2**), 4,7-dmphen (**3**), 5,6-dmphen (**4**), bpy (**5**), 4,4'-dmbpy (**6**)

Scheme 1.

compounds having the same molecular formula as **1** and **5** by Black *et al.* [3].

2.3. ^{1}H-NMR data

The ^{1}H-NMR spectra of all compounds synthesized (Tables 3 and 4) show two singlets, one in the range 1.50–1.88 ppm and the second between 2.02 and 2.20 ppm, attributed to the methyl protons of the acetato-group. The complex resonances of the nitrogen-containing ligands are in the range between 7.27 and 9.33 ppm. They may be assigned assuming the non-equivalence of the two pyridine rings.

The signals due to the protons of the phenanthroline ligands (complexes **1–4**, Table 3) may be assigned by assuming that all protons are not chemically equivalent. Furthermore, protons H2, H3 and H4 are mutually coupled but they do not couple with H7, H8 and H9. Proton H5 is coupled only to proton H6. These couplings were confirmed by selective decoupled spectra and by ^{1}H-NMR COSY spectra.

A simulation of the spectrum of **1** using the assignments in Table 3 gives a spectrum identical to that observed experimentally.

Black *et al.* [3] made similar assignments but they did not observe any difference between the two pyridine rings.

The signals of the protons of the bipyridine rings of compounds **5** and **6** (Table 4) may be assigned similarly assuming that the eight hydrogen atoms are not equivalent in pairs.

These assignments are consistent with the sequence of signals reported by Black *et al.* [3] for the compound having the same formula as **5** but they do not report any differences between the two pyridine rings. Orellana *et al.* [4] and Ohsawa *et al.* [5] report a different assignment of the signals of the protons H3' and H6' in the bipyridine in $[Ru(bpy)_3]^{2+}$. Our assignment is the same as that of Kelly and Young [6] in compounds such as $[Pt(bpy)R_2]$ [R = $-CH_2Si(CH_3)_2CH{=}CH_2$] for the low field signal arising from H6'.

There is no evidence from the chemical shifts of the protons in the 6 and 6' positions of an increase in acidity due to the distortion of the ring caused by the coordination of the nitrogen atoms, as reported by Constable [7,8] and as observed by us [1] for the binuclear carboxylatoruthenium carbonyls having the same nitrogen-containing ligand.

The ^{1}H-NMR spectra of compound **6** was assigned in the same way, but there is coupling between the H3 and H5 or H3' and H5' protons.

The lack of equivalence of the two methyl groups of the two acetato-ligands and between the two pyridine rings of the nitrogen-containing ligands may be explained by assuming an octahedral structure for these complexes with the equivalent ligands *cis* (Fig. 1).

When the substituents present *trans* to the two nitrogen-containing ligands are different, they may cause different chemical shifts in the two pyridine rings. The *cis* position of the carbonyl groups is consistent with the presence in the IR spectrum of two strong stretching frequencies of equal intensity [9–11].

Further support to this is that the starting polynuclear carboxylatoruthenium carbonyl (**7**) has both the carbonyl and carboxylato groups *cis* and that in the synthesis of mononuclear phosphine derivatives these relative positions remain unaffected [2,12,13].

This structure differs from that proposed by Black *et al.* [3] for their compounds. They suggested a *trans*

TABLE 1. Yields, analyses, and melting points of mononuclear acetatoruthenium carbonyls with nitrogen containing ligands.

	Yield [a] (%)	Elemental analysis [b]			mp (°C)
		C(%)	H(%)	N(%)	
$[Ru(CO)_2(CH_3COO)_2(phen)]$ (**1**)	39.4	48.07(47.48)	3.34(3.10)	5.66(6.15)	208–210
$[Ru(CO)_2(CH_3COO)_2(2,9\text{-dmphen})]$ (**2**)	36.5	48.73(49.69)	4.48 (3.75)	6.07(5.79)	260–264
$[Ru(CO)_2(CH_3COO)_2(4,7\text{-dmphen})]$ (**3**)	12.1	48.92(49.69)	4.26 (3.75)	5.73(5.79)	269–273
$[Ru(CO)_2(CH_3COO)_2(5,6\text{-dmphen})]$ (**4**)	40.9	49.44(49.69)	3.97 (3.75)	5.31(5.79)	250–254
$[Ru(CO)_2(CH_3COO)_2(bpy)]$ (**5**)	29.6	42.97(44.55)	3.24(3.27)	6.18 (6.49)	241–243
$[Ru(CO)_2(CH_3COO)_2(4,4'\text{-dmbpy})]$ (**6**)	25.3	43.89(47.06)	3.96 (3.95)	5.76(6.10)	228–231

[a] Recrystallized; [b] calculated values in parentheses.

TABLE 2. IR spectral data of mononuclear acetatoruthenium carbonyl with nitrogen-containing ligands [a]

	ν_{CO} (cm^{-1})	ν_{COO} (cm^{-1})
1	2060vs, 1993vs	1628s
2	2030vs, 1949vs	1580s
3	2058vs, 1990vs	1628s
4	2059vs, 1991vs	1615s
5	2060vs, 1993vs	1605s
6	2058vs, 1990vs	1619s

[a] Solvent CH_2Cl_2.

position for the two acetato ligands because their starting material [Ru(CO)$_2$(bpy)$_2$Cl$_2$] has two *trans* chloroligands and because the two pyridine rings of the bipyridine ligand are equivalent in the ^{1}H-NMR spectrum.

To check differences and analogies between our and their compounds we have synthesized the phenanthroline and bipyridine complexes using the method reported by Black *et al.* [3]. Their IR and ^{1}H-NMR spectra are identical to those of the products **1** and **5** that we have synthesized from [{Ru$_2$(CO)$_4$(MeCOO)$_2$}$_n$].

TABLE 3. ^{1}H-NMR spectral data of [Ru(CO)$_2$(MeCOO)$_2$(N-N)] {N-N = phenanthrolines} [a]

Group	1	2	3	4 [b]
CH_3COO	1.50, s	1.88, s	1.55, s	1.50, s
CH_3COO	2.16, s	2.02, s	2.20, s	2.02, s
CH_3-L °	–	3.02, s	2.97, s	2.81, s
CH_3-L °	–	3.03, s	3.05. s	2.84, s
H5	8.15, BC #	7.97, s	8.38, AB #	–
	J(5,6) = 9.2		J(5,6) = 9.3	
H6	8.22, BC #	8.10, s	8.45, AB #	–
	J(6,5) = 9.2		J(6,5) = 9.3	
H3	7.88, AMN #	7.76, d	7.78, d	7.78, dd
	J(3,2) = 5.3	J(3,4) = 8.4	J(3,2) = 5.2	J(3,2) = 5.2
	J(3,4) = 8.3			J(3,4) = 8.5
H8	8.16, dd	7.91, d	8.06, d	8.06, dd
	J(8,9) = 5.1	J(8,7) = 8.4	J(8,9) = 5.6	J(8,9) = 5.0
	J(8,7) = 8.3			J(8,7) = 8.6
H4	8.72, AMN #	8.48, d	–	8.66, dd
	J(4,2) = 1.2	J(4,3) = 8.4		J(4,2) = 1.3
	J(4,3) = 8.3			J(4,3) = 8.5
H7	8.88, dd	8.63, d	–	8.83, dd
	J(7,9) = 1.4	J(7,8) = 8.4		J(7,9) = 1.3
	J(7,8) = 8.3			J(7,8) = 8.6
H2	9.28, AMN #	–	9.15, d	9.28, dd
	J(2,4) = 1.2		J(2,3) = 5.2	J(2,4) = 1.3
	J(2,3) = 5.3			J(2,3) = 5.2
H9	9.31, dd	–	9.19, d	9.33, dd
	J(9,7) = 1.4		J(9,8) = 5.6	J(9,7) = 1.3
	J(9,8) = 5.1			J(9,8) = 5.0

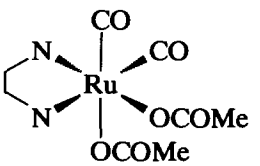
[a] Chemical shifts in ppm and coupling constants in Hz; solvent CD_3OD; [b] Solvent CD_2Cl_2.
° Methyl substituents of phenanthrolines in the specified complex; # Spin system.

TABLE 4. ^{1}H-NMR spectral data of [Ru(CO)$_2$(MeCOO)$_2$(N-N)] {N-N = bipyridines} [a]

Group	(5)	(6) [b]
CH_3COO	1.61, s	1.62, s
CH_3COO	2.10, s	2.13, s
CH_3-4 °	–	2.55, s
CH_3-4′ °	–	2.64, s
H5	7.54, ddd	7.27, dd
	J(5,3) = 1.4	J(5,3) = 1.2
	J(5,6) = 5.7	J(5,6) = 5.9
	J(5,4) = 7.8	
H5′	7.84, AMNX #	7.56, dd
	J(5′,3′) = 1.2	J(5′,3′) = 1.2
	J(5′,6′) = 5.5	J(5′,6′) = 5.8
	J(5′,4′) = 7.8	
H4	8.13, ddd	–
	J(4,6) = 1.5	
	J(4,5) = 7.8	
	J(4,3) = 7.9	
H4′	8.31, AMNX #	–
	J(4′,6′) = 1.6	
	J(4′,5′) = 7.8	
	J(4′,3′) = 8.0	
H3	8.48, ddd	7.94, d
	J(3,6) = 0.7	J(3,5) = 1.2
	J(3,5) = 1.4	
	J(3,4) = 7.9	
H3′	8.56, AMNX #	8.02, d
	J(3′,6′) = 0.7	J(3′,5′) = 1.2
	J(3′,5′) = 1.2	
	J(3′,4′) = 8.0	
H6	8.94, ddd	8.82, d
	J(6,3) = 0.7	J(6,5) = 5.9
	J(6,4) = 1.5	
	J(6,5) = 5.7	
H6′	8.98, AMNX #	8.90, d
	J(6′,3′) = 0.7	J(6′,5′) = 5.8
	J(6′,4′) = 1.6	
	J(6′,5′) = 5.5	

[a] Chemical shifts in ppm and coupling constants in Hz; solvent CD_3OD; [b] Solvent CD_2Cl_2;
° Methyl substituents of bipyridine in 4,4′ positions; # Spin system.

We conclude that our compounds are identical to those obtained by Black *et al.* [3]. The structures proposed by them on the basis of NMR spectra obtained with a 90 MHz spectrometer are not correct. The resolution is not sufficient to show the differences



N⌒N : phen (**1**), 2,9-dmphen (**2**), 4,7-dmphen (**3**), 5,6-dmphen (**4**), bpy (**5**), 4,4′-dmbpy (**6**)

Fig. 1. Structures suggested for compounds (**1**)–(**6**).

between the two pyridine rings, and only four resonances appear, instead of eight when using a 300 MHz instrument.

2.4. ^{13}C-NMR data

The ^{13}C-NMR spectra of the complexes are fully assigned in Tables 5 and 6.

The signals due to the nitrogen-containing ligands were assigned taking into account the corresponding signals of the free donors [1]. These resonances are shifted both to higher and to lower fields upon coordination. Every carbon atom, with very few exceptions, gives a specific resonance. The spectrum of **1** has been assigned assuming that the resonances of the C13 and C14 carbons are coincident, as happens in the free base. In the same way we have assigned the spectra **2–4** (Table 5).

The signals of the bipyridine **5** and **6** (Table 6) have been assigned with the same assumption and this is consistent with the assignment of Orellana *et al.* [4]. The signal at 159.3 ppm, in the spectrum of **5** assigned to the carbon atom in the 6′ position, is shifted to lower field than that due to the carbon in position 6, due to the different *trans* influences of the different *trans* ligands. Note that Akasheh *et al.* [14] report a sequence different from that reported by Orellana [4] for the chemical shifts of the carbon atoms in positions 3 and 5 both for the free bipyridine and in complexes such as [Ru(bpy)$_3$Cl$_2$].

TABLE 5. ^{13}C-NMR spectral data of [Ru(CO)$_2$(MeCOO)$_2$(N-N)] {N-N = phenanthrolines} [a]

	1	2	3	4 [b]
CH_3COO *	23.5	24.8	24.3	11.6
CH_3COO **	23.9	25.2	24.3	11.7
CH_3-L °	–	26.7	20.5	18.9
CH_3-L °	–	27.0	20.7	19.1
C3	125.9	128.4	126.7	121.2
C8	126.1	128.8	126.7	121.5
C5	127.9	129.3	129.0	127.3
C6	128.1	129.4	129.0	127.4
C13	130.8	131.2	133.1	128.1
C14	130.8	131.8	133.1	128.2
C4	138.2	140.0	148.5	131.0
C7	139.1	141.3	149.1	131.9
C11	146.6	151.6	153.3	141.6
C12	147.5	152.1	153.3	142.4
C2	151.2	170.6	152.5	145.2
C9	158.3	170.6	159.5	152.4
CH_3COO *	178.2	180.9	181.2	172.9
CH_3COO **	178.4	180.9	181.8	173.3
CO terminal	195.5	196.7	198.0	191.8
CO terminal	196.9	200.8	199.4	193.8

[a] Chemical shift in ppm; solvent CD_3OD; [b] Solvent CD_2Cl_2;
° Methyl substituents of phenanthrolines in the specified complex; * methyl and carboxylato-groups of the same ligand; ** methyl and carboxylato-groups of the same ligand.

TABLE 6. ^{13}C-NMR data of [Ru(CO)$_2$(CH_3COO)$_2$(N-N)] {N-N = bipyridines} [a]

	5	6 [b]
CH_3COO *	23.6	17.7
CH_3COO **	23.8	18.0
CH_3-4	–	18.9
CH_3-4′	–	19.2
C3	125.7	119.7
C3′	125.9	119.9
C5	129.1	123.6
C5′	129.2	123.9
C4	141.9	147.8
C4′	143.1	148.9
C6	151.9	145.6
C6′	159.3	152.9
C2	157.5	150.9
C2′	158.4	151.6
CH_3COO *	180.6	172.9
CH_3COO **	181.1	173.2
CO terminal	197.0	191.9
CO terminal	198.6	193.7

[a] Chemical shift in ppm; solvent CD_3OD; [b] Solvent CD_2Cl_2.
° Methyl substituents of 4.4′-dimethylbipyridine; * Methyl and carboxylato-groups of the same ligand; ** Methyl and carboxylato-groups of the same ligand.

2.5. Remarks concerning the spectroscopic data

The IR spectra of all compounds (Table 2) show two carbonyl stretches of equal intensity. The only exception concerns **2**, in which the methyl groups at positions 2 and 9 of the phenanthroline cause a shift to lower frequencies. The asymmetric stretches of the carboxylato-groups are also shifted to lower frequency than those of the other compounds.

Coordination causes the ^{1}H′ NMR resonances (Tables 3 and 4) of the nitrogen-containing ligands to shift to lower field. These shifts are less than those for the binuclear complexes [1] and different shifts are observed for resonances of the hydrogen atoms in corresponding positions of the two pyridine rings. For instance, in compound **5** the shifts are 0.11, 0.20, 0.19 and 0.30 ppm, for H5, H4, H3, and H6, respectively, and 0.41, 0.38, 0.37 and 0.34 ppm for H5′, H4′, H3′ and H6′, respectively.

The shifts of the resonances due to the carbon atoms upon coordination (Tables 5 and 6) show no systematic trends as is observed for the binuclear compounds [1]. The differences are also in the range between ± 6 ppm. The resonances corresponding to the carbon atoms of the methyl substituents are always at a higher field than those of the free nitrogen-containing bases.

The individual ^{13}C-NMR resonances for each carbon atom of phenanthroline or bipyridine and all the NMR data support the structures suggested for compounds **1–6** (Fig. 1).

3. Experimental section

3.1. Instruments

IR spectra were recorded with a FT-IR Perkin-Elmer 1760 instrument using KBr or CaF_2 windows for solutions and KBr pellets for solid samples. Elemental analyses were carried out using a Perkin-Elmer 240 C analyzer. ^{1}H-NMR spectra were recorded at 299.945 MHz on a Varian VXR 300 using tetramethylsilane as external reference. ^{13}C{^{1}H}-NMR spectra were recorded on the same instrument operating at 75.429 MHz using tetramethylsilane as external reference.

3.2. Materials

Methanol was a C. Erba product, purified by the Lund and Bijerrunn method reported by Vogel [15]. 2,2′-Bipyridine (Fluka), 4,4′-dimethyl-2,2′-bipyridine (Aldrich), 1,10-phenanthroline (Merck), 2,9-dimethyl-1,10-phenanthroline (Aldrich), 4,7-dimethyl-1,10-phenanthroline (Aldrich), 5,6-dimethyl-1,10-phenanthroline (Aldrich) and triruthenium dodecacarbonyl (Aldrich) were used as supplied. [{Ru$_2$(CO)$_4$(MeCOO)$_2$}$_n$] [16] and [Ru(CO)$_2$(N-N)Cl$_2$] [3] were synthesized as reported. [Ru(CO)$_2$(MeCOO)$_2$(N-N)] [N-N bpy or phen) were also synthesized according to Black *et al.* [3].

3.3. General procedure for the synthesis of [Ru(CO)$_2$(MeCOO)$_2$(N-N)]

All procedures were routinely performed under dry dinitrogen using the Schlenk technique.

Into a 100 ml flask equipped with a reflux condenser [{Ru$_2$(CO)$_4$(MeCOO)$_2$}$_n$] (500 mg, 2.381 mmol Ru), the nitrogen-containing ligand (2.660 mmol) and acetic acid (50 ml) were introduced. The suspension was heated under reflux for 60 h, avoiding the sun light. An orange solution was formed. The acetic acid was then distilled off under reduced pressure leaving a residue which was then dissolved in methanol and gave, on cooling to −5°C, the desired product in crystalline form.

Yields, elemental analysis and melting points are reported in Table 1; the IR data, in the 2200–1500 cm^{-1} range, are reported in Table 2 and the NMR data in Tables 3–6.

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References

1 P. Frediani, M. Bianchi, A. Salvini, R. Guarducci, L.C. Carluccio, F. Piacenti, S. Ianelli and M. Nardelli, *J. Organomet. Chem., 463* (1993) 187.
2 M. Bianchi, P. Frediani, U. Matteoli, G. Menchi, F. Piacenti, G. Petrucci, *J. Organomet. Chem., 259* (1983) 207.
3 D.S.C. Black, G.B. Deacon and N.C. Thomas, *Aust. J. Chem., 35* (1982) 2445.
4 G. Orellana, C.A. Ibarra and J. Santoro, *Inorg. Chem., 27* (1988) 1025.
5 Y. Oshawa, M.K. DeArmod, K.W. Hanck and C.G. Moreland, *J. Amer. Chem. Soc., 107* (1985) 5383.
6 R.D. Kelly and G.B. Young, *J. Organomet. Chem., 361* (1989) 123.
7 E.C. Constable, *Inorg. Chim. Acta, 145* (1988) 49.
8 E.C. Constable and T.A. Leese, *Inorg. Chim. Acta, 146* (1988) 55.
9 F.A. Cotton and C.S. Krainhanzel, *J. Amer. Chem. Soc., 84* (1962) 4432.
10 C.S. Krainhanzel and F.A. Cotton, *Inorg. Chem., 2* (1963) 533.
11 F.A. Cotton, *Inorg. Chem., 3* (1964) 702.
12 B.F.G. Johnson, R.D. Johnston, J. Lewis and I.G. Williams, *J. Chem. Soc., A,* (1971) 689.
13 S.D. Robinson and M.F. Uttley, *J. Chem. Soc., Dalton Trans.,* (1973) 1912.
14 T. Akasheh and K. Barqawi, *Inorg. Chim. Acta, 102* (1985) L33.
15 A.I. Vogel, *Vogel's Textbook of Practical Organic Chemistry*, IV edn., Longmans, London, 1978, p. 266.
16 G.R. Crooks, B.F.G. Johnson, J. Lewis, I.G. Williams and G. Gamlen, *J. Chem. Soc., A,* (1969) 2761.