

## Carbonyl–Carboxylato–Ruthenium Complexes Incorporating Diimine Ligands and Unexpected Cyclometalation of Carboxylate Ligands

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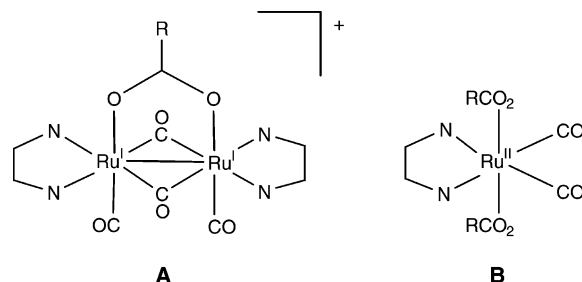
We report two new synthetic routes to the dinuclear Ru(I) complexes,  $[\text{Ru}_2(\text{RCO}_2)(\text{CO})_4(\text{N}^{\wedge}\text{N})_2]^+$  ( $\text{N}^{\wedge}\text{N} = 2,2'$ -bipyridine or 1,10-phenanthroline derivatives) that use  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  as a starting material. Direct addition of the bidentate diimine ligand to a methanolic solution of  $[\text{Ru}(\text{CO})_2\text{Cl}_2]_n$  and sodium acetate yielded a mixture of  $[\text{Ru}_2(\text{MeCO}_2)(\text{CO})_4(\text{N}^{\wedge}\text{N})_2]^+$  ( $\text{N}^{\wedge}\text{N} = 4,4'$ -dmbpy, and 5,6-dmphen), and  $[\text{Ru}^{\text{II}}(\text{MeCO}_2)_2(\text{CO})_2(\text{N}^{\wedge}\text{N})]$  ( $\text{N}^{\wedge}\text{N} = 4,4'$ -dmbpy and 5,5'-dmbpy). Single-crystal X-ray studies confirmed that the Ru(II) complexes had a *trans*-acetate–*cis*-carbonyl arrangement of the ligands. In contrast, the use of sodium benzoate resulted in the unexpected formation of a Ru–C bond producing *ortho*-cyclometalated complexes,  $[\text{Ru}^{\text{II}}(\text{O}_2\text{CC}_6\text{H}_4)(\text{CO})_2(\text{N}^{\wedge}\text{N})]$ , where  $\text{N}^{\wedge}\text{N} = \text{bpy}$  or phen. A second approach used ligand exchange between a bidentate ligand ( $\text{N}^{\wedge}\text{N}$ ) and the pyridine ligands of  $[\text{Ru}^{\text{I}}(\text{RCO}_2)(\text{CO})_2(\text{py})_2]$  to convert these neutral complexes into  $[\text{Ru}_2(\text{RCO}_2)(\text{CO})_4(\text{N}^{\wedge}\text{N})_2]^+$ . This method, although it involved more steps, was applicable for a wider variety of diimine ligands ( $\text{R} = \text{Me}$  and  $\text{N}^{\wedge}\text{N} = 4,4'$ -dmbpy, 5,5'-dmbpy, 5,6-dmphen;  $\text{R} = \text{Ph}$  and  $\text{N}^{\wedge}\text{N} = \text{bpy}$ , phen, 5,6-dmphen).

### Introduction

Carbonyl–carboxylato complexes of ruthenium(I) and (II), Figure 1, have been of interest due to their favorable catalytic properties, with respect to, for example, hydrogenation and carbonylation of organic substrates.<sup>1,2</sup> Unfortunately the high cost of existing syntheses based on  $\text{Ru}_3(\text{CO})_{12}$  has restricted the application of these complexes.

Previous syntheses involved reacting  $\text{Ru}_3(\text{CO})_{12}$  with carboxylic acids for prolonged periods at high temperature to produce the polymeric carboxylato complexes,  $[\text{Ru}^{\text{I}}(\text{RCO}_2)(\text{CO})_2]_n$ . These polymers were either directly reacted with a diimine ligand<sup>4</sup> or converted to the acetonitrile adduct prior to reaction with the bidentate ligand (Scheme 1).<sup>5</sup>

We have recently reported a new synthetic route to dimeric ruthenium(I) complexes incorporating unidentate ligands (L),



**Figure 1.** (A)  $[\text{Ru}_2(\text{RCO}_2)(\text{CO})_4(\text{N}^{\wedge}\text{N})_2]^+$  and (B)  $[\text{Ru}^{\text{II}}(\text{RCO}_2)_2(\text{CO})_2(\text{N}^{\wedge}\text{N})]$ , where  $\text{N}^{\wedge}\text{N}$  is a diimine ligand, such as 2,2'-bipyridine (bpy) or 1,10-phenanthroline (phen).

$[\text{Ru}^{\text{I}}(\text{RCO}_2)(\text{CO})_2(\text{L})_2]$ , which is based on the relatively inexpensive  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  precursor (Scheme 2).<sup>6</sup> An N-donor ligand, e.g., pyridine, was reacted with  $[\text{Ru}^{\text{II}}(\text{CO})_2\text{Cl}_2]_n$  in the presence of sodium carboxylate to yield  $[\text{Ru}^{\text{I}}(\text{RCO}_2)(\text{CO})_2(\text{L})_2]$ . Here, we report the extension of this synthetic approach to generate cationic  $[\text{Ru}_2(\text{RCO}_2)(\text{CO})_4(\text{N}^{\wedge}\text{N})_2]^+$

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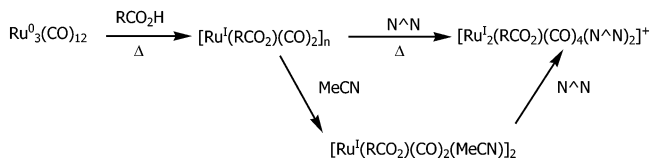
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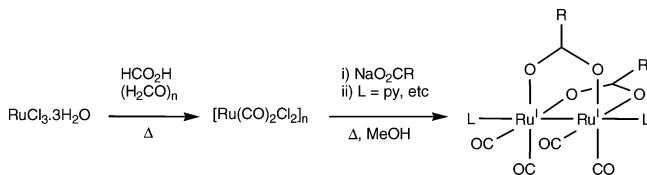
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## Scheme 1



## Scheme 2



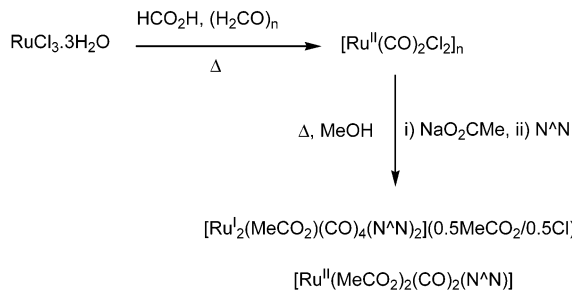
complexes. We further report the unexpected formation of cyclometalated benzoate complexes obtained when  $[\text{Ru}^II(\text{CO})_2\text{Cl}_2]_n$  was reacted with sodium benzoate and bpy or phen. Although cyclometalation of ligands, particularly phosphines and phosphites<sup>7,8</sup> by ruthenium complexes is known, and has been extended to, for example, heterocyclic amine ligands,<sup>9</sup> aromatic enolates<sup>10</sup> and Schiff bases,<sup>11</sup> Ru–cyclometalated benzoates have not been characterized by single-crystal X-ray diffraction studies. Solution rearrangement of an arylamidobenzoate led to an equilibrium with a Ru–cyclometalated anthranilate but the latter could not be obtained pure, and an attempted direct *ortho*-metalation of phenylacetate failed.<sup>12</sup> Although some cyclometalated ruthenium complexes incorporating aromatic alkanooates have been isolated, viz.,  $[\text{Ru}(\text{O}_2\text{CC}_6\text{H}_4)(\text{CO})_2(\text{PPh}_3)_2]$ <sup>13</sup> and  $[\text{Ru}(\text{O}_2\text{CC}_6\text{H}_3\text{Me})(\text{CO})_2(\text{PPh}_3)_2]$ ,<sup>13</sup> their characterization by spectroscopic studies leaves structural uncertainties.

## Results and Discussion

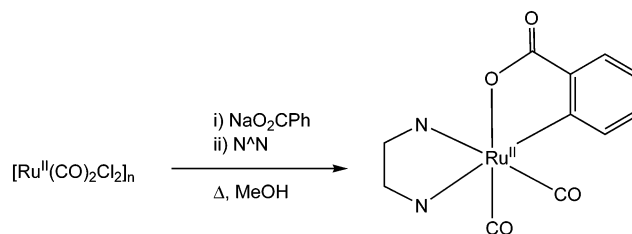
**Synthesis.** The first approach followed the procedure outlined in Scheme 2, the unidentate ligand, L, being replaced with a bidentate ligand,  $\text{N}^{\wedge}\text{N}$ . The reaction of 4,4'-dimethyl-2,2'-bipyridine (4,4'-dmbpy) with a refluxing solution of  $[\text{Ru}^II(\text{CO})_2\text{Cl}_2]_n/\text{NaO}_2\text{CMe}$  (Scheme 3) gave the dinuclear  $[\text{Ru}^I_2(\text{MeCO}_2)(\text{CO})_4(4,4'\text{-dmbpy})_2]^+$  complex which precipitated as a chloride/acetate salt (42% yield, cf. 55% for  $[\text{Ru}^I(\text{MeCO}_2)(\text{CO})_2(\text{py})_2]$ ) and was converted to the  $\text{PF}_6^-$  salt. Attempts to retrieve additional product from the reaction mixture yielded  $[\text{Ru}^II(\text{MeCO}_2)_2(\text{CO})_2(4,4'\text{-dmbpy})]$ , consistent with reports that  $[\text{Ru}^II(\text{RCO}_2)_2(\text{CO})_2(\text{L})_2]$  was formed in the reaction mixtures from  $[\text{Ru}^I(\text{RCO}_2)(\text{CO})_2(\text{L})_2]$  syntheses.<sup>6</sup>

When  $\text{N}^{\wedge}\text{N} = 5,5'\text{-dmbpy}$ , the major product was  $[\text{Ru}^II(\text{MeCO}_2)_2(\text{CO})_2(5,5'\text{-dmbpy})]$ , only trace amounts of the

## Scheme 3



## Scheme 4



expected dinuclear  $\text{Ru}^I$  complex being obtained. In the case of  $\text{N}^{\wedge}\text{N} = 5,6\text{-dmpen}$ , the precipitate obtained was a mixture of the  $\text{Ru}^I$  dinuclear complex, the  $\text{Ru}^II$  byproduct and the free ligand. This “direct addition” method is not general, the low yields and difficulty in separating the  $\text{Ru}^I$  and  $\text{Ru}^II$  products rendering it an unviable synthetic route to  $[\text{Ru}^I_2(\text{RCO}_2)(\text{CO})_4(\text{N}^{\wedge}\text{N})_2]^+$ . However, if the conditions could be optimized to selectively generate  $[\text{Ru}^II(\text{MeCO}_2)_2(\text{CO})_2(\text{N}^{\wedge}\text{N})]$ , this would be an improvement on existing syntheses that require either long reflux in acetic acid<sup>14</sup> or use of silver carboxylate salts.<sup>15</sup>

The attempted direct synthesis of  $[\text{Ru}^I_2(\text{PhCO}_2)(\text{CO})_4(\text{N}^{\wedge}\text{N})_2]^+$  by the addition of bpy and phen to refluxing solutions of  $[\text{Ru}(\text{CO})_2\text{Cl}_2]_n$  and sodium benzoate in methanol yielded crystalline ruthenium(II) complexes incorporating a cyclometalated benzoate (Scheme 4). The formation of these complexes was unexpected as the neutral pyridine complex,  $[\text{Ru}^I(\text{PhCO}_2)(\text{CO})_2(\text{py})_2]$ , had been successfully made from  $[\text{Ru}(\text{CO})_2\text{Cl}_2]_n$ .<sup>6</sup>

An approach that enabled the synthesis of  $[\text{Ru}^I_2(\text{RCO}_2)(\text{CO})_4(\text{N}^{\wedge}\text{N})_2]^+$  involved the use of  $\text{Ru}^I$  precursors.  $[\text{Ru}^I(\text{MeCO}_2)(\text{CO})_2(\text{py})_2]$  and  $[\text{Ru}^I(\text{PhCO}_2)(\text{CO})_2(\text{py})_2]$  were considered to be suitable synthons due to their relative ease of preparation and demonstrated lability of the pyridine ligands.<sup>6</sup> Ligand exchange reactions initially performed in refluxing alcohols resulted in decomposition of the dinuclear core. Prolonged reaction of an excess of a bidentate ligand with the complexes under milder conditions (40 °C) in methanol enabled the substitution of the axially coordinated pyridines (Scheme 5), hexafluorophosphate being used to precipitate the cationic product. Use of an aqueous solution of  $\text{NH}_4\text{PF}_6$ , instead of  $\text{KPF}_6$  (which coprecipitated other water insoluble compounds, e.g., unreacted  $[\text{Ru}(\text{RCO}_2)(\text{CO})_2(\text{py})_2]$  and diimine ligand), gave clean products, with clean electrospray

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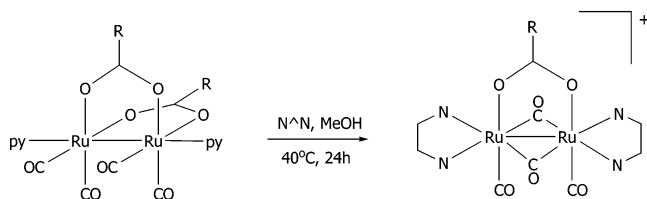
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Scheme 5



and NMR spectra. This approach uses mild conditions, eliminating the necessity for separation from Ru(II) byproducts, and was found to be general for  $[\text{Ru}^{\text{II}}_2(\text{RCO}_2)(\text{CO})_4(\text{N}^{\wedge}\text{N})_2]\text{PF}_6$  complexes: R = Me,  $\text{N}^{\wedge}\text{N}$  = 4,4'-dmbpy, 5,5'-dmbpy, 5,6-dmphen; R = Ph,  $\text{N}^{\wedge}\text{N}$  = bpy, phen, 5,6-dmphen.

**Characterization.** The IR spectra of the  $[\text{Ru}^{\text{II}}_2(\text{RCO}_2)(\text{CO})_4(\text{N}^{\wedge}\text{N})_2]^+$  complexes show two bands in the region 2100–1900  $\text{cm}^{-1}$ , which can be assigned to  $\nu(\text{CO}_{\text{terminal}})$ , and two bands between 1900 and 1700  $\text{cm}^{-1}$  attributable to  $\nu(\text{CO}_{\text{bridging}})$ . An absorption in the region 1550–1520  $\text{cm}^{-1}$  results from antisymmetric stretching ( $\nu_{\text{as}}$ ) of bridging acetate, while the symmetric stretch ( $\nu_{\text{s}}$ ) is found in the 1440–1400  $\text{cm}^{-1}$  region. A band at  $\sim 1600 \text{ cm}^{-1}$  is ascribed to C=C or C=N stretching of the diimine ligands. Frediani et al. have reported that the  $\nu_{\text{as}}$  stretch of the ionic acetate occurs in the 1655–1627  $\text{cm}^{-1}$  region,<sup>4</sup> more appropriate for unidentate acetate. It is expected to be much closer to  $\nu_{\text{as}}(\text{CO}_2)$  of sodium acetate (1578  $\text{cm}^{-1}$ ).<sup>16</sup>  $[\text{Ru}^{\text{II}}_2(\text{MeCO}_2)(\text{CO})_4(4,4'\text{-dmbpy})_2](0.5\text{MeCO}_2/0.5\text{Cl})$  displayed multiple bands in the region 1560–1520  $\text{cm}^{-1}$ , attributable to  $\nu_{\text{as}}$  of the pair of inequivalent acetates (bridging and anionic).

In the IR spectrum of  $[\text{Ru}^{\text{II}}_2(\text{MeCO}_2)(\text{CO})_4(5,6\text{-dmphen})_2]\text{PF}_6$  (prepared from the Ru(II) precursor)  $\nu(\text{CO})$  absorptions additional to those expected for this product were observed and are attributed to  $[\text{Ru}^{\text{II}}(\text{MeCO}_2)_2(\text{CO})_2(5,6\text{-dmphen})]$  with NMR analysis indicating a  $\sim 1:1$  ratio of products. These types of Ru(II) complexes typically display two strong CO stretching bands at  $\sim 2050$  and 1990  $\text{cm}^{-1}$ ,<sup>14,15</sup> which should obscure the weaker terminal  $\nu(\text{CO})$  absorptions of  $[\text{Ru}^{\text{II}}_2(\text{MeCO}_2)(\text{CO})_4(5,6\text{-dmphen})_2]\text{PF}_6$ . Characteristic bridging  $\nu(\text{CO})$  absorptions (at 1801 and 1731  $\text{cm}^{-1}$ ), however, prove the presence of  $[\text{Ru}^{\text{II}}_2(\text{MeCO}_2)(\text{CO})_4(5,6\text{-dmphen})_2]\text{PF}_6$ . The electrospray mass spectrum also displayed a signal at  $m/z$  791 corresponding to  $[\text{Ru}^{\text{II}}_2(\text{MeCO}_2)(\text{CO})_4(5,6\text{-dmphen})_2]^+$ .

The  $^1\text{H}$  NMR spectra of  $[\text{Ru}^{\text{II}}_2(\text{RCO}_2)(\text{CO})_4(\text{N}^{\wedge}\text{N})_2]^+$  indicate that these complexes have a high degree of symmetry so that the halves of the diimine ligands behave identically. Coordination of the diimine ligands to the diruthenium core caused the proton resonances to shift downfield relative to the free ligands (e.g., protons in the 5,5' and 6,6' positions of dmbpy by 0.9 and 1.5 ppm, respectively and by  $> 1.2$  ppm for the aromatic protons of 5,6-dmphen). When R = Me, the spectrum displayed singlets at ca. 1 and 1.9 ppm attributable to the methyl group of the bridging acetate and unbound acetate, respectively. For  $[\text{Ru}^{\text{II}}_2(\text{MeCO}_2)(\text{CO})_4(4,4'\text{-dmbpy})_2]^+$ , the integration of this

signal (half of that for coordinated acetate) and gravimetric chloride analysis<sup>17</sup> supported the formulation as  $[\text{Ru}^{\text{II}}_2(\text{MeCO}_2)(\text{CO})_4(4,4'\text{-dmbpy})_2](0.5\text{MeCO}_2/0.5\text{Cl})$ .

Analysis of the IR spectra of  $[\text{Ru}^{\text{II}}(\text{MeCO}_2)_2(\text{CO})_2(\text{N}^{\wedge}\text{N})]$  complexes revealed two strong bands attributable to  $\nu(\text{CO})$  of cis-terminal carbonyl ligands (2057 and 1996  $\text{cm}^{-1}$  for  $\text{N}^{\wedge}\text{N}$  = 4,4'-dmbpy, 2052 and 1983  $\text{cm}^{-1}$  for  $\text{N}^{\wedge}\text{N}$  = 5,5'-dmbpy; cf., 2058, 1995  $\text{cm}^{-1}$  for  $[\text{Ru}^{\text{II}}(\text{MeCO}_2)_2(\text{CO})_2(\text{bpy})]$  and 2060, 1993  $\text{cm}^{-1}$  for  $[\text{Ru}^{\text{II}}(\text{MeCO}_2)_2(\text{CO})_2(\text{phen})]$ <sup>15</sup>. Bands attributable to the  $\nu_{\text{as}}(\text{CO}_2)$  and  $\nu_{\text{s}}(\text{CO}_2)$  vibrational modes were observed at 1629, 1620, and 1315  $\text{cm}^{-1}$  for  $\text{N}^{\wedge}\text{N}$  = 4,4'-dmbpy or  $\text{N}^{\wedge}\text{N}$  = 5,5'-dmbpy. A large  $\nu(\text{COO})$  separation of ca. 310  $\text{cm}^{-1}$ , cf. ionic acetate ( $\sim 164 \text{ cm}^{-1}$ ), is indicative of unidentate acetate coordination<sup>18</sup> and is similar to that reported for bpy and phen analogues (320–330  $\text{cm}^{-1}$ ).<sup>15</sup>

The  $^1\text{H}$  NMR spectrum of  $[\text{Ru}^{\text{II}}(\text{MeCO}_2)_2(\text{CO})_2(4,4'\text{-dmbpy})]$  was consistent with a symmetrical geometry, showing only three resonances arising from the aromatic protons of the diimine ligand. Combined with the two  $\nu(\text{CO})$  frequencies, this indicates an isomer with trans acetate and cis carbonyl ligands. About 1 month later, the spectrum of the same NMR solution showed six additional aromatic signals, consistent with the presence of unsymmetrically bound 4,4'-dmbpy. An extra carbonyl stretch was observed in the IR spectrum at 1947  $\text{cm}^{-1}$ , which increased in intensity over time. This product was identified as  $[\text{Ru}(\text{MeCO}_2)_2(\text{CO})_2(4,4'\text{-dmbpy})_2]$  from the electrospray mass spectrum, which showed a peak due to  $[\text{Ru}(\text{MeCO}_2)_2(\text{CO})_2(4,4'\text{-dmbpy})_2]\text{H}^+$  at  $m/z$  865. Similar  $[\text{Ru}(\text{CO})_2\text{Cl}_2(\text{N}^{\wedge}\text{N})]$  complexes undergo photodecarbonylation to yield the dimers  $[\text{Ru}^{\text{II}}(\text{CO})_2\text{Cl}_2(\text{N}^{\wedge}\text{N})_2]$ , which display a single  $\nu(\text{CO})$  at  $\sim 1945 \text{ cm}^{-1}$ .<sup>19</sup>

The cyclometalated benzoate complexes,  $[\text{Ru}^{\text{II}}(\text{O}_2\text{CC}_6\text{H}_4)(\text{CO})_2(\text{N}^{\wedge}\text{N})]$  ( $\text{N}^{\wedge}\text{N}$  = bpy, phen), like the diacetate complexes, display two strong IR absorptions in the region 2050–1960  $\text{cm}^{-1}$ , attributable to  $\nu(\text{CO})$  of cis-terminal carbonyls. The  $\nu_{\text{as}}(\text{COO})$  and  $\nu_{\text{s}}(\text{COO})$  absorptions also showed large separations ( $\sim 300 \text{ cm}^{-1}$ ), relative to that of ionic benzoate (140  $\text{cm}^{-1}$ ), and in agreement with those observed for  $[(\text{C}_5\text{Me}_5)\text{M}(\text{O}_2\text{CC}_6\text{H}_4)(\text{DMSO})]$  (300–330  $\text{cm}^{-1}$  for M = Rh, Ir) which also contain O,C-bound benzoate(s).<sup>20</sup>

The  $^1\text{H}$  NMR spectra, assigned with reference to the chemical shifts and coupling constants for the benzoate resonances of  $[\text{Os}(\text{p-MeC}_6\text{H}_4\text{CHMe}_2)(\text{O}_2\text{CC}_6\text{H}_4)(\text{DMSO})]$ ,<sup>20</sup> exhibited the signals expected for cyclometalated benzoate complexes. The  $^{13}\text{C}$  NMR spectra of the cyclometalated products reported here showed a signal due to the ruthenium bound carbon at 165 ppm, the other benzene carbon signals being in the region 125–141 ppm. The former corresponded well to those of  $[\text{Os}(\text{p-MeC}_6\text{H}_4\text{CHMe}_2)(\text{O}_2\text{CC}_6\text{H}_4)(\text{DMSO})]$

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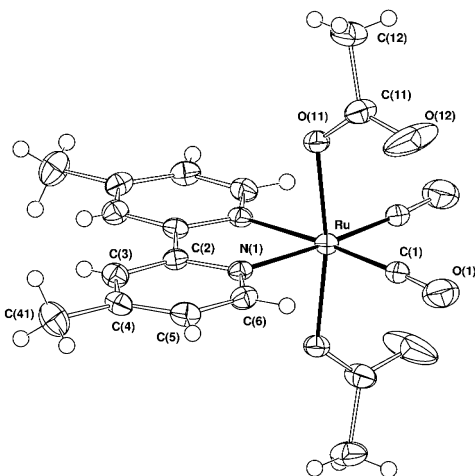
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**Table 1.** Ruthenium Environments,  $[\text{Ru}^{\text{II}}(\text{MeCO}_2)_2(\text{CO})_2(\text{N}^{\wedge}\text{N})]$ ,  $\text{N}^{\wedge}\text{N} = 4,4'/5,5'$ -dmbpy<sup>a</sup>

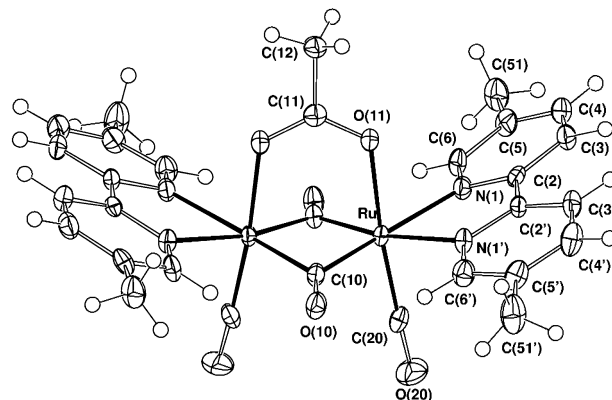
atom <sup>b</sup>	<i>r</i>	N(1*)	C(1)	C(1*)	O(11)	O(11*)
N(1)	2.103(3)	77.6(1)	96.7(1)	174.2(1)	87.5(1)	84.4(1)
N(11)	2.12(1)	78.1(4)	98.8(5)	174.8(5)	83.8(3)	87.2(3)
N(21)	2.12(1)	78.1(4)	96.5(5)	176.1(5)	85.7(4)	85.5(3)
N(1*)	(2.103(3))	(77.6(1))	(96.7(1))	(174.2(1))	(87.5(1))	(84.4(1))
N(11')	2.12(1)	176.9(5)	96.6(5)	85.9(3)	85.9(3)	
N(21')	2.13(1)	174.6(5)	98.0(5)	84.8(3)	86.6(3)	
C(1)	1.885(4)		89.1(2)	96.5(2)	90.9(2)	
C(110)	1.89(1)		86.5(6)	94.0(4)	93.8(4)	
C(210)	1.83(1)		87.4(6)	95.5(4)	92.4(4)	
C(1*)	(1.885(4))			(90.9(2))	(96.5(2))	
C(120)	1.86(1)			95.9(4)	92.6(4)	
C(220)	1.86(1)			93.7(5)	94.6(5)	
O(11)	2.072(3)				169.6(1)	
O(111)	2.092(7)				168.9(3)	
O(211)	2.063(8)				168.8(3)	
O(11*)	(2.072(3))					
O(121)	2.073(7)					
O(221)	2.073(7)					

<sup>a</sup> *r* (Å) is the Ru–ligand atom distance; other entries in the matrix are the angles (deg) subtended by the relevant entries at the head of the row and column. <sup>b</sup> The three values in each entry are for the  $\text{N}^{\wedge}\text{N} = 4,4'$ -dmbpy,  $\text{N}^{\wedge}\text{N} = 5,5'$ -dmbpy (two molecules) adducts respectively; the single “atom” entries across the head of the table imply the use of the other associates as appropriate. Asterisked atom entries for the  $4,4'$ -dmbpy adduct are generated by the intramolecular 2-axis, redundant entries being given in parentheses (see also Table 2).

**Figure 2.** Molecular projection of  $[\text{Ru}^{\text{II}}(\text{MeCO}_2)_2(\text{CO})_2(\text{N}^{\wedge}\text{N})]$ ,  $\text{N}^{\wedge}\text{N} = 4,4'$ -dmbpy (ruthenium site symmetry 2). The two molecules of the  $5,5'$ -dmbpy adduct are similar, albeit lacking crystallographic symmetry.

(156 ppm) and  $[\text{Ru}(\text{O}_2\text{CC}_6\text{H}_4)(\text{PPh}_3)_2(\text{CO})_2]$  (171 ppm).<sup>13</sup> Electrospray mass spectroscopy supported the formulation of  $[\text{Ru}^{\text{II}}(\text{O}_2\text{CC}_6\text{H}_4)(\text{CO})_2(\text{N}^{\wedge}\text{N})]$  with signals corresponding to  $[\text{complex}]\text{H}^+$  being observed at  $m/z$  435 (bpy) and 459 (phen).

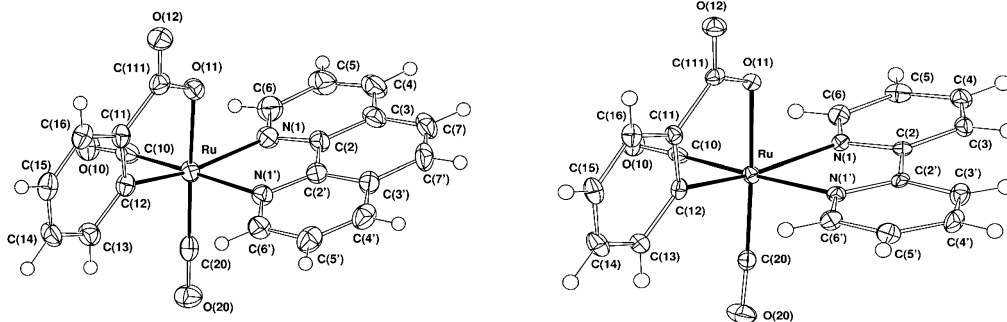
**Crystallography.** Single-crystal X-ray structure determinations were undertaken for  $[\text{Ru}^{\text{II}}(\text{MeCO}_2)_2(\text{CO})_2(4,4'$ -dmbpy)],  $[\text{Ru}^{\text{II}}(\text{MeCO}_2)_2(\text{CO})_2(5,5'$ -dmbpy)],  $[\text{Ru}^{\text{II}}(\text{O}_2\text{CC}_6\text{H}_4)(\text{CO})_2(\text{N}^{\wedge}\text{N})]$  ( $\text{N}^{\wedge}\text{N} = \text{bpy}$ , phen), and  $[\text{Ru}^{\text{II}}_2(\text{MeCO}_2)_2(\text{CO})_4(5,5'$ -dmbpy)<sub>2</sub>] $\text{PF}_6$ . The assignment of the stereochemistry of  $[\text{Ru}^{\text{II}}(\text{MeCO}_2)_2(\text{CO})_2(\text{N}^{\wedge}\text{N})]$  complexes on the basis of NMR spectroscopy has been debated. Black et al.<sup>15</sup> assigned the prevalent geometry as *trans*-carboxylate–*cis*-carbonyl, while Frediani et al.<sup>14</sup> proposed an all *cis*-

**Figure 3.** Molecular projection of the  $[\text{Ru}^{\text{II}}_2(\text{MeCO}_2)_2(\text{CO})_4(5,5'$ -dmbpy)<sub>2</sub>]<sup>+</sup> cation.**Table 2.** Ruthenium Environments,  $[\text{Ru}^{\text{II}}_2(\text{MeCO}_2)_2(\text{CO})_4(5,5'$ -dmbpy)<sub>2</sub>]<sup>+</sup>

atom	<i>r</i>	N(1')	C(10)	C(10*)	C(20)	O(11)
N(1)	2.190(4)	74.7(1)	169.1(2)	95.1(2)	95.4(2)	81.6(2)
N(1')	2.175(4)		95.3(2)	169.2(1)	91.0(2)	84.0(2)
C(10)	2.010(5)			94.5(2)	89.2(2)	93.2(2)
C(10*)	2.021(5)				93.8(2)	90.8(2)
C(20)	1.856(5)					174.7(2)
O(11)	2.109(5)					

arrangement. Since Ru(II) is kinetically inert ( $d^6$  configuration), undergoing only slow ligand exchange at room temperature, the solid state and initial solution structures should correspond within the <sup>1</sup>H NMR time frame. For the  $4,4'$ -dmbpy and  $5,5'$ -dmbpy complexes, X-ray studies showed a *trans*-acetato–*cis*-carbonyl ligand arrangement (Figures 2 and 3) in agreement with the structure proposed by Black et al.<sup>15</sup> and consistent with the <sup>1</sup>H NMR data. NMR studies of  $[\text{Ru}^{\text{II}}(\text{MeCO}_2)_2(\text{CO})_2(\text{bpy})]$ , prepared by the method of Black et al.<sup>15</sup> indicated that both *cis* and *trans* acetate complexes are present initially, but the *trans* isomer converts to the *cis* isomer over a prolonged time.

$[\text{Ru}^{\text{II}}(\text{MeCO}_2)_2(\text{CO})_2(4,4'$ -dmbpy)] crystallizes (modeled as a dichloromethane hemisolvate) with half of the formula unit comprising the asymmetric unit of the structure, the six-coordinate ruthenium being disposed on a crystallographic 2-axis which passes through the midpoint of the central C–C bond of the bipyridine component, relating the *cis*-carbonyl and *trans*-O-acetato pairs of ligands. The structure is more precisely established than that of its  $[\text{Ru}^{\text{II}}(\text{MeCO}_2)_2(\text{CO})_2(5,5'$ -dmbpy)] counterpart, wherein two complete molecules, pseudo symmetrically related, comprise the asymmetric unit of the structure. The geometries about the ruthenium atoms show no pronounced differences (Table 1). In both cases, the *trans*-acetato–O donors bow toward the aromatic chelate, presumably in consequence of its small bite (Figure 2); an interesting difference between the two structures is found in the relative dispositions of the pairs of acetate planes—in the  $5,5'$ -dmbpy adduct the uncoordinated acetate oxygen atoms lie disposed between the pair of *cis*-carbonyl groups, thus: O(12)⋯O(110, 120) 3.43(1), 3.16(1) Å; O(122)⋯O(110, 120) 3.12(1), 3.26(1) Å; O(212)⋯O(210, 220) 3.14(1), 3.34(1) Å; O(222)⋯O(210, 220) 3.23(1), 3.15(1) Å. The pairs within each molecule are thus slightly disposed to either side of the putative mirror plane passing through the



**Figure 4.** Molecular projection of  $[\text{Ru}^{\text{II}}(\text{C}_6\text{H}_4\text{CO}_2)(\text{CO})_2(\text{phen}, \text{bpy})]$ .

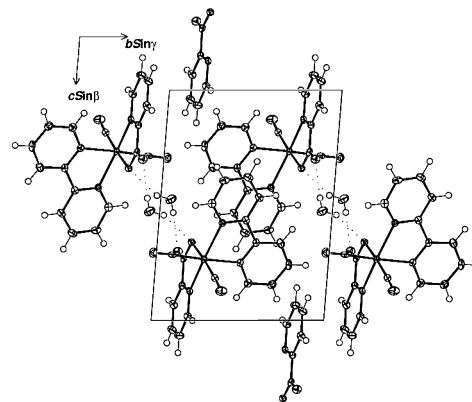
coordinated carboxylate oxygens, the overall molecular symmetry approaching  $2m$ . By contrast, in the 4,4'-dmbpy adduct, the carboxylates are twisted (necessarily, in opposite directions) about the O–Ru–O axis, so that the uncoordinated carboxylate oxygens lie outside the pair of *cis*-carbonyl groups—O(12)⋯O(1) is 2.970(7) Å, with  $\tau$  (C(11)–O(11)–Ru–C(1)) being 15.8(3)° and the overall symmetry reduced to 2. O–Ru–O angles are similar in both compounds, but Ru–O–C in the 4,4'-dmbpy complex (124.6(3)°) is larger than the counterparts in the 5,5'-dmbpy adduct (range 120.8(8)–122.1(7)°). No significant concomitant change is observed in Ru–O lengths. The O–Ru–O angle, ca. 169° in these complexes, may be contrasted with the Cl–Ru–Cl angle (176.3(1)°) in the chloro counterpart  $[\text{Ru}^{\text{II}}\text{Cl}_2(\text{CO})_2(\text{bpy})]$ ;<sup>21</sup> Ru–C, N in the latter (1.83(2), 2.11(1) Å ( $\langle \rangle$ )) are similar to the present values. The 4,4'-dmbpy ligand itself, for which a redetermination of superior precision is reported herein,<sup>22,23</sup> (see Supporting Information) adopts, as might be expected, a centrosymmetric *trans* conformation.  $[\text{Ru}_2(\text{MeCO}_2)(\text{CO})_4(5,5'\text{-dmbpy})_2](\text{PF}_6)$  (Table 2, Figure 3) crystallizes (modeled as a  $1/3$  methanol solvate) with half of the formula unit comprising the asymmetric unit of the structure, the binuclear cation disposed with a crystallographic 2-axis passing through the C–C bond of the acetate ligand and the midpoint of the Ru⋯Ru line. The  $\text{C}_2\text{O}_2$  skeleton of the acetate is thus obligate planar; of smaller “bite” (O⋯O 2.243(5) Å) than the Ru⋯Ru distance (2.7021(5) Å). Concomitant with its bridging function we find the *trans* axes through the two  $\mu$ -carbonyl groups divergent and the Ru( $\mu$ -CO)<sub>2</sub>Ru four-membered ring nonplanar, the “fold” dihedral angle at the C⋯C line being 18.5(2)°, with the carbonyl groups essentially collinear ( $\chi^2 = 1143$ ). Geometries about the metal are otherwise similar to those found in the counterpart species  $[\text{Ru}_2(\text{MeCO}_2)(\text{CO})_4(\text{N}^{\wedge}\text{N})_2]^+$ ,  $\text{N}^{\wedge}\text{N} = \text{phen},^4 \text{bpy},^{24}$  and “dpa” (=bis(2-pyridyl)amine).<sup>25</sup>

The structures of  $[\text{Ru}^{\text{II}}(\text{O}_2\text{CC}_6\text{H}_4)(\text{CO})_2(\text{bpy}, \text{phen})]$  establish the formation of cyclometalated benzoate products, resolve the isomer issue (–C(O)O– *trans* to CO or N), and

**Table 3.** Ruthenium Environments,  $[\text{Ru}^{\text{II}}(\text{C}_6\text{H}_4\text{CO}_2)(\text{CO})_2\text{L}]$ , L = Bpy, Phen<sup>a</sup>

atom	<i>r</i>	N(1')	C(10)	C(20)	O(11)	C(12)
N(1)	2.171(3)	76.8(1)	101.1(1)	99.7(2)	86.4(1)	163.7(1)
	2.165(3)	77.4(1)	102.4(1)	99.6(1)	82.9(1)	161.7(1)
N(1')	2.133(3)		177.7(1)	92.2(1)	85.2(1)	92.6(1)
	2.133(3)		178.0(1)	90.0(1)	84.8(1)	93.4(1)
C(10)	1.890(4)			88.9(2)	93.9(2)	89.4(1)
	1.874(4)			88.1(2)	97.2(1)	87.4(1)
C(20)	1.860(5)				172.8(1)	93.0(2)
	1.857(4)				173.6(1)	96.2(1)
O(11)	2.102(3)					80.4(1)
	2.091(2)					80.5(1)
C(12)	2.062(4)					
	2.065(3)					

<sup>a</sup>Values for the bpy complex are above those for the phen adduct.



**Figure 5.** Unit cell projection of  $[\text{Ru}^{\text{II}}(\text{O}_2\text{CC}_6\text{H}_4)(\text{CO})_2(\text{bpy})]$ , down a showing the hydrogen-bonding interactions.

confirm their isolation as solvates. A few examples of ruthenium cyclometalated aromatic carboxylates are known,  $[\text{Ru}(\text{O}_2\text{CC}_6\text{H}_3\text{NH}_2)(\text{PPh}_3)_4]$ ,<sup>12</sup>  $[\text{Ru}(\text{O}_2\text{CC}_6\text{H}_4)(\text{CO})_2(\text{PPh}_3)_2]$ <sup>13</sup> and  $[\text{Ru}(\text{O}_2\text{CC}_6\text{H}_3\text{Me})(\text{CO})_2(\text{PPh}_3)_2]$ ,<sup>13</sup> but  $[\text{Ru}^{\text{II}}(\text{O}_2\text{CC}_6\text{H}_4)(\text{CO})_2(\text{bpy}, \text{phen})]$  appear to be the first to be structurally characterized. Other transition metal complexes incorporating a O,C-chelating benzoate to be structurally characterized include  $[\text{Ir}(\text{O}_2\text{CC}_6\text{H}_4)(\text{Cp}^*)(\text{DMSO})]$ <sup>26</sup> (O–Ir–C 78.4(10)°, Ir–C 2.08(3) Å, Ir–O 2.09(2) Å);  $[\text{Pt}(\text{O}_2\text{CC}_6\text{F}_4)(\text{PPh}_3)(2,6\text{-Me}_2\text{py})]$ <sup>27</sup> (Pt–C 2.01(2), Pt–O 2.06(1), C–O 1.28(2), C=O, 1.24(2) Å, C–Pt–O 81.9(5)°). A comparison of the geometric features of the benzoate chelate in  $[\text{Ru}^{\text{II}}(\text{O}_2\text{CC}_6\text{H}_4)(\text{CO})_2(\text{bpy}, \text{phen})]$  (Table 3, Figure 4) with those exhibited

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by these complexes shows similar chelate angles and M—C and M—O distances despite differences in the metal centers.

In the present complexes, as in the other structures, the interleaving or overlapping of the planar bidentate ligands are dominant motifs throughout the lattice arrays (representative cell projections have been deposited). Also of significance is the hydrogen bonding in the hydrated bpy cyclometalated adduct, the water molecules bridging successive inversion related substrate molecules via their carboxylate groups into a string parallel to the *b* axis (Figure 5). This structure lends credence to the claim (from microanalyses) that  $[\text{Ru}^{\text{II}}(\text{XC}_6\text{H}_3\text{CO}_2)(\text{CO})_2(\text{PPh}_3)_2]$  ( $\text{X} = \text{H}, \text{Me}$ ) were isolated as hydrates.

## Experimental Section

**Physical Measurements.** Infrared spectra were recorded using a Perkin-Elmer 1640 FTIR spectrophotometer.  $^1\text{H}$  NMR spectra were recorded on a Bruker DPX300 spectrometer or Varian Mercury 300 spectrometer, both operating at 300 MHz. Unresolved doublets of doublets giving rise to apparent triplets are denoted by an asterisk. Electrospray mass spectra were recorded on Micromass Platform Quadrupole mass spectrometer fitted with an electrospray source. Peaks are listed according to the most intense signal within an isotopic distribution pattern. For  $\text{Ru}_2$  containing ions, this is one of two nearly equal intensity peaks, corresponding to the natural isotopic distribution of constituent elements.

**Materials and Reagents.** Most materials and reagents were of reagent or analytical reagent grade and used as received without further purification. 3-Methylpyridine was distilled prior to use.  $[\text{Ru}(\text{CO})_2\text{Cl}_2]_n$ <sup>28</sup> and 5,5'-dmbpy<sup>29</sup> were synthesized according to literature methods.

**Syntheses.  $\mu$ -O, $O'$ -Acetatodi- $\mu$ -C,C-carboxyl-di-C,C-carboxylbis(4,4'-dimethyl-2,2'-bipyridine)diruthenium(I) Acetate/Chloride.**  $[\text{Ru}(\text{CO})_2\text{Cl}_2]_n$  (274 mg, 1.20 mmol) was added to a degassed solution of sodium acetate (1.20 g, 14.6 mmol) in methanol (25 mL). The reaction mixture was refluxed under nitrogen, at a bath temperature of 110°C. After 4 h, 4,4'-dmbpy (264 mg, 1.43 mmol) was added to the pale orange solution, resulting in an instant color change to bright red/orange. After heating for a further 15 min, the reaction mixture was cooled overnight in a refrigerator, giving a yellow precipitate in an orange solution. The product,  $[\text{Ru}_2(\text{MeCO}_2)(\text{CO})_4(4,4'\text{-dmbpy})_2](0.5\text{MeCO}_2/0.5\text{Cl})$  (yield: 199 mg, 42%), was collected by filtration and dried in air at 70 °C (the filtrate yielded  $[\text{Ru}^{\text{II}}(\text{MeCO}_2)(\text{CO})_2(4,4'\text{-dmbpy})]$ ). It was converted to the hexafluorophosphate salt as indicated below. Infrared spectrum (KBr disk),  $\text{cm}^{-1}$ : 2017 s, 1968 m, 1801 w, 1734 s, 1619 m, 1562 m, 1494 m, 1419 m, b, 1243 w, 1020 w, 834 w, 714 m, 623 w, 514 w.  $^1\text{H}$  NMR spectrum ( $d_4$ -methanol): 0.99 (3H, s,  $\mu$ - $\text{CH}_3\text{CO}_2$ ), 1.89 (1.5H, s,  $\text{CH}_3\text{CO}_2^-$ ), 2.70 (12H, s, bpy- $\text{CH}_3$ ), 7.87 (4H, d, bpy- $\text{H}_5$ ), 8.61 (4H, s, bpy- $\text{H}_3$ ), 10.05 (4H, d, bpy- $\text{H}_6$ ). Electrospray mass spectrum (methanol):  $m/z$  743 (100%,  $[\text{Ru}_2(\text{MeCO}_2)(\text{CO})_4(4,4'\text{-dmbpy})_2]^+$ ). Chloride analysis. Found:  $\text{Cl}^-$ , 2.1. Calcd for  $\text{C}_{30}\text{H}_{27}\text{ClN}_4\text{O}_6\text{Ru}_2\{[\text{Ru}_2(\text{MeCO}_2)(\text{CO})_4(4,4'\text{-dmbpy})_2](\text{Cl})\}$ :  $\text{Cl}^-$ , 4.6. Calcd for  $\text{C}_{31}\text{H}_{28.5}\text{Cl}_{0.5}\text{N}_4\text{O}_6\text{Ru}_2\{[\text{Ru}_2(\text{MeCO}_2)(\text{CO})_4(4,4'\text{-dmbpy})_2](0.5\text{MeCO}_2/0.5\text{Cl})\}$ :  $\text{Cl}^-$ , 2.3.

**$\mu$ -O, $O'$ -Acetatodi- $\mu$ -C,C-carboxyl-di-C,C-carboxylbis(4,4'-dimethyl-2,2'-bipyridine)diruthenium(I) Hexafluorophosphate.**

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**Method 1.**  $[\text{Ru}_2(\text{MeCO}_2)(\text{CO})_4(4,4'\text{-dmbpy})_2](0.5\text{MeCO}_2/0.5\text{Cl})$  (89 mg, 0.11 mmol) was dissolved in methanol (15 mL) by heating the mixture in a water bath at 50 °C with stirring. Addition of a methanolic solution (5 mL) of  $\text{KPF}_6$  (28 mg, 1.5 mmol) immediately precipitated pale yellow  $[\text{Ru}_2(\text{MeCO}_2)(\text{CO})_4(4,4'\text{-dmbpy})_2](\text{PF}_6)$  (Yield: 79 mg, 80%). Anal. Calcd for  $\text{C}_{30}\text{H}_{27}\text{F}_6\text{N}_4\text{O}_6\text{PRu}_2\{[\text{Ru}_2(\text{MeCO}_2)(\text{CO})_4(4,4'\text{-dmbpy})_2](\text{PF}_6)\}$ : C, 40.6; H, 3.1; N, 6.3. Found: C, 40.6; H, 3.3; N, 6.4. Infrared Spectrum (KBr disk),  $\text{cm}^{-1}$ : 2021 s, 1961 m, 1804 w, 1737 s, 1620 m, 1527 m, 1493 m, 1448 m, 1421 m, 1318 w, 1242 w, 1021 w, 916 w, 847 s, 709 m, 670 w, 559 m, 515 w, 422 w.  $^1\text{H}$  NMR spectrum ( $d_6$ -acetone): 1.00 (3H, s,  $\mu$ - $\text{CH}_3\text{CO}_2$ ), 2.73 (12H, s, bpy- $\text{CH}_3$ ), 8.03 (4H, d, bpy- $\text{H}_5$ ), 8.77 (4H, s, bpy- $\text{H}_3$ ), 10.08 (4H, d, bpy- $\text{H}_6$ ). Electrospray mass spectrum (acetone:methanol 1:1):  $m/z$  743 (100%,  $[\text{Ru}_2(\text{MeCO}_2)(\text{CO})_4(4,4'\text{-dmbpy})_2]^+$ ).

**Method 2.**  $[\text{Ru}^{\text{I}}(\text{MeCO}_2)(\text{CO})_2(\text{py})_2]$  (78 mg, 0.13 mmol) and 4,4'-dimethyl-2,2'-bipyridine (100 mg, 0.54 mmol) were suspended in HPLC grade methanol (20 mL) in a quickfit round-bottomed flask. The suspension was sonicated for several minutes until the 4,4'-dimethyl-2,2'-bipyridine had dissolved and the sealed vessel was incubated in a thermostatically controlled water bath at 40 °C for 24 h. The addition of aqueous potassium hexafluorophosphate (5 mL, 1.0 M) induced the precipitation of a fine orange/yellow powder which was collected by filtration and washed with cold ethanol and diethyl ether before drying in air at 70 °C. (Yield: 0.109 g, 87%.) Anal. Calcd for  $\text{C}_{30}\text{H}_{27}\text{F}_6\text{K}_{1/3}\text{N}_4\text{O}_6\text{P}_{4/3}\text{Ru}_2\{[\text{Ru}_2(\text{MeCO}_2)(\text{CO})_4(4,4'\text{-dmbpy})_2]\text{PF}_6 \cdot 1/3\text{KPF}_6\}$ : C, 38.0; H, 2.9; N, 5.9. Found: C, 38.1; H, 2.9; N, 6.0. Infrared spectrum (Nujol)  $\text{cm}^{-1}$ : 3132 w, 3078 w, 2012 s, 1958 s, 1805 m, 1737 s, 1617 s, 1529 s, 1491 s, 1318 m, 1296 m, 1242 m, 1140 w, 1038 w, 1022 m, 986 w, 916 m, 850 s  $\nu(\text{PF}_6)$ ; 739 s.  $^1\text{H}$  NMR spectrum ( $d_6$ -acetone): 1.01 (3H, s,  $\text{CH}_3\text{CO}_2$ ); 2.73 (12H, s, bpy- $\text{CH}_3$ ); 8.03 (4H, dd,  $\text{H}_5, \text{H}_5'$ ); 8.77 (4H, s,  $\text{H}_3, \text{H}_3'$ ); 10.08 (4H, d,  $\text{H}_6, \text{H}_6'$ ). Electrospray mass spectrum (acetone):  $m/z$  743 (100%,  $[\text{Ru}_2(\text{MeCO}_2)(\text{CO})_4(4,4'\text{-dmbpy})_2]^+$ ).

**$\mu$ -O, $O'$ -Acetatodi- $\mu$ -C,C-carboxyl-di-C,C-carboxylbis(5,5'-dimethyl-2,2'-bipyridine)diruthenium(I) Hexafluorophosphate.** Method 2 for the preparation of  $[\text{Ru}_2(\text{MeCO}_2)(\text{CO})_4(4,4'\text{-dmbpy})_2](\text{PF}_6)$  was followed using  $[\text{Ru}^{\text{I}}(\text{MeCO}_2)(\text{CO})_2(\text{py})_2]$  (82 mg, 0.14 mmol) with 5,5'-dimethyl-2,2'-bipyridine (0.146 g, 0.79 mmol). The less soluble hexafluorophosphate salt was formed on addition of ammonium hexafluorophosphate (0.125 mg, 0.68 mmol), followed by sonication for a period of 5 min.  $[\text{Ru}_2(\text{MeCO}_2)(\text{CO})_4(5,5'\text{-dmbpy})_2](\text{PF}_6)$  was then isolated as previously described. (Yield: 0.126 g, 96%.) Anal. Calcd for  $\text{C}_{30}\text{H}_{27}\text{F}_6\text{N}_4\text{O}_6\text{PRu}_2\{[\text{Ru}_2(\text{MeCO}_2)(\text{CO})_4(5,5'\text{-dmbpy})_2](\text{PF}_6)\}$ : C, 40.6; H, 3.1; N, 6.3. Found: C, 40.3; H, 3.1; N, 6.5. Infrared spectrum (Nujol)  $\text{cm}^{-1}$ : 2017 s, 1974 s, 1811 m, 1755 s, 1602 w, 1584 w, 1525 s, 1482 s, 1348 w, 1326 w, 1321 w, 1298 w, 1243 m, 1164 m, 1144 w, 1068 w, 1050 m, 1029 w, 932 w, 844 s, 730 w (sh), 706 s, 652 w, 620 w.  $^1\text{H}$  NMR spectrum ( $d_6$ -acetone): 1.01 (3H, s,  $\text{CH}_3\text{CO}_2$ ); 2.79 (12H, s, bpy- $\text{CH}_3$ ); 8.33 (4H, dd,  $\text{H}_4, \text{H}_4'$ ); 8.73 (4H, d,  $\text{H}_3, \text{H}_3'$ ); 10.08 (4H, m,  $\text{H}_6, \text{H}_6'$ ). Electrospray mass spectrum (acetone):  $m/z$  743 (100%,  $[\text{Ru}_2(\text{MeCO}_2)(\text{CO})_4(5,5'\text{-dmbpy})_2]^+$ ).

**$\mu$ -O, $O'$ -Acetatodi- $\mu$ -C,C-carboxyl-di-C,C-carboxylbis(5,6-dimethyl-1,10-phenanthroline)diruthenium(I) Acetate/Chloride.**

**Method 1.**  $[\text{Ru}_2(\text{MeCO}_2)(\text{CO})_4(5,6\text{-dmpphen})_2](\text{MeCO}_2/\text{Cl})$  was synthesized in a fashion similar to  $[\text{Ru}_2(\text{MeCO}_2)(\text{CO})_4(4,4'\text{-dmbpy})_2](\text{MeCO}_2/\text{Cl})$  by reaction between  $[\text{Ru}(\text{CO})_2\text{Cl}_2]_n$  (185 mg, 0.81 mmol) and  $\text{NaO}_2\text{CMe}$  (900 mg, 110 mmol), followed by addition of 5,6-dmpphen (173 mg, 0.830 mmol) after 5.5 h. The mixture was refrigerated overnight giving a pale orange precipitate of  $[\text{Ru}_2(\text{MeCO}_2)(\text{CO})_4(5,6\text{-dmpphen})_2](\text{MeCO}_2/\text{Cl})$  and colorless

crystals (169 mg crude). Infrared spectrum (KBr disk),  $\text{cm}^{-1}$ : 2055 vs, 2016 m (sh), 1989 vs, 1801 vw, 1731 m, 1630 m, 1600 m, 1524 w, 1433 m, 1376 m, 1313 m, 1020 w, 814 m, 728 m, 695 m. A methanol suspension of the solid was gently heated on a water bath at 40 °C until the solid had completely dissolved. Addition of a methanolic solution (10 mL) of  $\text{KPF}_6$  (140 mg, 0.76 mmol) to the solution containing  $[\text{Ru}^{\text{II}}(\text{MeCO}_2)(\text{CO})_4(5,6\text{-dmphen})_2](\text{MeCO}_2/\text{Cl})$  deposited a precipitate. Filtration of the mixture yielded a gray precipitate and an orange filtrate. Reduction of the volume of the filtrate under vacuum precipitated a solid mixture of  $[\text{Ru}^{\text{I}}(\text{MeCO}_2)(\text{CO})_4(5,6\text{-dmphen})_2](\text{PF}_6)$  and  $[\text{Ru}^{\text{II}}(\text{MeCO}_2)_2(\text{CO})_2(5,6\text{-dmphen})]$  in ~1:1 ratio, which was collected by filtration and dried in vacuo (yield: 67 mg, ~9% of  $\text{Ru}^{\text{I}}$  complex, ~8% of  $\text{Ru}^{\text{II}}$  complex). Infrared spectrum (KBr disk),  $\text{cm}^{-1}$ : 3413 w, 3085 w, 2929 w, 2055 vs, 2013 s (sh), 1990 vs, 1803 w, 1733 s, 1630 s, 1603 s, 1544 w, 1524 w, 1483 vw, 1434 s, 1377 m, 1312 s, 1174 w, 1040 w, 844 s, 813 m (sh), 728 m, 682 m, 636 w, 596 w, 559 w, 522 w.  $^1\text{H}$ NMR spectrum ( $d_6$ -acetone):  $[\text{Ru}^{\text{I}}(\text{MeCO}_2)(\text{CO})_4(5,6\text{-dmphen})_2](\text{PF}_6)$ : 0.82 (3H, s,  $\mu\text{-CH}_3\text{CO}_2$ ), 3.00 (12H, s, phen-**CH**<sub>3</sub>), 8.57 (4H, dd, **H3,H8**), 9.28 (4H, dd, **H4,H7**), 10.61 (4H, dd, **H2,H9**). Other product  $\{[\text{Ru}^{\text{II}}(\text{MeCO}_2)_2(\text{CO})_2(5,6\text{-dmphen})]\}$ : 1.43 (6H, s,  $\text{CH}_3\text{CO}_2^-$ ), 2.96 (6H, s, phen-**CH**<sub>3</sub>), 8.17 (2H, dd, **H3',H8'**), 9.08 (2H, dd, **H4',H7'**), 9.59 (2H, dd, **H2',H9'**). Electrospray mass spectrum (acetone):  $m/z$  791 (100%,  $[\text{Ru}^{\text{I}}_2(\text{MeCO}_2)(\text{CO})_4(5,6\text{-dmphen})_2]^+$ ).

**Method 2.** 5,6-Dimethyl-1,10-phenanthroline (138 mg, 0.66 mmol) and  $[\text{Ru}^{\text{I}}(\text{MeCO}_2)(\text{CO})_2(\text{py})_2]$  (118 mg, 0.200 mmol) were reacted according to the process used to prepare  $[\text{Ru}^{\text{I}}_2(\text{MeCO}_2)(\text{CO})_4(5,5'\text{-dmbpy})_2](\text{PF}_6)$ , resulting in the isolation of fine, pale orange needles of  $[\text{Ru}^{\text{I}}_2(\text{MeCO}_2)(\text{CO})_4(5,6\text{-dmphen})_2](\text{PF}_6)$ . (Yield: 176 mg, 72%.) Anal. Calcd for  $\text{C}_{34}\text{H}_{27}\text{F}_6\text{N}_4\text{O}_6\text{PRu}_2 \cdot 1/6\text{NH}_4\text{PF}_6$   $\{[\text{Ru}^{\text{I}}_2(\text{MeCO}_2)(\text{CO})_4(5,6\text{-dmphen})_2](\text{PF}_6) \cdot 1/6\text{NH}_4\text{PF}_6\}$ : C, 42.5; H, 2.9; N, 6.1. Found: C, 42.6; H, 2.9; N, 6.1. Infrared spectrum (Nujol)  $\text{cm}^{-1}$ : 2023 s, 1992 m, 1984 w (sh), 1968 m, 1806 m, 1732 s, 1600 w, 1586 w, 1548 m, 1440 s, 1348 w, 1310 w, 1201 w, 1176 w, 1118 w, 1084 w, 1040 w, 960 w, 846 s, 816 w (sh), 804 w (sh), 646 w, 619 w.  $^1\text{H}$  NMR and mass spectra were in agreement with those for the product from method 1.

**$\mu\text{-O, O'}$ -Benzoatodi- $\mu\text{-C, C}$ -carbonyldi- $\text{C, C}$ -carbonylbis(2,2'-bipyridine)diruthenium(I) Hexafluorophosphate.** The conditions used to prepare  $[\text{Ru}^{\text{I}}_2(\text{MeCO}_2)(\text{CO})_4(5,5'\text{-dmbpy})_2](\text{PF}_6)$  were employed to form  $[\text{Ru}^{\text{I}}_2(\text{PhCO}_2)(\text{CO})_4(\text{bpy})_2](\text{PF}_6)$ . The product was collected as a light orange powder after the reaction between  $[\text{Ru}^{\text{I}}(\text{PhCO}_2)(\text{CO})_2(\text{py})_2]$  (129 mg, 0.181 mmol) and 2,2'-bipyridine (164 mg, 1.05 mmol). (Yield: 0.135 g; 84%.) Anal. Calcd for  $\text{C}_{31}\text{H}_{21}\text{F}_6\text{N}_4\text{O}_6\text{PRu}_2 \cdot 1/6\text{NH}_4\text{PF}_6$   $\{[\text{Ru}^{\text{I}}_2(\text{PhCO}_2)(\text{CO})_4(\text{bpy})_2](\text{PF}_6) \cdot 1/6\text{NH}_4\text{PF}_6\}$ : C, 41.7; H, 2.4; N, 6.3. Found: C, 41.3; H, 2.2; N, 6.4. Infrared spectrum (Nujol)  $\text{cm}^{-1}$ : 2013 s, 1983 m, 1809 m, 1741 s, 1602 m, 1594 w, 1567 w, 1531 s, 1461 m, 1444 m, 1417 s, 1236 m, 1246 w, 1176 w, 1162 w, 1076 w, 1045 w, 1025 w, 917 w, 897 w, 856 s, 840 s, 767 m, 717 m, 653 w.  $^1\text{H}$  NMR spectrum ( $d_6$ -acetone): 6.68 (2H, dd, benz-**H2**); 6.89 (2H, t\*d, benz-**H3**); 7.18 (1H, tt, benz-**H4**); 8.21 (4H, ddd, bpy-**H5,H5'**); 8.56 (4H, t\*d, bpy-**H4,H4'**); 8.98 (4H, d, bpy-**H3,H3'**); 10.31 (4H, dt\*, bpy-**H6,H6'**). Electrospray mass spectrum (acetone):  $m/z$  693 (65%,  $[\text{Ru}^{\text{I}}_2(\text{PhCO}_2)(\text{CO})_4(\text{bpy})_2]^+$ ), 721 (40%,  $[\text{Ru}^{\text{I}}_2(\text{PhCO}_2)(\text{CO})_3(\text{bpy})_2]^+$ ), 749 (100%,  $[\text{Ru}^{\text{I}}_2(\text{PhCO}_2)(\text{CO})_4(\text{bpy})_2]^+$ ).

**$\mu\text{-O, O'}$ -Benzoatodi- $\mu\text{-C, C}$ -carbonyldi- $\text{C, C}$ -carbonylbis(1,10-phenanthroline)diruthenium(I) Hexafluorophosphate.** Formation of the 1,10-phenanthroline analogue of  $[\text{Ru}^{\text{I}}_2(\text{PhCO}_2)(\text{CO})_4(\text{bpy})_2](\text{PF}_6)$ ,  $[\text{Ru}^{\text{I}}_2(\text{PhCO}_2)(\text{CO})_4(\text{phen})_2](\text{PF}_6)$ , was achieved by replacement of 2,2'-bipyridine with 1,10-phenanthroline (174 mg, 0.88 mmol) in the reaction with  $[\text{Ru}^{\text{I}}(\text{PhCO}_2)(\text{CO})_2(\text{py})_2]$  (136 mg, 0.191

mmol). (Yield: 115 mg, 64%.) Infrared spectrum (Nujol)  $\text{cm}^{-1}$ : 2019 s, 1978 s, 1808 m, 1741 s, 1630 w, 1603 w, 1593 w, 1538 s, 1520 m, 1434 m, 1413 s, 1307 w, 1227 w, 1175 w, 1149 w, 1026 w, 976 w, 931 w, 861 s, 851 s, 785 w, 717 m.  $^1\text{H}$  NMR spectrum ( $d_6$ -acetone): 6.33 (2H, d, benz-**H2**); 6.69 (2H, t\*, benz-**H3**); 7.04 (1H, t, benz-**H4**); 8.52 (4H, s, phen-**H5,H6**); 8.58 (4H, dd, phen-**H3,H8**); 9.18 (4H, dd, phen-**H4,H7**); 10.67 (4H, dd, phen-**H2,H9**). Electrospray mass spectrum (acetone):  $m/z$  797 (100%,  $[\text{Ru}^{\text{I}}_2(\text{PhCO}_2)(\text{CO})_4(\text{phen})_2]^+$ ), 769 (30%,  $[\text{Ru}^{\text{I}}_2(\text{PhCO}_2)(\text{CO})_3(\text{phen})_2]^+$ ), 740 (32%,  $[\text{Ru}^{\text{I}}_2(\text{PhCO}_2)(\text{CO})_2(\text{phen})_2]^+$ ).

**$\mu\text{-O, O'}$ -Benzoatodi- $\mu\text{-C, C}$ -carbonyldi- $\text{C, C}$ -carbonylbis(5,6-dimethyl-1,10-phenanthroline)diruthenium(I) Hexafluorophosphate.**  $[\text{Ru}^{\text{I}}_2(\text{PhCO}_2)(\text{CO})_4(5,6\text{-dmphen})_2](\text{PF}_6)$  was synthesized in a fashion similar to  $[\text{Ru}^{\text{I}}_2(\text{MeCO}_2)(\text{CO})_4(5,5'\text{-dmbpy})_2](\text{PF}_6)$  by reaction between  $[\text{Ru}^{\text{I}}(\text{PhCO}_2)(\text{CO})_2(\text{py})_2]$  (143 mg, 0.152 mmol) and 5,6-dimethyl-1,10-phenanthroline (148 mg, 0.711 mmol). The product was isolated as a brown/orange powder. (Yield: 132 mg, 87%.) Infrared spectrum (Nujol)  $\text{cm}^{-1}$ : 2016 s, 1974 m, 1808 m, 1740 s, 1612 w, 1529 m, 1415 s, 1310 w, 1177 w, 1130 w, 1087 w, 1037 w, 879 w, 844 s, 729 m, 697 m.  $^1\text{H}$  NMR spectrum ( $d_6$ -acetone): 3.02 (12H, s, phen-**CH**<sub>3</sub>); 6.33 (2H, dd, benz-**H2**); 6.69 (2H, t\*, benz-**H3**); 7.04 (1H, t, benz-**H4**); 8.56 (4H, dd, phen-**H3,H8**); 9.29 (4H, dd, phen-**H4,H7**); 10.64 (4H, dd, phen-**H2,H9**). Electrospray mass spectrum (acetone):  $m/z$  853 (100%,  $[\text{Ru}^{\text{I}}_2(\text{PhCO}_2)(\text{CO})_4(5,6\text{-dmphen})_2]^+$ ).

***trans*-Di- $\text{O, O}$ -acetato-*cis*-di- $\text{C, C}$ -carbonyl(4,4'-dimethyl-2,2'-bipyridine)ruthenium(II).** The orange filtrate from  $[\text{Ru}^{\text{I}}_2(\text{MeCO}_2)(\text{CO})_4(4,4'\text{-dmbpy})_2](0.5\text{MeCO}_2/0.5\text{Cl})$  was evaporated to dryness, resulting in a mixture of sodium acetate and  $[\text{Ru}^{\text{II}}(\text{MeCO}_2)_2(\text{CO})_2(4,4'\text{-dmbpy})]$ . Suspension of the residue by addition of  $\text{CH}_2\text{Cl}_2$ , and filtration yielded an orange solution of  $[\text{Ru}^{\text{II}}(\text{MeCO}_2)_2(\text{CO})_2(4,4'\text{-dmbpy})]$ . On evaporation, the orange complex still contained a light colored solid. The residue was suspended in  $\text{CH}_2\text{Cl}_2$  and filtered to yield a yellow powder of  $[\text{Ru}^{\text{II}}(\text{MeCO}_2)_2(\text{CO})_2(4,4'\text{-dmbpy})]$  (yield: 160 mg, 29%). Infrared spectrum (KBr disk),  $\text{cm}^{-1}$ : 2057 s, 1996 s, 1620 s, b, 1376 m, 1315 m, 1036 w, 834 w, 678 w, 513 w. After exposure to light the powder started to change to an orange color and was recrystallized from methanol, giving a yellow/orange crystalline substance. Recrystallization was repeated from  $\text{CH}_2\text{Cl}_2$  to give single crystals suitable for X-ray crystallography. Infrared spectrum (KBr disk),  $\text{cm}^{-1}$ : 2058 s, 1991 s, {1947 m  $\nu(\text{CO})$  of  $[\text{Ru}^{\text{II}}(\text{MeCO}_2)_2(\text{CO})_2(4,4'\text{-dmbpy})_2]$ }, 1702 w, 1620 s, b, 1544 w, 1382 m, 1323 m, 671 s.  $^1\text{H}$  NMR spectrum ( $d_6$ -acetone): *trans-cis*- $[\text{Ru}^{\text{II}}(\text{MeCO}_2)_2(\text{CO})_2(4,4'\text{-dmbpy})]$ : 1.57 (6H, s,  $\text{CH}_3\text{CO}_2^-$ ); 2.64 (6H, s, bpy-**CH**<sub>3</sub>); 7.60 (2H, d, **H5,H5'**); 8.47 (2H, s, **H3,H3'**); 9.05 (2H, d, **H6,H6'**). One month later,  $^1\text{H}$  NMR spectrum ( $d_6$ -acetone): {~1:1 mixture of (i) *trans-cis*- $[\text{Ru}^{\text{II}}(\text{MeCO}_2)_2(\text{CO})_2(4,4'\text{-dmbpy})]$  and (ii)  $[\text{Ru}^{\text{II}}(\text{MeCO}_2)_2(\text{CO})_2(4,4'\text{-dmbpy})_2]$ : (i) 1.53 (6H, s,  $\text{CH}_3\text{CO}_2^-$ ), 2.65 (6H, s, bpy-**CH**<sub>3</sub>), 7.65 (2H, d, **H5,H5'**), 8.55 (2H, s, **H3,H3'**), 9.09 (2H, d, **H6,H6'**), and (ii) 1.51 (6H, s,  $\text{CH}_3\text{CO}_2^-$ ), 2.60 (3H, s, bpy-**CH**<sub>3</sub>), 2.72 (3H, s, bpy-**CH**<sub>3</sub>), 7.36 (1H, d, **H5'**), 7.81 (1H, d, **H5**), 8.46 (1H, s, **H3'**), 8.60 (1H, s, **H3**); 8.90 (1H, d, **H6'**), 9.22 (1H, d, **H6**). Infrared spectrum (Nujol)  $\text{cm}^{-1}$ : 2056 s, 1989 s, {1946 s  $\nu(\text{CO})$  of  $[\text{Ru}^{\text{II}}(\text{MeCO}_2)_2(\text{CO})_2(4,4'\text{-dmbpy})_2]$ }, 1620 s, b, 1318 m, 837 w, 721 w. Electrospray mass spectrum (methanol):  $m/z$  405 (100%,  $[\text{M} - 2\text{CO} + \text{H}]^+$ ), 437 (55%,  $[\text{M} - 2\text{CO} + \text{MeOH} + \text{H}]^+$ ), 461 (30%,  $[\text{M} + \text{H}]^+$ ), 483 (35%,  $[\text{M} + \text{Na}]^+$ ), 865 (5%,  $[\text{Ru}^{\text{II}}(\text{MeCO}_2)_2(\text{CO})_2(4,4'\text{-dmbpy})_2\text{H}]^+$ ).

***trans*-Di- $\text{O, O}$ -acetato-*cis*-di- $\text{C, C}$ -carbonyl(5,5'-dimethyl-2,2'-bipyridine)ruthenium(II).** In an attempt to prepare  $[\text{Ru}^{\text{I}}_2(\text{MeCO}_2)(\text{CO})_4(5,5'\text{-dmbpy})_2]^+$ , degassed methanol (25 mL) containing  $[\text{Ru}(\text{CO})_2\text{Cl}_2]_n$  (320 mg, 1.4 mmol) and  $\text{MeCO}_2\text{Na}$  (780 mg, 9.4

Table 4. Crystal/Refinement Data<sup>a</sup>

compound <sup>b</sup> formula	A <sup>c</sup> C <sub>18</sub> H <sub>18</sub> N <sub>2</sub> O <sub>6</sub> Ru· 0.5CH <sub>2</sub> Cl <sub>2</sub>	B C <sub>18</sub> H <sub>18</sub> N <sub>2</sub> O <sub>6</sub> Ru	C C <sub>19</sub> H <sub>12</sub> N <sub>2</sub> O <sub>4</sub> Ru·H <sub>2</sub> O	D C <sub>21</sub> H <sub>12</sub> N <sub>2</sub> O <sub>4</sub> Ru·MeOH	E C <sub>30</sub> H <sub>27</sub> N <sub>4</sub> O <sub>6</sub> Ru <sub>2</sub> PF <sub>6</sub> · 1/3MeOH	F <sup>a</sup> C <sub>12</sub> H <sub>12</sub> N <sub>2</sub>
Mr	501.9	459.4	451.4	489.5	897.4	184.2
cryst syst	monoclinic	triclinic	triclinic	monoclinic	rhombohedral	orthorhombic
space group	C2/c (No. 15)	P $\bar{1}$ (No. 2)	P $\bar{1}$ (No. 2)	P2 <sub>1</sub> /c (No. 14)	R $\bar{3}c$ (No. 167, hex.)	(D <sub>2h</sub> <sup>15</sup> ) (No. 51)
a/Å	15.792(2)	9.2447(8)	8.001(2)	8.7171(2)	28.7660(3)	11.9978(6)
b/Å	17.579(3)	12.256(1)	9.208(2)	10.7983(2)		10.7508(8)
c/Å	7.915(1)	16.403(1)	12.673(3)	20.1286(6)	21.1130(3)	7.4927(9)
α/deg		99.362(1)	91.27(3)			
β/deg	112.437(3)	98.224(1)	107.50(3)	97.110(3)		
γ/deg		90.164(1)	100.31(3)			
V/Å <sup>3</sup>	2031	1814	873.2	1880	15 141	966.5
D <sub>c</sub> /g cm <sup>-3</sup>	1.64 <sub>1</sub>	1.68 <sub>2</sub>	1.71 <sub>7</sub>	1.72 <sub>9</sub>	1.77 <sub>1</sub>	1.26 <sub>6</sub>
Z	4	4	2	4	18	4
μ <sub>Mo</sub> /mm <sup>-1</sup>	0.94	0.90	0.93	0.87	1.03	0.08
“T” <sup>min/max</sup>	0.74	n/a	n/a	n/a	n/a	0.81
2θ <sub>min</sub> /deg	68	50	55	56.6	60	75
N <sub>t</sub>	17 549	7969	10 793	12 467	9845	20 080
N (R <sub>int</sub> )	4213 (0.097)	5946 (0.050)	4102 (0.057)	4624 (0.047)	4925 (0.077)	2563 (0.042)
N <sub>0</sub>	2580	2370	3233	3371	3427	1743
R	0.052	0.056	0.042	0.040	0.053	0.045
R <sub>w</sub>	0.048	0.053	0.044	0.042	0.075	0.052
Δρ <sub>max</sub>  /e Å <sup>-3</sup>	1.6(4)	1.0(1)	1.2(1)	0.8(1)	1.0(1)	0.57(9)

<sup>a</sup> Variations in procedures: (A) A solvent component was modeled as dichloromethane, disordered about a center of symmetry, site occupancy set at 0.5 after trial refinement. (B) Weak and limited data would support meaningful anisotropic displacement parameter refinement for Ru only. (C) A difference map residue was modeled as a water molecule oxygen atom, associated hydrogen atoms also being credibly located. (D) Solvent residues were modeled in terms of methanol, disordered over two sets of sites, occupancies refining to 0.707(6) and complement. (E) Solvent residues were modeled in terms of methanol disordered about the  $\bar{3}$  axis; the PF<sub>6</sub> was modeled as disordered about an axis defined by a pair of opposed fluorines, site occupancies of the two components refining to 0.62(2) and complement. <sup>b</sup> A is [Ru<sup>II</sup>(MeCO<sub>2</sub>)<sub>2</sub>(CO)<sub>2</sub>(4,4'-dmbpy)]·0.5CH<sub>2</sub>Cl<sub>2</sub>; B is [Ru<sup>II</sup>(MeCO<sub>2</sub>)<sub>2</sub>(CO)<sub>2</sub>(5,5'-dmbpy)]; C is [Ru<sup>II</sup>(C<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>)(CO)<sub>2</sub>(bpy)]·H<sub>2</sub>O; D is [Ru<sup>II</sup>(C<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>)(CO)<sub>2</sub>(phen)]·MeOH; E is [Ru<sup>II</sup><sub>2</sub>(MeCO<sub>2</sub>)(CO)<sub>4</sub>(5,5'-dmbpy)<sub>2</sub>](PF<sub>6</sub>); F is the 4,4'-dimethyl-2,2'-bipyridine ligand. <sup>c</sup> Specimen sizes: 0.20 × 0.12 × 0.35 mm (A); 0.20 × 0.12 × 0.035 mm (B); 0.40 × 0.60 × 0.80 mm (C); 0.40 × 0.50 × 0.30 mm (D); 0.30 × 0.20 × 0.18 mm (F).

mmol) was heated for 4 h at 120 °C under nitrogen before 5,5'-dimethyl-2,2'-bipyridine (310 mg, 1.7 mmol) was added, and heating was continued for 15 min. The flask was then sealed and cooled to 2 °C. A few orange crystals (of presumably [Ru<sup>II</sup><sub>2</sub>(MeCO<sub>2</sub>)(CO)<sub>4</sub>(5,5'-dmbpy)<sub>2</sub>](MeCO<sub>2</sub>/Cl) and a larger amount of very pale yellow crystals of *trans*-diacetato-*cis*-dicarbonyl(5,5'-dimethyl-2,2'-bipyridine)ruthenium(II) ([Ru<sup>II</sup>(MeCO<sub>2</sub>)<sub>2</sub>(CO)<sub>2</sub>(5,5'-dmbpy)]) precipitated overnight. (Yield: 0.14 g, 21%.) Anal. Calcd for C<sub>18</sub>H<sub>18</sub>N<sub>2</sub>O<sub>6</sub>Ru {[Ru<sup>II</sup>(MeCO<sub>2</sub>)<sub>2</sub>(CO)<sub>2</sub>(5,5'-dmbpy)]}: C, 47.1; H, 3.9; N, 6.1. Found: C, 46.8; H, 4.1; N, 6.2. Infrared spectrum (KBr disk), cm<sup>-1</sup>: 2052 s, 1983 s, 1629 s, 1597 s, 1545 w, 1478 m, 1376 s, 1315 s, 1240 m, 1169 w, 1147 w, 1062 w, 1042 w, 1014 w, 839 m, 679 m. <sup>1</sup>H NMR spectrum (*d*<sub>4</sub>-methanol): 1.78 (6H, s, CH<sub>3</sub>CO<sub>2</sub>); 2.67 (6H, s, bpy-CH<sub>3</sub>); 8.21 (2H, d, H<sub>4</sub>,H<sub>4'</sub>); 8.55 (2H, d, H<sub>3</sub>,H<sub>3'</sub>); 9.18 (2H, s, H<sub>6</sub>,H<sub>6'</sub>). Electro spray mass spectrum (MeOH): *m/z* 401 (83%, [M - MeCO<sub>2</sub>]<sup>+</sup>), 483 (100%, [M + Na]<sup>+</sup>), 943 (91%, [2M + Na]<sup>+</sup>).

**μ-C,O-o-Phenylencarboxylato-C,C-carbonyl(2,2'-bipyridine)-ruthenium(II).** Sodium benzoate (1.03 g, 7.15 mmol), [Ru(CO)<sub>2</sub>Cl<sub>2</sub>]<sub>n</sub> (175 mg, 0.767 mmol), and 2,2'-bipyridine (175 mg, 1.12 mmol) were heated in degassed methanol (25 mL), at a bath temperature of 120 °C for 5 h, as outlined for [Ru<sup>II</sup>(MeCO<sub>2</sub>)<sub>2</sub>(CO)<sub>2</sub>(5,5'-dmbpy)]. The reaction mixture was filtered to remove any impurities and then evaporated to dryness. The residue was suspended in CH<sub>2</sub>Cl<sub>2</sub> and the excess sodium benzoate extracted into water. The yellow solution of CH<sub>2</sub>Cl<sub>2</sub> was then left to evaporate, resulting in nearly colorless diamond-shaped crystals in a bulk yellow oily substance. Infrared spectrum of mixture (KBr disk), cm<sup>-1</sup>: 2047 s, 1962 s, 1749 w, 1704 w, 1600 s, 1494 w, 1474 w, 1444 m, 1324 m, 1244 w, 1141 w, 1069 w, 1023 w, 850 w, 768 m, 738 m, 645 w, 614 w, 519 w.

A small volume of CH<sub>2</sub>Cl<sub>2</sub> was used to dissolve the yellow oil leaving the crystals behind. The crystals, [Ru<sup>II</sup>(O<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>)(CO)<sub>2</sub>-

(bpy)] (yield: 104 mg, 31%) were washed with a little more CH<sub>2</sub>Cl<sub>2</sub> (5 mL) and water (5 mL). Anal. Calcd for C<sub>19</sub>H<sub>14</sub>N<sub>2</sub>O<sub>5</sub>Ru {[Ru<sup>II</sup>(O<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>)(CO)<sub>2</sub>(bpy)]·H<sub>2</sub>O}: C, 50.6; H, 3.1; N, 6.2. Found: C, 51.1; H, 3.0; N, 6.3. Infrared spectrum (KBr disk), cm<sup>-1</sup>: 2047 vs, 1962 vs, 1703 vw, 1630 s, 1599 s, 1580 s, 1494 w, 1474 w, 1444 m, 1324 s, 1246 w, 1182 w, 1142 m, 1073 vw, 1023 w, 852 w, 819 vw, 769 s, 740 s, 701 w, 643 w, 614 w, 560 vw, 519 w, 475 w, 455 w, 412 w. <sup>1</sup>H NMR spectrum (*d*<sub>4</sub>-methanol): 7.18 (1H, td, benz-H<sub>4</sub>), 7.42 (1H, td, benz-H<sub>5</sub>), 7.46 (1H, ddd, bpy-H<sub>5</sub>), 7.61 (1H, ddd, benz-H<sub>3</sub>), 7.77 (1H, ddd, benz-H<sub>6</sub>), 7.77 (1H, ddd, bpy-H<sub>5'</sub>), 7.89 (1H, ddd, bpy-H<sub>6</sub>), 8.18 (1H, ddd, bpy-H<sub>4</sub>), 8.28 (1H, ddd, bpy-H<sub>4'</sub>), 8.60 (2H, t\*, sH<sub>3</sub>, H<sub>3'</sub>), 9.14 (1H, ddd, bpy-H<sub>6'</sub>). <sup>13</sup>C NMR spectrum (*d*<sub>4</sub>-methanol): 124.9 (bpy-C<sub>3</sub>/C<sub>3'</sub>), 125.3 (benz-C<sub>4</sub>), 128.1 (bpy-C<sub>5</sub>), 128.8 (bpy-C<sub>5'</sub>), 131.1 (benz-C<sub>3</sub>), 133.8 (benz-C<sub>5</sub>), 139.6 (benz-C<sub>6</sub>), 141.1 (benz-C<sub>2</sub>), 141.3 (bpy-C<sub>4</sub>), 141.9 (bpy-C<sub>4'</sub>), 151.5 (bpy-C<sub>6</sub>), 155.6 (bpy-C<sub>6'</sub>), 156.1 (bpy-C<sub>2</sub>), 157.9 (bpy-C<sub>2'</sub>), 165.5 (benz-C<sub>1</sub>-Ru), 182.5 (CO<sub>2</sub>), 198.3 (CO), 199.5 (CO'). Electro spray mass spectrum (MeOH): *m/z* 435 (55%, [M + H]<sup>+</sup>), 457 (90%, [M + Na]<sup>+</sup>), 473 (50%, [M + K]<sup>+</sup>), 563 (10%, [M + I + 2H]<sup>+</sup>), 869 (30%, [2M + H]<sup>+</sup>), 891 (100%, [2M + Na]<sup>+</sup>), 906 (30%, [2M + K]<sup>+</sup>).

**μ-C,O-o-Phenylencarboxylato-C,C-carbonyl(1,10-phenanthroline)ruthenium(II).** Sodium benzoate (1.05 g, 7.29 mmol), [Ru(CO)<sub>2</sub>Cl<sub>2</sub>]<sub>n</sub> (175 mg, 0.767 mmol), and 1,10-phenanthroline (173 mg, 0.96 mmol) were heated in degassed methanol (25 mL), at a bath temperature of 130 °C for 24 h as outlined for [Ru<sup>II</sup>(MeCO<sub>2</sub>)<sub>2</sub>(CO)<sub>2</sub>(5,5'-dmbpy)]. The reaction mixture was filtered to remove any impurities and then evaporated to dryness under vacuum. The pale orange residue was suspended in CH<sub>2</sub>Cl<sub>2</sub> and the solid sodium benzoate was removed by filtration. The filtrate was evaporated to give an orange solid which was dissolved in methanol and left in the dark to evaporate giving a yellow powder of [Ru<sup>II</sup>(O<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>)(CO)<sub>2</sub>(phen)] (yield: 88 mg, 23%). Anal. Calcd for C<sub>22</sub>H<sub>16</sub>N<sub>2</sub>O<sub>5</sub>-



Ru {[Ru<sup>II</sup>(O<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>)(CO)<sub>2</sub>(phen)].MeOH}: C, 54.0; H, 3.3; N, 5.7. Found: C, 54.9; H, 3.4; N, 5.9. Infrared spectrum (KBr disk), cm<sup>-1</sup>: 2038 s, 1962 s, 1747 w, 1703 m, 1620 s, 1575, 1425 m, 1402 m, 1342 w, 1314 m, 1258 w, 1142 w, 846 m, 718 m. <sup>1</sup>H NMR spectrum (*d*<sub>4</sub>-methanol): 7.24 (1H, td, <sup>4</sup>*J*<sub>H<sub>4</sub>,H<sub>6</sub></sub> 1.2, <sup>3</sup>*J*<sub>H<sub>3</sub>,H<sub>4</sub></sub> = <sup>3</sup>*J*<sub>H<sub>4</sub>,H<sub>5</sub></sub> 7.5 Hz, benz-**H4**), 7.48 (1H, td, benz-**H5**), 7.66 (1H, ddd, benz-**H3**), 7.78 (1H, dd, phen-**H3**), 7.88 (1H, ddd, benz-**H6**), 8.10 (1H, dd, <sup>3</sup>*J*<sub>H<sub>8</sub>,H<sub>9</sub></sub> 5.0, <sup>3</sup>*J*<sub>H<sub>7</sub>,H<sub>8</sub></sub> 8.3 Hz, phen-**H8**), 8.18 (2H, q\*, phen-**H5**,**H6**), 8.17 (1H, dd, phen-**H2**), 8.73 (1H, dd, phen-**H4**), 8.84 (1H, dd, phen-**H7**), 9.51 (1H, dd, phen-**H9**). <sup>13</sup>C NMR spectrum (*d*<sub>4</sub>-methanol): 125.4 (benz-**C4**), 126.7 (phen-**C3**), 127.6 (phen-**C8**), 128.7 (phen-**C5**), 129.2 (phen-**C6**), 131.1 (benz-**C3**), 132.2 (phen-**C13**), 132.3 (phen-**C14**), 133.8 (benz-**C5**), 139.7 (benz-**C6**), 140.3 (phen-**C4**), 141.0 (phen-**C7**), 141.2 (benz-**C2**), 147.0 (phen-**C11**), 148.4 (phen-**C12**), 152.0 (phen-**C2**), 155.9 (phen-**C9**), 165.3 (benz-**C1**-Ru), 182.4 (benz-CO<sub>2</sub>), 198.4 (CO), 199.6 (CO'). Electro spray mass spectrum (MeOH): *m/z* 459 (65%, [M + H]<sup>+</sup>), 481 (85%, [M + Na]<sup>+</sup>), 497 (25%, [M + K]<sup>+</sup>), 917 (20%, [2M + H]<sup>+</sup>), 939 (100%, [2M + Na]<sup>+</sup>), 955 (10%, [2M + K]<sup>+</sup>).

**Structure Determinations.** Full spheres of CCD diffractometer data were measured at low temperature (for 4,4'-dmbpy, [Ru(MeCO<sub>2</sub>)<sub>2</sub>(CO)<sub>2</sub>(4,4'-dmbpy)], Bruker AXS instrument, *T* ca. 153 K, "empirical"/multiscan absorption correction; for [Ru(O<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>)(CO)<sub>2</sub>(bpy)], a Bruker *P4* instrument (*ω*-scans, *T* ca. 153 K); for the remainder, an Enraf-Nonius Kappa instrument (*T* ca. 123 K), no absorption corrections; all structures, monochromatic Mo K $\alpha$  radiation,  $\lambda = 0.7107 \text{ \AA}$ ). *N*<sub>(total)</sub> reflections were obtained,

merging to *N* unique (*R*<sub>int</sub> cited), *N*<sub>o</sub> with  $I > 2\sigma(I)/F > 4\sigma(F)$  considered "observed" and used in the full-matrix least-squares refinements (anisotropic displacement parameter forms for the non-hydrogen atoms, (*x*, *y*, *z*, *U*<sub>iso</sub>)<sub>H</sub> constrained at estimated values (exception: 4,4'-dmbpy in which they were refined). Conventional residuals *R* (=  $\sum\Delta/\sum F_o$ ), *R*<sub>w</sub> (=  $(\sum w\Delta^2)/\sum wF_o^2$ )<sup>1/2</sup> (weights:  $(\sigma^2(F_o) + 0.0003F_o^2)^{-1/2}$ ) are cited at convergence. Neutral atom complex scattering factors were employed, within the Xtal 3.7 program system.<sup>30</sup> Pertinent results are given in the tables and figures, the latter showing 50% probability amplitude displacement envelopes for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å; see Supporting Information for full .cif depositions. Individual variations in procedure are noted in footnote *a* of Table 4.

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**Supporting Information Available:** Crystallographic files for the five X-ray structure determinations in CIF format, figures showing unit cell projections, and text giving further details of <sup>1</sup>H NMR spectra including coupling constants. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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