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Ruthenium carbonyl carboxylates with nitrogen-containing ligands

I. Syntheses and characterization of binuclear compounds *

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Abstract

Several ruthenium carbonyl carboxylato-complexes containing bipyridine or phenanthroline have been synthesized and spectroscopically characterized. The structures of these compounds have been assigned on the basis of spectroscopic data and by X-ray analysis in one case. Crystals of μ-acetato-di-μ-carbonyl-bis[(1,10-phenanthroline)-carbonylruthenium(I)](*Ru-Ru*) tetraphenylborate contain one molecule of CH_2Cl_2. The cation is dinuclear with two Ru atoms bridged by two carbonyls and an acetate and there is a metal–metal bond of 2.701(1) Å. Octahedral coordination around each Ru is completed by a terminal carbonyl and a chelating phenanthroline. The binuclear cation has approximate local *mm* symmetry.

1. Introduction

Phosphine-substituted carboxylatocarbonylruthenium complexes are good catalysts for the hydrogenation and hydroformylation of unsaturated organic substrates containing C=C and C=O bonds [1–5].

In hydrogenation reactions performed at relatively high temperatures, the phosphine ligands may be dealkylated, giving rise to the formation of the corresponding phosphido-derivatives though they are then generally less active [6–10]. Moreover, phosphines free in solution can easily be oxidized giving products which further complicate the separation of the crude reaction product. Furthermore, phosphines are toxic.

In order to avoid the difficulties created by the phosphines in these complexes, we used analogous complexes with nitrogen-containing ligands such as bipyridine, phenanthroline, and their alkyl substituted derivatives in similar reactions. These ligands besides being π-acids and therefore capable, like phosphines, of stabilizing metals in their lower oxidation states, are chemically stable, have low volatility and are less toxic than phosphines. They are water soluble and may therefore render water soluble the complexes containing them. Furthermore, they may be considered model compounds and, when incorporating an asymmetric substituent in a catalyst precursor [11–13], may act as promoters of asymmetric syntheses.

Ruthenium complexes with nitrogen-containing ligands are photosensitizing agents [14–18], or catalysts in reactions such as the water gas shift reaction [19–22], the reduction or carbonylation of nitrobenzene [23,24], CO_2 reduction [25] and the selective oxidation of aromatic compounds to carboxylic acids [26].

The aim of this work was to synthesize carboxylatocarbonylruthenium complexes with nitrogen-containing ligands such as 1,10-phenanthroline (phen), 2,2′-bipyridine (bipy) and their dimethylsubstituted deriva-

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* Dedicated to Professor Gian Paolo Chiusoli, University of Parma, on the occasion of his 70th birthday.

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$$[Ru_2(CO)_4(MeCOO)_2]_n + 2N\text{–}N \xrightarrow{\Delta} \xrightarrow{NaBPh_4} \longrightarrow n[Ru_2(CO)_4(MeCOO)(N\text{–}N)_2](BPh_4) + nMeCOONa$$

N–N: phen (**1**), 4,7-dmphen (**2**), 5,6-dmphen (**3**), bipy (**4**), 4,4′-dmbipy (**5**)

Scheme 1

$$[Ru_2(CO)_4(MeCOO)_2]_n + 2N\text{–}N \xrightarrow{\Delta} n[Ru_2(CO)_4(MeCOO)(N\text{–}N)_2](MeCOO)$$

N–N: phen (**7**), 4,7-dmphen (**8**), 5,6-dmphen (**9**), bipy (**10**), 4,4′-dmbipy (**11**)

Scheme 2

tives [4,7-dimethyl-1,10-phenanthroline (4,7-dmphen), 5,6-dimethyl-1,10-phenanthroline (5,6-dmphen), and 4,4′-dimethyl-2,2′-bipyridine (4,4′-dmbipy)].

2. Results and discussion

2.1. Syntheses of complexes

The syntheses of $[Ru_2(CO)_4(MeCOO)(N\text{-}N)_2](BPh_4)$ were performed using the procedure of Steyn and Singleton [27] (Scheme 1).

The N-N is added in a 1/1 = Ru/N-N molar ratio to an ethanol suspension of $\{Ru_2(CO)_4(MeCOO)_2\}_n$ (**6**). After heating the suspension at 60°C for 3 h, sodium tetraphenylborate is added in a $Ru/NaBPh_4$ = 2:1 molar ratio. The solution is heated under reflux for 3 h, the solvent then distilled off under reduced pressure and the residue crystallized from CH_2Cl_2/C_2H_5OH. The analytical data of the products obtained are in Table 1.

The syntheses of $[Ru_2(CO)_4(MeCOO)(N\text{-}N)_2](MeCOO)$ from **6** were carried out as described by Crooks *et al.* [28] for the corresponding trialkylphosphine derivatives (Scheme 2).

The N-N is added in a Ru/N-N = 1/1 molar ratio to an ethanol suspension of **6**. After heating for 3 h at 60°C, the solvent is evaporated and the solid residue purified by TLC. The analytical data of the products are also reported in Table 1.

In these ionic compounds, a molecule of N-N ligand chelates each ruthenium atom and the counter anion is acetate or tetraphenylborate.

2.2. IR data

The IR spectra of **1–5** and **7–11** (Table 2), show two bands in the range 2200–1500 cm^{-1} (the first very strong, the second very weak) which may be attributed to $\nu(CO)_{terminal}$, and two bands at lower frequencies (the first very weak, the second very strong) associated with $\nu(CO)_{bridging}$. A weak absorption in the 1550–1539 cm^{-1} region may be attributed to the asymmetric stretching of the coordinated acetate. The asymmetric stretching of the acetate anion (compounds **7–11**) is found in the 1655–1627 cm^{-1} region. The absorption around 1600 cm^{-1} is due to the nitrogen-containing ligands.

For compound **4** Steyn and Singleton [27] report absorptions at 2025, 1996 and 1747sh cm^{-1} due to $\nu(CO)$ and two absorptions at 1539 and 1479 cm^{-1} due to the carboxylato ligand. There are only small differences between this reported spectrum and those of the

TABLE 1. Binuclear carbonylcarboxylatoruthenium containing nitrogen ligands. Elemental analysis, decomposition temperature and conductivity data

Compound	Code	Chemical yield (%)	Elemental analysis [a]			T_d [b] °C	Conductivity [c] $10^4\ \Omega^{-1}\ cm^{-1}$
			C(%)	H(%)	N(%)		
$[Ru_2(CO)_4(MeCOO)(phen)_2](BPh_4)(CH_2Cl_2)$	**1**	68.2	60.13(58.10)	3.68(3.63)	5.22(4.92)	225–227	0.79
$[Ru_2(CO)_4(MeCOO)(4,7\text{-dmphen})_2](BPh_4)$	**2**	79.9	58.21(62.81)	4.43(4.29)	5.10(4.78)	270–272	0.73
$[Ru_2(CO)_4(MeCOO)(5,6\text{-dmphen})_2](BPh_4)$	**3**	77.6	62.88(62.81)	4.43(4.27)	5.10(5.05)	235–238	0.79
$[Ru_2(CO)_4(MeCOO)(bipy)_2](BPh_4)$	**4**	78.5	59.33(59.77)	3.93(3.91)	6.65(6.65)	237–239	0.75
$[Ru_2(CO)_4(MeCOO)(4,4'\text{-dmbipy})_2](BPh_4)$	**5**	76.2	61.73(61.13)	4.48(4.46)	4.63(5.28)	231–235	0.83
$[Ru_2(CO)_4(MeCOO)(phen)_2](MeCOO)$	**7**	64.3	47.37(48.49)	3.22(2.80)	7.28(7.07)	209–211	1.09
$[Ru_2(CO)_4(MeCOO)(4,7\text{-dmphen})_2](MeCOO)$	**8**	64.9	47.25(50.94)	3.74(3.56)	5.93(6.60)	254–259	0.76
$[Ru_2(CO)_4(MeCOO)(5,6\text{-dmphen})_2](MeCOO)$	**9**	65.2	47.19(50.94)	3.73(3.56)	6.13(6.60)	261–265	0.66
$[Ru_2(CO)_4(MeCOO)(bipy)_2](MeCOO)$	**10**	61.0	44.73(45.16)	3.04(2.98)	7.05(7.52)	205–207	1.08
$[Ru_2(CO)_4(MeCOO)(4,4'\text{-dmbipy})_2](MeCOO)$	**11**	62.4	45.20(48.00)	3.58(3.78)	6.76(7.00)	250–254	0.69

[a] Calculated values in parentheses. [b] T_d: Decomposition temperature. [c] c = 1.00 M in MeOH, 27°C.

new compounds. The band at 1747 cm^{-1} is very strong in our spectra, but was reported [27] to be only a shoulder.

2.3. ^{1}H-NMR data

The ^{1}H-NMR spectra (Tables 3 and 4) show a singlet in the range 0.82–1.01 ppm attributed to the methyl protons of the acetate ligand. Another singlet in the spectra of compounds **7–11**, between 1.82 and 1.91 ppm, is attributed to the methyl group of the acetate anion. The signals at 6.85, 7.02 and 7.35 ppm in the spectra of compounds **1–5** are assigned to the *para*, *ortho* and *meta* hydrogen atoms of the aromatic rings in the BPh_4 anion.

The resonances of the nitrogen-containing ligands are in the range 6.5–11.0 ppm, and are assigned assuming that each pyridine ring is equivalent to the other.

The signals in the spectrum of **4** (Table 4) due to the protons on the nitrogen-containing ligand we assigned by assuming that this is a second-order spectrum which was simulated [29] (Fig. 1). Due to coordination the resonances of the protons in the 5,5′ and 6,6′ positions are shifted, to lower field compared to the free base (0.49 and 1.60 ppm, respectively), and their coupling is higher (0.5 Hz). The shift of the resonances due to the 4,4′ protons is small (0.25 ppm), and the resonance of the 3,3′ protons is practically unchanged (0.05 ppm).

In the spectrum of **8**, there is no coupling between the methyl protons in the substituents in positions 4 and 7 of phenanthroline with the protons in 3 and 8 positions, respectively. This coupling is present in the free base.

In the spectrum of free 4,4′-dimethylbipyridine there is a coupling between the 3,3′ and the 5,5′ protons which is not apparent in the spectrum of **11**.

2.4. ^{13}C-NMR data

The ^{13}C-NMR spectra (Tables 5–7) show two singlets due to the coordinated acetate; one may be attributed to the carbon atom of the methyl group (between 17.5 and 22.6 ppm), and the other to the carbon of the carboxylate group (between 176.5 and 183.2 ppm). The resonances due to the carbon atoms of the coordinated N-N are or at a higher, or at a lower field than those of the free base. Two singlets, one in the 189.4–196.6 ppm range and the other in the 254.0–261.2 ppm range, may be attributed to the carbon atoms of the terminal and of the bridging carbonyl groups, respectively. These assignments are in keeping with those reported by Howell and Rowan for $[Cp_2Ru_2(CO)_3(CNR)]$ [30].

The resonances due to the carbon atoms of the tetraphenylborate anion of the phenanthroline complexes **1–3**, are shifted to higher values than those of the same anion in the bipyridine derivatives **4**, **5**.

Considering the ^{13}C NMR resonances assigned to carboxylate in all the complexes, we attribute in the spectrum of **10** the signals, that have the same intensity, at 22.6 and 183.2 ppm to the coordinated acetate, and the signals at 25.8 and 181.6 ppm, that have the same, but lower, intensity, to the anionic acetate. These attributions are in agreement with those reported for the spectrum of $Ru(CO)_2(MeCOO)_2(bipy)$ [31].

The resonances associated with the methyl group of the acetate anion are at the same frequency as those of the coordinated acetate in compounds **8** and **11**. In the spectra of these compounds and also in that of **7**, the resonances of the two different carboxylate groups are coincident.

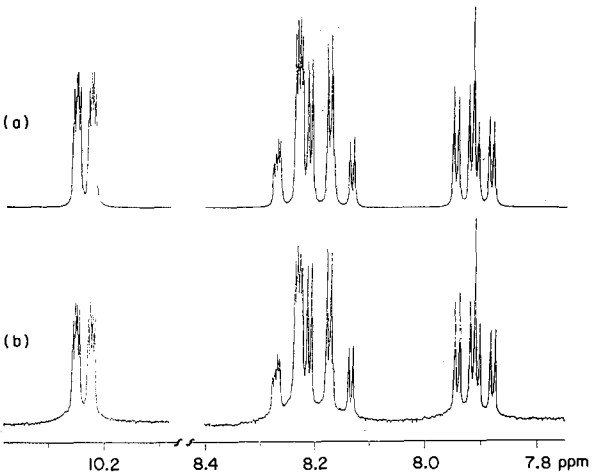

Fig. 1. Experimental (bottom) and computed (top) ^{1}H-NMR spectra of **4** (199.945 MHz, CD_2Cl_2).

TABLE 2. Binuclear carbonylcarboxylatoruthenium containing nitrogen ligands. Frequencies of the IR stretching bands of carbonyl and carboxylato groups in the 2200–1500 cm^{-1} region [a]

Code	ν(CO) (cm^{-1})	ν(COO) (cm^{-1})
1	2025vs, 1984vw, 1803vw, 1746vs	1539w
2	2022vs, 1980vw, 1799vw, 1743vs	1542m
3	2023vs, 1982w, 1801vw, 1744vs	1541w
4	2025vs, 1984vw, 1803vw, 1747vs	1539w
5	2022vs, 1981vw, 1800vw, 1744vs	1540w
7 *	2025vs, 1983vw, 1805vw, 1750vs	1655m, 1549w
8	2022vs, 1980vw, 1800vw, 1743vs	1627sh, 1545w
9	2023vs, 1982vw, 1802vw, 1744vs	1653w, 1544s
10 *	2024vs, 1984vw, 1804vw, 1750vs	1654m, 1550w
11	2022vs, 1981vw, 1801vw, 1744vs	1653w, 1540w

[a] Solvent CH_2Cl_2. * Solvent MeOH.

2.5. Remarks on spectroscopic data

The ^{1}H-NMR data of the Ru^I complexes in Tables 3 and 4 show that the resonances due to the bipyridine and phenanthroline protons are shifted to higher frequencies upon coordination. These shifts are more

TABLE 3. ^{1}H-NMR spectral data of $[Ru_2(CO)_4(MeCOO)(N\text{-}N)_2]X$ {N-N: phenanthrolines; X: BPh_4 or MeCOO} and free phenanthrolines [a]

Code	MeCOO *	MeCOO **	Me-L [†]	H5, H6	H3, H8	H4, H7	H2, H9	H_{para}	H_{ortho}	H_{meta}
phen	–	–		7.86, s	7.72, dd $J(3,2) = J(8,9) = 4.4$ $J(3,4) = J(8,7) = 8.1$	8.38, dd $J(4,2) = J(7,9) = 1.7$ $J(4,3) = J(7,8) = 8.1$	9.06, dd $J(2,4) = J(9,7) = 1.7$ $J(2,3) = J(9,8) = 4.4$	–	–	–
1 [b]	0.87, s	–		8.14, s	8.25, dd $J(3,2) = J(8,9) = 5.2$ $J(3,4) = J(8,7) = 8.2$	8.71, dd $J(4,2) = J(7,9) = 1.4$ $J(4,3) = J(7,8) = 8.2$	10.59, dd $J(2,4) = J(9,7) = 1.4$ $J(2,3) = J(9,8) = 5.2$	6.87, m	7.03, m	7.37, m
4,7-dmphen [c]	–	–	2.79, d $J(Me4,3) = J(Me7,8) = 0.9$	8.02, s	7.45, dq $J(3,Me4) = J(8,Me7) = 0.9$ $J(3,2) = J(8,9) = 4.5$	–	9.04, d $J(2,3) = J(9,8) = 4.5$	–	–	–
2 [b]	0.84, s	–	3.04, s	8.35, s	8.12, d $J(3,2) = J(8,9) = 5.5$	–	10.44, d $J(2,3) = J(9,8) = 5.5$	6.87, m	7.04, m	7.32, m
5,6-dmphen [c]	–	–	2.73, s	–	7.64, dd $J(3,2) = J(8,9) = 4.3$ $J(3,4) = J(8,7) = 8.5$	8.44, dd $J(4,2) = J(7,9) = 1.7$ $J(4,3) = J(7,8) = 8.5$	9.13, dd $J(2,4) = J(9,7) = 1.7$ $J(2,3) = J(9,8) = 4.3$	–	–	–
3 [b]	0.82, s	–	2.89, s	–	8.26, dd $J(3,2) = J(8,9) = 5.1$ $J(3,4) = J(8,7) = 8.5$	8.90, dd $J(4,2) = J(7,9) = 1.3$ $J(4,3) = J(7,8) = 8.5$	10.56, dd $J(2,4) = J(9,7) = 1.3$ $J(2,3) = J(9,8) = 5.1$	6.93, m	6.99, m	7.32, m
7	0.84, s	1.88, s	–	8.35, s	8.43, dd $J(3,2) = J(8,9) = 5.1$ $J(3,4) = J(8,7) = 8.2$	9.00, dd $J(4,2) = J(7,9) = 1.4$ $J(4,3) = J(7,8) = 8.2$	10.61, dd $J(2,4) = J(9,7) = 1.4$ $J(2,3) = J(9,8) = 5.1$			
8	0.82, s	1.89, s	3.08, s	8.51, s	8.26, d $J(3,2) = J(8,9) = 5.2$	–	10.45, d $J(2,3) = J(9,8) = 5.2$			
9	0.82, s	1.89, s	2.95, s	–	8.42, dd $J(3,2) = J(8,9) = 5.0$ $J(3,4) = J(8,7) = 8.5$	9.17, dd $J(4,2) = J(7,9) = 1.3$ $J(4,3) = J(7,8) = 8.5$	10.58, dd $J(2,4) = J(9,7) = 1.3$ $J(2,3) = J(9,8) = 5.0$			

[a] Chemical shifts in ppm and coupling constants in Hz; solvent CD_3OD. [b] Solvent CD_2Cl_2. [c] Solvent $CDCl_3$. * Coordinated. ** Uncoordinated. [†] Specified methyl substituents of phenanthrolines.

TABLE 4. ^{1}H-NMR spectral data of $[Ru_2(CO)_4(MeCOO)(N\text{-}N)_2]X$ {N-N: bipyridines; X = BPh_4 or MeCOO} and free bipyridines [a]

Code	MeCOO *	MeCOO **	Me-L [†]	H5, H5′	H4, H4′	H3, H3′	H6, H6′	H_{para}	H_{ortho}	H_{meta}
bipy	–	–	–	7.43, ddd $J(5,3) = J(5',3') = 1.1$ $J(5,6) = J(5',6') = 4.9$ $J(5,4) = J(5',4') = 7.7$	7.93, ddd $J(4,6) = J(4',6') = 1.8$ $J(4,5) = J(4',5') = 7.7$ $J(4,3) = J(4',3') = 7.9$	8.29, ddd $J(3,6) = J(3',6') = 1.0$ $J(3,5) = J(3',5') = 1.1$ $J(3,4) = J(3',4') = 7.9$	8.64, ddd $J(6,3) = J(6',3') = 1.0$ $J(6,4) = J(6',4') = 1.8$ $J(6,5) = J(6',5') = 4.9$			
4 [b]	0.99, s	–	–	7.912, amno [#] $J(5,3) = J(5',3') = 1.24$ $J(5,6) = J(5',6') = 5.48$ $J(5,4) = J(5',4') = 7.60$	8.175, amno [#] $J(4,6) = J(4',6') = 1.59$ $J(4,5) = J(4',5') = 7.60$ $J(4,3) = J(4',3') = 8.13$	8.243, amno [#] $J(3,6) = J(3',6') = 0.76$ $J(3,5) = J(3',5') = 1.24$ $J(3,4) = J(3',4') = 8.13$	10.236, amno [#] $J(6,3) = J(6',3') = 0.76$ $J(6,4) = J(6',4') = 1.59$ $J(6,5) = J(6',5') = 5.48$	6.85, m	7.02, m	7.35, m
4,4′-dmbipy [c]	–	–	2.44, s	7.12, dd $J(5,3) = J(5',3') = 1.0$ $J(5,6) = J(5',6') = 4.8$	–	8.21, d $J(3,5) = J(3',5') = 1.0$	8.52, d $J(6,5) = J(6',5') = 4.8$			
5 [b]	1.01, s	–	2.63, s	7.72, d $J(5,6) = J(5',6') = 5.8$	–	8.12, s	10.06, d $J(6,5) = J(6',5') = 5.8$	6.86, m	7.02, m	7.36, m
10	0.90, s	1.82, s	–	7.99, ddd $J(5,3) = J(5',3') = 1.2$ $J(5,6) = J(5',6') = 5.5$ $J(5,4) = J(5',4') = 7.7$	8.32, ddd $J(4,6) = J(4',6') = 1.6$ $J(4,5) = J(4',5') = 7.7$ $J(4,3) = J(4',3') = 7.7$	8.68, ddd $J(3,6) = J(3',6') = 1.0$ $J(3,5) = J(3',5') = 1.2$ $J(3,4) = J(3',4') = 7.7$	10.18, ddd $J(6,3) = J(6',3') = 1.0$ $J(6,4) = J(6',4') = 1.6$ $J(6,5) = J(6',5') = 5.5$			
11	0.99, s	1.91, s	2.70, s	7.89, d $J(5,6) = J(5',6') = 5.9$	–	8.62, s	10.06, d $J(6,5) = J(6',5') = 5.9$			

[a] Chemical shifts in ppm and coupling constants in Hz, solvent CD_3OD. [b] Solvent CD_2Cl_2. [c] Solvent $CDCl_3$. * Coordinated. ** Uncoordinated. [†] Methyl substituents of bipyridine in 4,4′. [#] Assigned on the basis of an amno spin system.

TABLE 5. ^{13}C-NMR spectral data of $[Ru_2(CO)_4(MeCOO)(N\text{-}N)_2](BPh_4)$ {N-N: phenanthrolines} and free phenanthrolines [a]

	phen	1 [b]	4,7-dmphen [c]	2 [b]	5, 6-dmphen [c]	3 [b]
*Me*COO	–	17.5	–	17.5	–	17.4
Me-L$^+$	–	–	19.1	15.6	15.3	11.8
C3, C8	126.2	118.2	122.0	120.1	122.9	121.7
C5, C6	129.4	122.1	124.0	122.8	128.9	127.5
C13, C14	131.8	122.2	127.8	126.6	129.4	128.1
C4, C7	139.4	132.4	144.2	143.6	132.2	132.2
C11, C12	148.2	142.9	146.2	142.8	145.4	142.0
C2, C9	152.5	144.3	149.9	145.8	148.9	142.8
C_{para}	–	124.0	–	118.1	–	118.0
C_{ortho}	–	127.1	–	122.0	–	122.0
C_{meta}	–	135.7	–	132.3	–	132.2
C_{ipso}	–	160.1	–	160.2	–	159.0
MeCOO	–	176.4	–	176.1	–	176.1
$CO_{terminal}$	–	189.6	–	190.0	–	189.6
$CO_{bridging}$	–	254.0	–	255.2	–	254.8

[a] Chemical shift in ppm; carbon atoms indicated by *ortho*, *meta*, *para* and *ipso* are those of aromatic rings of BPh_4^-; solvent CD_3OD. [b] Solvent CD_2Cl_2. [c] Solvent $CDCl_3$. [†] Specified methyl substituents of phenanthrolines.

evident for the *ortho*-protons, in the 6,6′ positions in bipyridine and the 2,9 positions in phenanthroline. These shifts are in the range 1.2–2.2 ppm. The proton resonances due to the methyl substituent on the N-N are also shifted, though less (0.2–0.3 ppm). The proton resonances of the coordinated acetate group are at the same frequency in every complex and are shifted to lower frequencies by about 1 ppm if compared with those of the phosphine-substituted compounds [28]. The same behaviour is shown by the protons of the anion; the resonances associated with the protons of

TABLE 6. ^{13}C-NMR data of $[Ru_2(CO)_4(MeCOO)(N\text{-}N)_2]X$ {N-N: bipyridines, X: BPh_4 or MeCOO} and free bipyridines [a]

	bipy	10	4 [b]	4,4′-dmbipy [c]	11	5 [b]
*Me*COO *	–	22.6	17.6	–	22.6	17.6
*Me*COO **	–	25.8	–	–	22.6	–
Me-L [†]	–	–	–	21.2	23.0	17.9
C3, C3′	124.2	125.6	118.2	122.0	127.1	118.2
C5, C5′	126.9	129.9	119.7	124.7	130.5	120.3
C4, C4′	140.3	143.5	136.7	148.2	149.4	143.4
C6, C6′	151.8	150.2	144.1	148.9	156.2	149.1
C2, C2′	158.7	158.4	151.6	156.0	158.1	151.3
C_{para}	–	–	122.1	–	–	122.1
C_{ortho}	–	–	123.4	–	–	124.2
C_{meta}	–	–	132.4	–	–	132.4
C_{ipso}	–	–	160.5	–	–	160.6
MeCOO *	–	183.2	176.5	–	182.9	176.3
MeCOO **	–	181.9	–	–	182.9	–
$CO_{terminal}$	–	196.1	189.4	–	196.4	189.8
$CO_{bridging}$	–	260.4	254.1	–	261.0	254.7

[a] Chemical shift in ppm; carbon atoms indicated by *ortho*, *meta*, *para* and *ipso* are those of aromatic rings of BPh_4^-; solvent CD_3OD. [b] Solvent CD_2Cl_2. [c] Solvent $CDCl_3$. * Coordinated. ** Uncoordinated. [†] Methyl substituents of 4,4′-dimethylbipyridine.

TABLE 7. ^{13}C-NMR data of $[Ru_2(CO)_4(MeCOO)(N\text{-}N)_2](MeCOO)$ {N-N: phenanthrolines} [a]

	7	8	9
*Me*COO *	22.5	22.5	21.2
*Me*COO **	25.8	22.5	24.6
Me-L [†]	–	20.7	15.8
C3, C8	128.6	126.6	127.0
C5, C6	130.4	129.1	132.9
C13, C14	133.9	133.1	133.5
C4, C7	142.5	149.9	137.9
C11, C12	149.2	149.1	147.2
C2, C9	150.6	153.0	148.0
MeCOO *	183.1	182.9	181.8
MeCOO **	183.1	182.9	181.0
$CO_{terminal}$	196.2	196.6	195.1
$CO_{bridging}$	260.1	261.2	259.6

[a] Chemical shifts in ppm; solvent CD_3OD. * Coordinated. ** Uncoordinated. [†] Specified methyl substituents of phenanthrolines.

both the acetate and the BPh_4 anions are independent of complex.

The ^{13}C-NMR resonances (Tables 5–7) for the tetraphenylborate complexes are at lower frequencies than those of the acetate complexes containing the same N-N.

There is no systematic trend in the changes of the ^{13}C shifts due to the carbon atoms of N-N upon coordination. The differences are between +6 and −6 ppm, but resonances corresponding to the carbon atoms of the methyl substituents are always at a higher frequency than those of the free bases.

2.6. *Crystal structure of* $[Ru_2(CO)_4(MeCOO)(phen)_2](BPh_4) \cdot CH_2Cl_2$

The crystals are built of bioctahedral edge-sharing $[Ru_2(\mu\text{-}O_2CMe)(CO)_4(phen)_2]^+$ cations packed with BPh_4^- anions in such a way as to leave holes in which molecules of CH_2Cl_2 are located. The structures of the two ions shown in Fig. 2 are quite similar to those of the corresponding ions present in the analogous 2,2′-bipyridine derivative [27] (hereafter, data referring to the latter compound will be quoted in square brackets). Relevant parameters are given in Table 8.

The metal-coordination octahedra are joined by the carboxylato- and carbonyl bridging ligands giving a Ru–Ru distance (2.701(1) [2.709(1)] Å) corresponding to a single metal–metal bond. The largest angular distortions from the ideal octahedral angles are found in those formed by the chelating phenanthroline ligands at Ru (75.2(1) and 75.1(1)° [74.8(1) and 74.4(1)°]) that are imposed by the Ru–N distances and the bite of the ligand. The other angles at Ru do not deviate by more than 5° from 90°.

The central $Ru(\mu\text{-}CO)_2Ru$ quadrilateral is slightly but significantly deformed from planarity (total puckering amplitude [32]: $Q_T = 0.038(1)$ [0.034(1)] Å, with

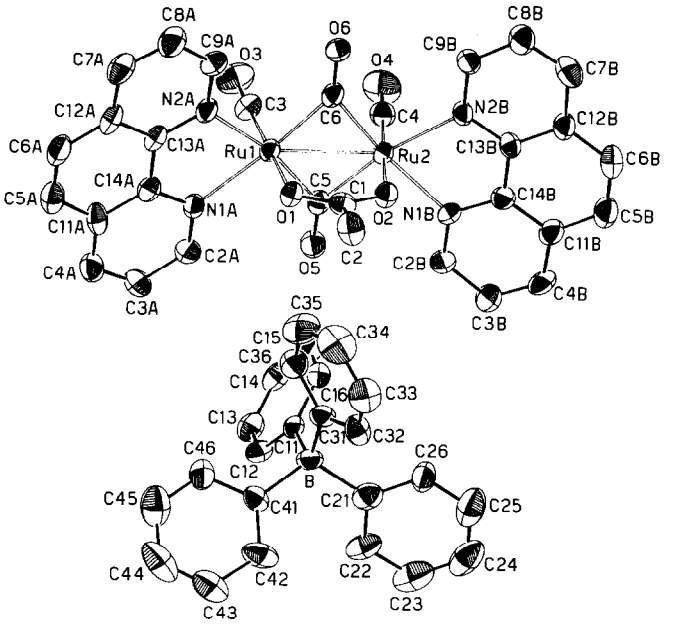

Fig. 2. ORTEP drawings of the $[Ru_2(CO)_4(MeCOO)(phen)_2]^+$ and $(BPh_4)^-$ ions. Ellipsoids at 50%.

endocyclic angles of 84.6(2) [84.0(4)]° av. at C and 94.8(2) [95.6(2)]° av. at Ru). The equatorial planes of the two octahedra containing the phenanthroline ligands and the bridging carbonyls are not exactly coplanar, but form a dihedral angle of 159.3(1) [161.1(2)]°. This is related to the combined effects of the bridging action of the acetato-group and the interference between the two terminal carbonyls (C3 ··· C4 = 3.213(7) [3.266(8)], O3 ··· O4 = 3.512(5) [3.590(5)] Å). In fact, the terminal carbonyls are colinear with the corresponding $Ru–O_{acetate}$ bonds and, being approximately perpendicular to these planes, define two lines forming an angle approximately supplementary (15.3(1) [17.3 (1)]°) to that formed by the planes.

As shown by Fig. 2 and Table 9, the complex cation has an approximate local *mm* symmetry with one mirror plane running along the bridging carbonyls, the C1–C2 acetate bond and through the midpoint of the Ru1–Ru2 bond, and the other containing the axial carbonyls and the acetato- ligand and running perpendicular to the phenanthroline planes along the Ru1–Ru2 direction through the midpoints of the C13–C14 bond.

The tetraphenylborate anion is packed between cations with contacts involving hydrogen atoms of the phenyl and phenanthroline groups, the shortest of them being H12 ··· $H2B^{i}$ = 2.31(1), H16 ··· $H5B^{ii}$ = 2.53(1), H15 ··· $H5B^{ii}$ = 2.62(1), H12 ··· $H7A^{iii}$ = 2.66(1), H34 ··· $H9A^{i}$ = 2.68(1) (i = 1 − *x*, *y* − 1/2, 1/2 − *z*; ii = 1 − *x*, −*y*, 1 − *z*; iii = 1 + *x*, *y*, *z*). It is worth noting that the angular deformations observed in the phenyl

TABLE 8. $[Ru_2(CO)_4(CH_3COO)(phen)_2](BPh_4)\cdot CH_2Cl_2$: atomic fractional co-ordinates (×10⁴) and equivalent isotropic displacement parameters (Å² ×10⁴) (one third trace of the diagonalized matrix), with e.s.d.'s in parentheses.

Atom	*x*	*y*	*z*	U_{eq}
Ru1	702.7(3)	1083.7(2)	2314.5(2)	306(1)
Ru2	1929.1(3)	1066.7(2)	3692.3(2)	303(1)
O1	1161(2)	62(2)	2313(2)	374(12)
O2	2154(2)	37(2)	3472(2)	377(12)
O3	−161(3)	2481(2)	2296(2)	675(18)
O4	1518(3)	2481(2)	4063(2)	699(19)
O5	2927(3)	1561(2)	2569(2)	450(14)
O6	−357(3)	796(2)	3465(2)	513(14)
C1	1712(4)	−240(2)	2870(3)	377(19)
C2	1846(4)	−994(3)	2812(3)	540(22)
C3	191(4)	1952(3)	2296(3)	425(20)
C4	1700(4)	1940(3)	3921(3)	418(20)
C5	2205(4)	1362(2)	2768(3)	343(18)
C6	386(3)	931(2)	3259(3)	362(18)
N1A	847(3)	1137(2)	1199(2)	353(14)
N2A	−788(3)	709(2)	1639(2)	374(15)
C2A	1649(4)	1371(3)	988(3)	445(20)
C3A	1646(4)	1381(3)	268(3)	538(23)
C4A	809(4)	1145(3)	−254(3)	519(22)
C11A	−50(4)	905(3)	−55(3)	455(21)
C5A	−994(5)	648(3)	−553(3)	527(23)
C6A	−1813(4)	421(3)	−334(3)	537(23)
C12A	−1773(4)	431(3)	411(3)	424(20)
C7A	−2589(4)	208(3)	685(3)	554(24)
C8A	−2494(4)	226(3)	1395(3)	545(23)
C9A	−1586(4)	490(3)	1865(3)	467(21)
C13A	−882(4)	678(2)	917(3)	343(18)
C14A	−1(4)	913(2)	680(3)	372(19)
N1B	3608(3)	1036(2)	4298(2)	369(14)
N2B	1951(3)	730(2)	4773(2)	340(14)
C2B	4416(4)	1216(3)	4068(3)	465(21)
C3B	5456(4)	1159(3)	4495(3)	541(22)
C4B	5651(4)	920(3)	5175(3)	533(23)
C11B	4822(4)	722(3)	5445(3)	441(20)
C5B	4945(4)	469(3)	6152(3)	562(24)
C6B	4104(4)	309(3)	6388(3)	563(24)
C12B	3059(4)	388(3)	5936(3)	438(20)
C7B	2167(4)	262(3)	6166(3)	525(23)
C8B	1212(4)	392(3)	5716(3)	501(22)
C9B	1121(4)	620(3)	5015(3)	430(20)
C13B	2919(4)	626(2)	5231(3)	353(18)
C14B	3799(4)	799(2)	4983(3)	359(18)
B	4876(4)	−1644(3)	1433(3)	371(22)
C11	4554(3)	−845(2)	1428(2)	333(17)
C12	4823(3)	−364(3)	979(3)	423(21)
C13	4672(4)	320(3)	1037(3)	448(20)
C14	4228(4)	565(3)	1553(3)	475(21)
C15	3938(4)	115(3)	2002(3)	444(20)
C16	4107(4)	−567(3)	1945(3)	418(20)
C21	6048(4)	−1689(3)	2001(3)	480(22)
C22	6950(4)	−1490(3)	1817(3)	608(25)
C23	7936(5)	−1494(3)	2296(4)	801(34)
C24	8083(6)	−1701(3)	2989(4)	829(33)
C25	7227(6)	−1871(3)	3208(4)	769(31)
C26	6240(5)	−1858(3)	2732(3)	570(24)
C31	4040(4)	−2152(3)	1673(3)	389(19)
C32	4324(4)	−2783(3)	1989(3)	476(22)
C33	3622(5)	−3232(3)	2144(3)	635(28)
C34	2585(6)	−3059(3)	1993(4)	785(33)

TABLE 8 (continued)

Atom	x	y	z	U_{eq}
C35	2273(5)	−2446(3)	1687(3)	696(28)
C36	2969(4)	−2005(3)	1531(3)	501(22)
C41	4832(4)	−1881(3)	604(3)	408(21)
C42	5622(5)	−2226(3)	396(3)	558(25)
C43	5531(6)	−2429(3)	−310(4)	690(30)
C45	3850(6)	−1968(3)	−662(4)	750(31)
C44	4648(7)	−2298(3)	−834(4)	853(38)
C46	3940(5)	−1771(3)	34(3)	568(25)
Cl1	8426(1)	3851(1)	253(1)	1158(11)
Cl2	9476(3)	2618(2)	272(2)	2547(23)
C17	8313(8)	3038(5)	84(6)	1699(63)

rings (the endocyclic angle at the *para* and, even more so, at the *ipso* carbon atoms are significantly less than 120°, see Table 9) are consistent with the findings of Domenicano *et al.* [33].

The CH_2Cl_2 molecules are disordered, as indicated by their exceptionally high atomic displacement coefficients and anisotropies. The contacts formed between the chlorine atoms and the surrounding atoms are all greater than 3 Å, and the only short contact formed by its CH_2 group involves one H atom which is 2.6 Å from the phenyl carbon C35 at $1-x$, $-y$, $-z$.

2.7. Remarks on the structure of the compounds

The formulation $[Ru_2(CO)_4(MeCOO)(N\text{-}N)_2]X$, where $X = BPh_4$ or MeCOO, may be attributed to all the complexes. Such a general formulation is supported by the following data and considerations: i) the analytical results, ii) the X-ray structure of **1** we determined (Fig. 2), similar to that of **4** [27]; iii) the similar spectroscopic characteristics of the two series of products (Tables 2–7); and iv) the syntheses of $[Ru_2(CO)_4(MeCOO)(N\text{-}N)_2](BPh_4)$ from $[Ru_2(CO)_4(MeCOO)(N\text{-}N)_2](MeCOO)$ by metathetical substitution of the acetate anion by tetraphenylborate. All compounds are 1:1 electrolytes in methanol solution (Table 1): an equimolar solution of sodium acetate in the same solvent has almost the same conductance. The general structure of the complexes $[Ru_2(CO)_4(MeCOO)(N\text{-}N)_2](MeCOO)$ is presented in Fig. 3.

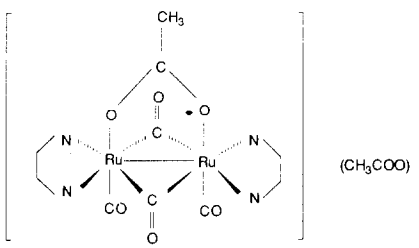

Fig. 3. General structure of $[Ru_2(CO)_4(MeCOO)(N\text{-}N)_2](MeCOO)$.

3. Experimental section

3.1. Spectroscopy and conductivity determinations

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 or at 199.975 MHz on a Varian Gemini-200 spectrometer, using tetramethylsilane as external reference. ^{13}C-NMR spectra were recorded at 75.429 MHz on a Varian VXR 300 instrument; all ^{13}C-NMR spectra were proton-decoupled, using tetramethylsilane as external reference.

Conductivity determinations: an Analytical Instrument 111 conductivity meter with Orion 99.01.01 cell, having a cell-constant 1.00 cm^{-1}, was used.

3.2. Materials

All preparations and manipulations were routinely performed under a dry dinitrogen atmosphere using Schlenk tube techniques.

Methanol (C. Erba) was purified by the Lund and Bijerrunn method reported by Vogel [34]. Tetrahydrofuran (C. Erba RPE grade) (900 ml) was dried by refluxing over $LiAlH_4$ (10 g). The product collected by fractional distillation had b.p. 65°C.

Acetone (C. Erba, RPE-ACS grade) was purified according to Vogel [35]. Other reagents were supplied as follows: 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), triruthenium dodecacarbonyl (Aldrich). The ^{1}H-NMR spectrum, in CD_3OD, of sodium tetraphenylborate (C. Erba RPE-ACS grade) showed signals at: 6.84 (m, 4H, H_{para}), 6.97 (m, 8H, H_{ortho}), 7.30 (m, 8H, H_{meta}) ppm. The ^{13}C-NMR spectrum, in CD_3OD, showed signals at: 124.4 (s, 4C, C_{para}), 128.1 (s, 8C, C_{ortho}), 138.9 (s, 8C, C_{meta}), 166.9 (m, 4C, C_{ipso}, $J(C,B) = 49.4$ Hz) ppm. $\{Ru_2(CO)_4(MeCOO)_2\}_n$ was synthesized according to Crooks *et al.* [28].

3.3. Syntheses

3.3.1. General procedure for synthesis of $[Ru_2(CO)_4(MeCOO)(N\text{-}N)_2](BPh_4)$

The base N-N (0.923 mmol), ethanol (30 ml) and $[Ru_2(CO)_4(MeCOO)_2]_n$ (200 mg, 0.925 mmol Ru were introduced into a 100 ml flask equipped with a reflux condenser. The suspension was heated under reflux for 3 h, giving an orange solution. The solution was cooled

TABLE 9. $[Ru_2(CO)_4(CH_3COO)(phen)_2](BPh_4) \cdot CH_2Cl_2$: bond distances (Å) and angles (°). E.s.d.'s in parentheses

Metal coordination				av.
Ru1–Ru2	2.701(1)			–
Ru1–O1	2.111(3)	Ru2–O2	2.119(3)	2.115(4)
Ru1–C3	1.844(5)	Ru2–C4	1.829(6)	1.838(7)
Ru1–C5	2.017(5)	Ru2–C5	2.002(5)	2.010(8)
Ru1–C6	2.001(5)	Ru2–C6	2.003(4)	2.002(3)
Ru1–N1A	2.212(4)	Ru2–N1B	2.210(3)	2.211(2)
Ru1–N2A	2.174(4)	Ru2–N2B	2.177(4)	2.176(3)
N1A–Ru1–N2A	75.2(1)	N1B–Ru2–N2B	75.1(1)	75.2(1)
C6–Ru1–N2A	96.2(2)	C6–Ru2–N2B	95.6(2)	95.9(3)
C6–Ru1–N1A	170.9(2)	C6–Ru2–N1B	168.6(2)	169.8(11)
C5–Ru1–N2A	167.8(2)	C5–Ru2–N2B	169.1(2)	168.4(6)
C5–Ru1–N1A	93.7(2)	C5–Ru2–N1B	94.1(2)	93.9(2)
C5–Ru1–C6	94.6(2)	C5–Ru2–C6	95.0(2)	94.8(2)
C3–Ru1–N2A	92.1(2)	C4–Ru2–N2B	91.0(2)	91.6(5)
C3–Ru1–N1A	93.8(2)	C4–Ru2–N1B	96.3(2)	95.0(12)
C3–Ru1–C6	89.4(2)	C4–Ru2–C6	90.4(2)	89.9(5)
C3–Ru1–C5	93.9(2)	C4–Ru2–C5	91.2(2)	92.6(13)
O1–Ru1–N2A	83.5(1)	O2–Ru2–N2B	86.1(1)	84.8(12)
O1–Ru1–N1A	86.7(1)	O2–Ru2–N1B	84.4(1)	85.6(11)
O1–Ru1–C6	89.4(2)	O2–Ru2–C6	88.4(2)	88.9(5)
O1–Ru1–C5	90.7(2)	O2–Ru2–C5	91.8(2)	91.2(6)
O1–Ru1–C3	175.3(2)	O2–Ru2–C4	176.8(2)	176.0(7)
Ru2–Ru1–N2A	141.6(1)	Ru1–Ru2–N2B	142.0(1)	141.8(2)
Ru2–Ru1–N1A	139.8(1)	Ru1–Ru2–N1B	139.7(1)	139.8(1)
Ru2–Ru1–C6	47.6(1)	Ru1–Ru2–C6	47.6(1)	47.6(1)
Ru2–Ru1–C5	47.6(1)	Ru1–Ru2–C5	48.0(1)	47.8(2)
Ru2–Ru1–C3	98.6(2)	Ru1–Ru2–C4	97.4(2)	98.0(6)
Ru2–Ru1–O1	83.9(1)	Ru1–Ru2–O2	84.0(1)	84.0(1)
Ru1–O1–C1	123.2(3)	Ru2–O2–C1	122.8(3)	123.0(2)
Ru1–C3–O3	177.0(5)	Ru2–C4–O4	177.4(5)	177.2(4)
Ru1–C5–O5	137.4(4)	Ru2–C5–O5	138.0(4)	137.7(3)
Ru1–C5–Ru2	84.4(2)	Ru1–C6–Ru2	84.8(2)	84.6(2)
Ru1–C6–O6	137.7(4)	Ru2–C6–O6	137.4(4)	137.6(3)
Ru1–N1A–C14A	114.9(3)	Ru2–N1B–C14B	114.3(3)	114.6(3)
Ru1–N1A–C2A	127.6(3)	Ru2–N1B–C2B	127.7(3)	127.6(2)
Ru1–N2A–C13A	115.9(3)	Ru2–N2B–C13B	115.3(3)	115.6(3)
Ru1–N2A–C9A	126.3(3)	Ru2–N2B–C9B	126.4(3)	126.4(2)
Acetate ligand				
O1–C1	1.268(6)	O2–C1	1.268(6)	1.268(4)
C1–C2	1.511(7)			–
O1–C1–O2	125.7(4)			–
O1–C1–C2	117.0(4)	O2–C1–C2	117.3(4)	117.2(3)
Carbonyl ligands				
O3–C3	1.145(7)	O4–C4	1.146(7)	1.146(5)
O5–C5	1.193(7)	O6–C6	1.191(6)	1.192(5)
Phenanthroline ligands				
N1A–C2A	1.323(7)	N1B–C2B	1.316(7)	1.320(5)
N1A–C14A	1.356(5)	N1B–C14B	1.356(6)	1.356(4)
N2A–C9A	1.325(7)	N2B–C9B	1.328(7)	1.326(5)
N2A–C13A	1.362(7)	N2B–C13B	1.357(5)	1.359(4)
C2A–C3A	1.385(8)	C2B–C3B	1.401(6)	1.395(8)
C3A–C4A	1.358(7)	C3B–C4B	1.348(8)	1.354(5)
C4A–C11A	1.384(9)	C4B–C11B	1.396(8)	1.391(6)
C11A–C5A	1.443(7)	C11B–C5B	1.417(8)	1.432(13)
C11A–C14A	1.400(7)	C11B–C14B	1.410(6)	1.406(5)
C5A–C6A	1.346(9)	C5B–C6B	1.353(9)	1.350(6)
C6A–C12A	1.421(8)	C6B–C12B	1.426(7)	1.424(5)
C12A–C7A	1.401(8)	C12B–C7B	1.396(9)	1.399(6)
C12A–C13A	1.395(6)	C12B–C13B	1.400(7)	1.397(5)
C7A–C8A	1.339(8)	C7B–C8B	1.347(7)	1.344(5)
C8A–C9A	1.390(7)	C8B–C9B	1.397(8)	1.393(5)
C13A–C14A	1.444(8)	C13B–C14B	1.422(8)	1.433(11)

TABLE 9 (continued)

Phenanthroline ligands				
C2A–N1A–C14A	117.5(4)	C2B–N1B–C14B	118.1(4)	117.8(3)
C9A–N2A–C13A	117.8(4)	C9B–N2B–C13B	118.2(4)	118.0(3)
N1A–C2A–C3A	122.3(5)	N1B–C2B–C3B	122.8(5)	122.6(4)
C2A–C3A–C4A	120.8(5)	C2B–C3B–C4B	119.4(5)	120.1(7)
C3A–C4A–C11A	118.6(5)	C3B–C4B–C11B	120.1(5)	119.4(7)
C4A–C11A–C14A	117.8(5)	C4B–C11B–C14B	117.0(5)	117.4(4)
C4A–C11A–C5A	124.5(5)	C4B–C11B–C5B	124.4(5)	124.4(4)
C5A–C11A–C14A	117.7(5)	C5B–C11B–C14B	118.6(5)	118.2(4)
C11A–C5A–C6A	122.5(5)	C11B–C5B–C6B	121.3(5)	121.9(6)
C5A–C6A–C12A	120.3(5)	C5B–C6B–C12B	121.5(5)	120.9(6)
C6A–C12A–C13A	119.8(5)	C6B–C12B–C13B	118.2(5)	119.0(8)
C6A–C12A–C7A	124.1(5)	C6B–C12B–C7B	123.5(5)	123.8(4)
C7A–C12A–C13A	116.1(5)	C7B–C12B–C13B	118.2(5)	117.2(10)
C12A–C7A–C8A	120.9(5)	C12B–C7B–C8B	119.3(5)	120.1(8)
C7A–C8A–C9A	119.6(5)	C7B–C8B–C9B	119.8(5)	119.7(4)
N2A–C9A–C8A	122.4(5)	N2B–C9B–C8B	122.4(5)	122.4(4)
N2A–C13A–C12A	123.3(5)	N2B–C13B–C12B	122.0(5)	122.6(6)
C12A–C13A–C14A	119.7(4)	C12B–C13B–C14B	120.5(5)	120.0(4)
N2A–C13A–C14A	117.1(4)	N2B–C13B–C14B	117.5(4)	117.3(3)
C11A–C14A–C13A	120.1(5)	C11B–C14B–C13B	119.9(5)	120.0(4)
N1A–C14A–C13A	116.9(4)	N1B–C14B–C13B	117.5(4)	117.2(3)
N1A–C14A–C11A	123.0(5)	N1B–C14B–C11B	122.6(5)	122.8(4)
Tetraphenylborate anion				
B–C11	1.636(7)	B–C21	1.637(7)	1.636(5)
B–C31	1.656(8)	B–C41	1.651(8)	1.654(6)
C_{ipso}–C_{ortho}				1.397(3)
C_{ortho}–C_{meta}				1.375(3)
C_{metal}–C_{para}				1.359(4)
C11–B–C41	109.3(4)	C21–B–C31	111.5(4)	110.4(11)
C11–B–C31	113.2(4)	C21–B–C41	113.8(5)	113.4(3)
C11–B–C21	104.7(4)	C31–B–C41	104.5(4)	104.6(3)
B–C–C				123.1(5)
$\hat{C}_{ipso}$				113.6(2)
$\hat{C}_{ortho}$				123.3(2)
$\hat{C}_{meta}$				120.5(2)
$\hat{C}_{para}$				118.7(3)

at room temperature and $NaBPh_4$ (158 mg, 0.462 mmol) was added; the suspension was then heated under reflux for 3 h and the solvent distilled off under reduced pressure leaving a residue which was then dissolved in CH_2Cl_2 and crystallized by adding ethanol.

The yields, elemental analyses and the conductivity data are reported in Table 1; the IR data are in Table 2 and the NMR data in Tables 3–6.

3.3.2. General procedure for synthesis of $[Ru_2(CO)_4(MeCOO)(N\text{-}N)_2](MeCOO)$

The base N-N (0.923 mmol), ethanol (30 ml) and $[Ru_2(CO)_4(MeCOO)_2]_n$ (200 mg, 0.925 mmol Ru) were introduced into a flask (100 ml) fitted with reflux condenser and the suspension heated under reflux for 3 h, giving an orange solution. After removal by distillation of the solvent under reduced pressure, a brown residue was obtained. This was purified by preparative TLC (Al_2O_3 as stationary phase, methanol as eluent), collecting the middle fraction.

The yields, elemental analyses and conductivity data are reported in Table 1; the IR data in Table 2 and the NMR data in Tables 3, 4, 6, and 7.

3.4. Crystal structure analysis of $[Ru_2(CO)_4(MeCOO)(phen)_2](BPh_4) \cdot CH_2Cl_2$

The crystal structure analysis is summarized in Table 10. The lattice parameters were refined by a least-squares procedure [37] using the Nelson and Riley [38] extrapolation function. The intensities were measured at room temperature and the intensity variations of the standard reflections were never greater than the statistical fluctuations. The individual reflection profiles were analysed using the method of Lehmann and

TABLE 10. Experimental data for the crystal structure analysis of $[Ru_2(CO)_4(CH_3COO)(phen)_2](BPh_4)\cdot CH_2Cl_2$

Formula	$C_{55}H_{41}BCl_2N_4O_6Ru_2$
M	1137.81
Space group	$P2_1/c$
a/Å	13.267(3)
b/Å	19.778(3)
c/Å	19.262(6)
β/°	106.132
V/Å^3	4855(2)
Z	4
D_c/Mg m^{-3}	1.556
Reflections for number	25
Lattice parameters θ range/°	11/17
Crystal data, radiation, wavelength/Å	Mo-Kα_1, 0.709300
F(000)	2296
Temperature/K	293(2)
Crystal size/mm	0.21×0.32×0.41
Diffractometer	Enraf-Nonius CAD4
μ/mm^{-1}	0.775
Scan speed/° min^{-1}	3.3
Scan width/°	1.20+0.35 tan θ
Radiation for intensity measurements	Mo-Kα mean
θ-range/°	3–25
h range	−15/15
k range	0/23
l range	0/22
Standard reflections	4 11 4, −2 9 9, 3 0 12
Intensity variation	none
No. of measured reflections	9053
No. of independent reflections	8516
No. of reflections omitted ($\lvert F_o^2 - F_c^2\rvert$/e.s.d. > 5)	7
No. of reflections used in refinement (N)	8509
R(int)	0.0222
Anisotropic least-squares on F^2	full matrix
Mean L.S. shift to error ratio	0.002
Min./Max. height in final $\Delta\rho/e$ Å^{-3}	−0.58/0.59(6)
No. of refined parameters (P)	636
$wR_2 = [\Sigma w(\Delta F^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ for 8509 data	0.0812
wR_2 for all 8516 data	0.0818
$R1 = \Sigma\lvert\Delta F\rvert/\Sigma\lvert F_o\rvert$ for 3694 with $F_o > 4\sigma F_o$	0.0303
$R1$ for all 8516 data	0.0972
$S = [\Sigma w(\Delta F)^2/(N-P)]^{1/2}$ for all data	0.439
S for obs. data	0.538
w, $g = [\max(F_o^2, 0)+2F_c^2]/3$	$1/[\sigma^2(F_o^2)+0.0133\ g^2]$

Larsen [39], and the intensity data were corrected for Lorentz and polarization effects, but no correction for absorption or extinction was applied.

The structure was solved by the Patterson and Fourier methods of SHELX86 [40], and refined by block-diagonal least squares on F^2, using the SHELXL92 [41] program. The non-hydrogen atoms were all refined anisotropically, while the hydrogen atoms were put in calculated positions riding on the attached carbon atoms. The CH_2Cl_2 molecule was found from a final difference map; its abnormally high atomic displacement coefficients and anisotropies are indicative of disorder.

The geometrical aspects of the structure were analysed by using the PARST [42], ORTEP [43] and PLUTO [44] programs. Atomic scattering factors and anomalous scattering coefficients were taken from ref. [45]; final atomic coordinates are given in Table 8.

Throughout the paper the averaged values are means, weighted according to the reciprocals of the variances, and the corresponding e.s.d.'s are the largest of the values of the "external" and "internal" standard deviations [46]. The crystallographic calculations were carried out on the Encore-Powernode 6040 and Encore-91 computers of the Centro di Studio per la Strutturistica Diffrattometrica del CNR (Parma).

Complete lists of bond distances, bond angles, torsion angles, hydrogen coordinates, anisotropic parameters and structure factor tables are available from the authors, and from the Cambridge Crystallographic Data Centre.

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