

Synthesis, Characterization, and Reactions of Ruthenium Phenanthroline Complexes Bearing C₁ Ligands: Formyl, Metallo-carboxylate, and CO₂-Bridged Complexes

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A new formyl complex, *cis*-Ru(phen)₂(CO)(CHO)(PF₆) (**8**), has been characterized, and some of its reactions have been compared with those of its bipyridyl analogue. Reactions of **8** with MeOH can be photoassisted and lead to a metalloester, **7**; reaction rates are comparable to those of the bipyridyl analogue. Reactions of **8** in DME/H₂O require O₂ and can be photoassisted; the reactions lead to a μ_2 - η^2 -type CO₂-bridged complex, **10**. Reactions of **8** with water are slower than those of the bipyridyl analogue and allow observation of an intermediate metallo-carboxylic acid, *cis*-Ru(phen)₂(CO)(COOH)(PF₆) (**6**), which has been structurally characterized. A related CO₂-bridged complex, *cis,cis*-[Ru(phen)₂(CO₂)Ru(bpy)₂(CO)](2PF₆) (**11**), has also been prepared and structurally characterized; its spectral properties support the formulation of **10** and its bipyridyl analogue.

Introduction

Ruthenium and rhenium polypyridyl complexes with C₁ ligands are implicated as important intermediates in photocatalytic and electrocatalytic reductions of CO₂ to formate and CO,¹ but few such compounds are known² and little is known of their chemistry. Recently, we reported^{2g} that certain reactions of *cis*-[Ru(bpy)₂(CO)(CHO)](PF₆) (**1**; bpy = 2,2'-bipyridyl) could be pho-

toassisted. The motivation for the present work was to determine the reactivity of analogues containing the more rigid, fused-ring 1,10-phenanthroline ligand rather than 2,2'-bipyridine. Also, there have been reports of differences in product distributions (CO versus formate) in the CO₂ conversion reactions with changes in the polypyridine ligands;³ thus, it is important to define the differences in reactivity, promoted by ligand changes, that may have bearing on the catalytic reactions.

Results and Discussion

Compound **1** was prepared first by Tanaka et al.^{2c} and reported to react with MeOH to yield the corresponding metalloester, *cis*-[Ru(bpy)₂(CO)(COOMe)](PF₆) (**2**); we determined that photoassistance was required for this reaction, and we also probed additional reactions of compound **1**.^{2g} The pathway we proposed^{2g} for the reaction with MeOH is illustrated in Scheme 1. A critical step involves temporary dechelation of the bidentate bipyridyl ligand followed by hydride migration from the formyl group to the new vacant site. Monodentate complexes such as **A** in Scheme 1 have been suggested⁴ as intermediates in photochemically promoted ligand substitution reactions of Ru(bpy)₃²⁺, and spectral evidence has been obtained for one such compound.^{4b} Also, the dynamic behavior of bipyridyl-like ligands in square-planar complexes is well-docu-

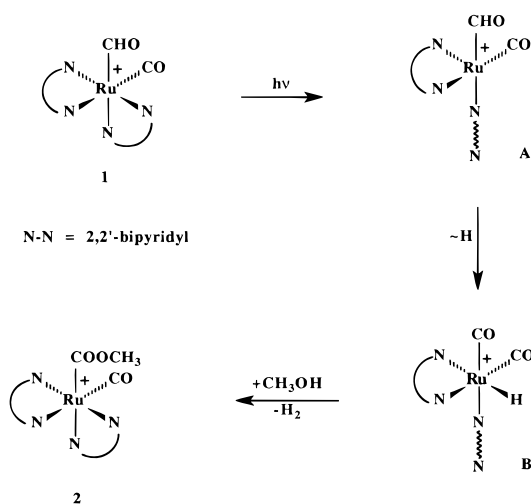
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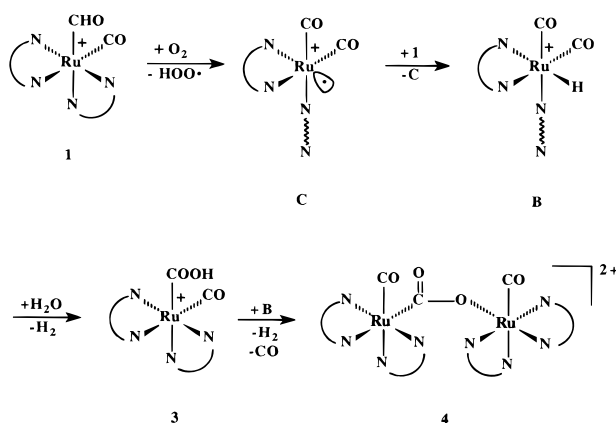
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Scheme 1



Scheme 2



mented.⁵ Furthermore, there is structural data supporting monodentate coordination of a phenanthroline ligand in a platinum complex.⁶ We also showed that the reaction of **1** with H_2O required the presence of O_2 ; the pathway is proposed to be initiated by H atom abstraction from the formyl group, a well-known characteristic of metal formyl complexes.⁷ The full path is illustrated in Scheme 2 and leads, through an intermediate metalcarboxylic acid, $\text{cis}[\text{Ru}(\text{bpy})_2(\text{CO})(\text{COOH})](\text{PF}_6)$ (**3**), to a CO_2 -bridged complex, $\text{cis},\text{cis}[\text{Ru}(\text{bpy})_2(\text{CO})(\text{CO}_2)\text{Ru}(\text{bpy})_2(\text{CO})](\text{PF}_6)_2$ (**4**). Note that the same intermediate hydride, **A**, is proposed here as well as in Scheme 1. We observed that the reaction with water could be photoassisted, but would proceed in the dark in the presence of O_2 . The proposed intermediate acid, **3**, could not be observed; however, reaction of **1** with **3** afforded CO_2 -bridged complex **4** much more rapidly than in reactions of the formyl complex alone. We sought to explore the reactivity of the closely related formyl complex bearing phenanthroline, rather than bipyridyl,

ligands to establish any differences that might be linked to the more rigid nature of the fused-ring phenanthroline ligands. Thus, the synthesis of several new compounds was required.

Reaction of $\text{cis}[\text{Ru}(\text{phen})_2(\text{CO})_2](\text{PF}_6)_2$ (**5**) with aqueous Na_2CO_3 afforded the metalcarboxylic acid, $\text{cis}[\text{Ru}(\text{phen})_2(\text{CO})(\text{COOH})](\text{PF}_6)$ (**6**), which has been characterized by elemental analysis, spectral data, and X-ray structure determination (see discussion below). Similarly, treatment of **5** with sodium methoxide afforded $\text{cis}[\text{Ru}(\text{phen})_2(\text{CO})(\text{COOMe})](\text{PF}_6)$ (**7**); the metalloester has been characterized by spectral data and by elemental analysis.

Treating cation **5** with Et_4NBH_4 in a manner similar to that used for the corresponding bipyridyl cation^{2g} afforded the new formyl complex, $\text{cis}[\text{Ru}(\text{phen})_2(\text{CO})(\text{CHO})](\text{PF}_6)$ (**8**), as a yellow solid in 80% yield; it has been characterized by elemental analysis and spectral data (see Experimental Section).

The new carbon dioxide complex, $\text{cis}[\text{Ru}(\text{phen})_2(\text{CO})(\text{CO}_2)]$ (**9**), was prepared by reaction of cation **5** with excess aqueous Et_4NOH , in a manner similar to the analogous compound with bipyridyl ligands prepared previously.^{2a} The compound was characterized by elemental analysis and spectral data, which indicated that it is obtained as the trihydrate as is the bipyridyl analogue.

Reaction of **8** with water in the presence of oxygen afforded the CO_2 -bridged complex, $\text{cis},\text{cis}[\text{Ru}(\text{phen})_2(\text{CO})(\text{CO}_2)\text{Ru}(\text{phen})_2(\text{CO})](\text{PF}_6)_2$ (**10**), in 83% yield after 4 days (see discussion below); it has been characterized by elemental analysis and spectral data; the DRIFTS data showed ν_{OCO} at 1500 and 1174 cm^{-1} , indicating that the carboxyl bridge is of the $\mu_2\text{-}\eta^2$ type.⁹

Also, the mixed CO_2 -bridged complex, $\text{cis},\text{cis}[\text{Ru}(\text{phen})_2(\text{CO})(\text{CO}_2)\text{Ru}(\text{bpy})_2(\text{CO})](\text{PF}_6)_2$ (**11**), was prepared by reaction of CO_2 complex **9** with $\text{cis}[\text{Ru}(\text{bpy})_2(\text{CO})(\text{H}_2\text{O})](\text{PF}_6)_2$.¹⁰ Compound **11** has been characterized by elemental analysis, spectral data, and X-ray structure determination (as discussed below). DRIFTS data show the ν_{OCO} bands at 1499 and 1183 cm^{-1} , and structural data are consistent with $\mu_2\text{-}\eta^2$ bonding of the carboxyl bridge in this complex, thus providing support for the assignment of this bonding mode for the CO_2 ligand in compound **10** (and for that in **4**^{2g}).

An ORTEP diagram for $\text{cis}[\text{Ru}(\text{phen})_2(\text{CO})(\text{COOH})](\text{PF}_6)$ (**6**) is shown in Figure 1. Crystallographic data are summarized in Table 1; selected bond distances and bond angles are shown in Table 2. The X-ray data show fractional diethyl ether units in the crystal, but there is no evidence for hydrogen bonding of the carboxyl proton to additional centers as has been observed with the closely related $\text{cis}[\text{Ru}(\text{bpy})_2(\text{CO})(\text{COOH})](\text{OTf})_2$ ^{2f} and $\text{cis}[\text{Ru}(\eta^2\text{-tpy})(\text{bpy})(\text{CO})(\text{COOH})](\text{PF}_6)$ ¹¹ ($\text{tpy} = 2,2';6',2''\text{-terpyridyl}$). Also, **6** does not form dimers as the result of intermolecular hydrogen bonding involving the carboxyl groups as shown by the platinum complexes $\text{trans-Pt}(\text{Ph})(\text{PET}_3)_2\text{COOH}$ and $\text{trans-Pt}[(\text{C}_6\text{H}_3\text{PPh}_2)_2\text{-2,6}]\text{COOH}$

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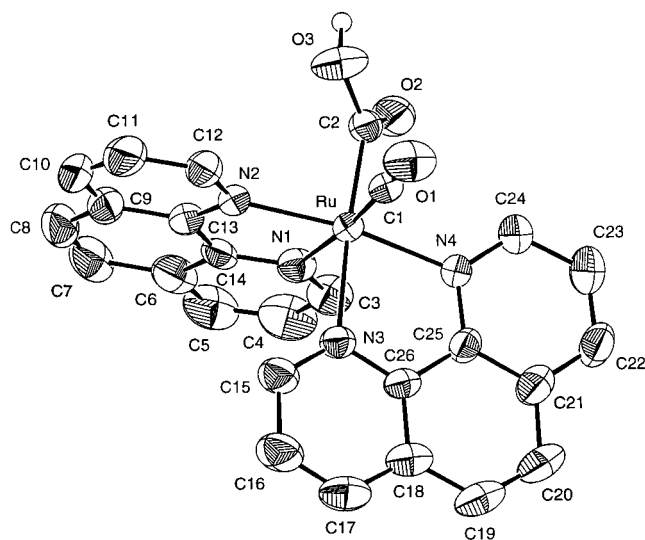
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Table 1. Summary of Crystallographic Data

	6	11
formula	C ₂₉ H _{24.50} F ₆ N ₄ O _{3.75} PRu	C _{53.5} H _{40.6} N _{10.1} O ₄ Ru ₂ P ₂ F ₆
fw	735.07	1381.04
cryst dimens, mm	0.49 × 0.36 × 0.20	0.50 × 0.43 × 0.20
cryst descriptn	yellow block	orange, triangular
cryst system	monoclinic	triclinic
space group	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>P</i> 1 (No. 2)
<i>a</i> , Å	11.323(3)	14.305(3)
<i>b</i> , Å	14.062(4)	14.580(4)
<i>c</i> , Å	19.296(5)	13.687(3)
α, deg		103.45(2)
β, deg	90.46(2)	90.62(2)
γ, deg		93.94(2)
vol, Å ³	3072(1)	2768(1)
<i>Z</i>	4	2
<i>D</i> _c , g/cm ³	1.59	1.66
μ(Mo Kα), cm ⁻¹	6.39	6.99
diffractometer	Enraf-Nonius CAD4	same
monochromator	graphite crystal	same
radiation (λ, Å)	Mo Kα (λ = 0.710 73)	same
temp, °C	23(1)	-80(1)
scan range, deg	0.80 + 0.35 tan θ	same
scan speed, deg/min	1-5	same
maximum 2θ, deg	50.0	50.1
abs corr	psi scans	same
transmission factors: min/max	0.86/1.00	0.93/1.00
no. of unique reflns collected	5683	9717
no. of reflns included (<i>I</i> _o > 3σ(<i>I</i> _o))	4161	7628
no. of params	439	758
computer hardware	Silicon Graphics	same
computer software	teXsan (msc)	same
residuals: <i>R</i> ; <i>R</i> _w	0.043; 0.055	0.069; 0.078
GOF	2.71	5.50
least-squares weights	[σ ² (<i>F</i> _o)] ⁻¹	same
max peak in final diff map, e/Å ³	0.67	1.21
min peak in final diff map, e/Å ³	-0.51	-1.49

**Figure 1.** ORTEP diagram of **6** (cation only) with thermal ellipsoids shown at the 50% probability level.

characterized by Bennett et al.¹² Thus **6** is unique among the few structurally characterized metallocarboxylic acids. Structural data for **6** show that the coordination geometry about the ruthenium atom is slightly distorted from a regular octahedron. All of the ruthenium–nitrogen bond distances are slightly longer in **6** as compared to the bipyridyl analogue.^{2f} Furthermore, the longest such bond in **6** is Ru–N3, the one

Table 2. Selected Bond Distances (Å) and Angles (deg) for [Ru(phen)₂((CO)(COOH))(PF₆)₂] (6**)**

Bond Distances			
Ru–N(1)	2.129(4)	Ru–N(2)	2.073(4)
Ru–N(3)	2.169(4)	Ru–N(4)	2.089(4)
Ru–C(1)	1.845(6)	Ru–C(2)	2.022(5)
O(1)–C(1)	1.127(6)	O(2)–C(2)	1.215(6)
O(3)–C(2)	1.363(6)		
Bond Angles			
N(1)–Ru–N(2)	79.2(2)	N(1)–Ru–N(3)	86.8(2)
N(1)–Ru–N(4)	93.7(2)	N(1)–Ru–C(1)	174.8(2)
N(1)–Ru–C(2)	88.0(2)	N(2)–Ru–N(3)	94.8(2)
N(2)–Ru–N(4)	170.4(2)	N(2)–Ru–C(1)	96.3(2)
N(2)–Ru–C(2)	90.5(2)	N(3)–Ru–N(4)	78.2(2)
N(3)–Ru–C(1)	96.2(2)	N(3)–Ru–C(2)	171.7(2)
N(4)–Ru–C(1)	91.0(2)	N(4)–Ru–C(2)	95.8(2)
Ru–C(1)–O(1)	177.7(5)	Ru–C(2)–O(2)	125.8(4)
Ru–C(2)–O(3)	117.3(4)	O(2)–C(2)–O(3)	116.8(5)

trans to the carboxyl group; as in other acyl complexes of ruthenium,^{2f,h,11} this σ-donor group exerts a strong trans effect. The O–C–O angle in the carboxyl group is also larger (116.8(5)°) in **6** than in the bipyridyl analogue (114.9(6)°).^{2f}

An ORTEP diagram for *cis,cis*-[Ru(phen)₂(CO)(CO₂)-Ru(bpy)₂(CO)](PF₆)₂ (**11**) is shown in Figure 2. Crystallographic data are summarized in Table 1; selected bond distances and bond angles are shown in Table 3. The X-ray data for **11** show fractional solvent molecules (acetonitrile and benzene) but clearly indicate μ₂-η²-coordination of the bridging CO₂ ligand. The data show slightly distorted octahedral ruthenium centers; again, the carboxyl group exerts a strong trans effect, with the Ru1–N1 bond being longer than other ruthenium–nitrogen bonds involving either ruthenium atom. The

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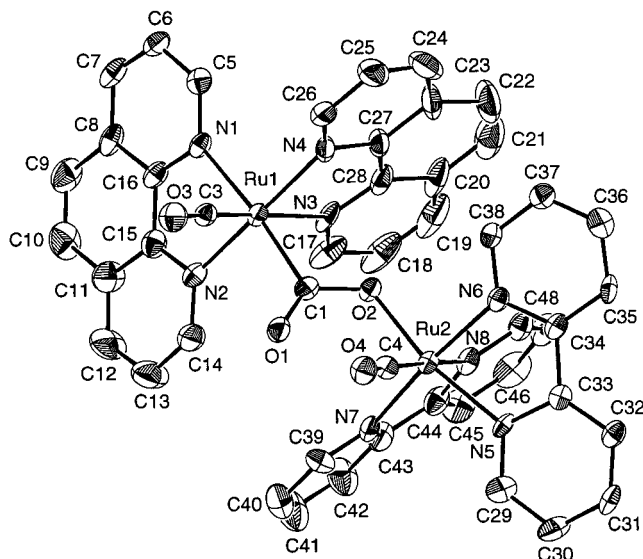


Figure 2. ORTEP diagram of **11** (cation only) with thermal ellipsoids shown at the 50% probability level.

Table 3. Selected Bond Distances (Å) and Angles (deg) for [Ru(phen)₂(CO)(CO₂Ru(bpy)₂CO)](2PF₆) (**11**)

Bond Distances			
Ru(1)–N(1)	2.182(5)	Ru(2)–O(2)	2.065(4)
Ru(1)–N(2)	2.080(6)	Ru(2)–N(5)	2.074(5)
Ru(1)–N(3)	2.124(6)	Ru(2)–N(6)	2.055(6)
Ru(1)–N(4)	2.050(6)	Ru(2)–N(7)	2.053(6)
C(1)–O(1)	1.234(8)	Ru(2)–N(8)	2.120(5)
C(1)–O(2)	1.318(8)		
Bond Angles			
O(1)–C(1)–O(2)	122.3(6)	Ru(2)–C(4)–O(4)	176.7(6)
Ru(1)–C(3)–O(3)	177.8(7)	N(5)–Ru(2)–N(6)	78.8(2)
N(1)–Ru(1)–N(2)	78.3(2)	N(7)–Ru(2)–N(8)	78.4(2)
N(3)–Ru(1)–N(4)	79.2(2)	Ru(1)–C(1)–O(1)	122.9(5)

O–C–O angle in the carboxyl group in **11** is much larger (122.3(6)°) than in **6** and is typical of the values observed for this type of CO₂-bridged ligand.⁹

A sample of **8** was dissolved in MeOH under N₂ and allowed to stand for 7 h under laboratory fluorescent lights; during this time, conversion to the methyl ester, *cis*-[Ru(phen)₂(CO)(COOMe)](PF₆) (**7**), occurred (identical to the sample prepared by methoxide addition to cation **5**), and the ester was isolated in 81% yield. As in the case of **1**,^{2g} reaction of **7** with MeOH occurred quickly (20 min) when promoted by a 450 W Hg arc lamp (through Pyrex). Both of these conversions of **8** are comparable to the corresponding ones for **1**.

Reaction of **8** in DME/H₂O (DME = dimethoxyethane) in the presence of O₂ required 4 days for completion, but provided the CO₂-bridged compound *cis,cis*-[Ru(phen)₂(CO)(CO₂Ru(phen)₂(CO))](PF₆)₂ (**10**) in 83% yield. Unlike the reactions of **1**, where the suspected metal-carboxylic acid **3** could not be observed, acid **6** was observed as an intermediate (which later disappeared) during the transformation of **8**, thus supporting the proposed intermediacy of **3** in the analogous reactions of formyl complex **1** suggested earlier.^{2g} The conversion of **8** to **10** is much slower than the corresponding conversion of **1**, which requires only 3 h for completion.^{2g} The conversion of **8** can be photoassisted, proceeding to completion in 2 h as the result of irradiation with the 450 W lamp through Pyrex. The analogous reaction

with **1** proceeded to completion, giving mainly the CO₂-bridged compound, after only 5 min.

A probe reaction was done, using compounds from both series, to test the reactivity differences further. Thus, formyl complex **1** (with bipyridyl ligands) was allowed to react with oxygen in DME/H₂O in the presence of acid **6** (phenanthroline ligands); the product mixture contained unreacted **6**, CO₂-bridged compound **4** (all bpy ligands), and a small amount of the mixed ligand CO₂-bridged compound, **11**, resulting from reaction of a small amount of **6** with **1**. Although acid **3** is believed to be an intermediate in the reactions of **1** leading to **4**,^{2g} it was not observed as a product here either. We conclude from the results of this experiment, and the one above involving the conversion of **8** to **10**, that compound **6** is a weaker acid than **3** and is unable to compete with it in reactions with **1** (for the presumed intermediate hydride of type **A** shown in Scheme 2).

Conclusions

The reactivity of formyl complex **8** toward methanol is directly comparable to the reactivity of its bipyridyl analogue, **1**. The more rigid fused-ring phenanthroline ligand does not provide a barrier to the transformation to metalloester **9**. However, the two formyl complexes differ greatly in the ease of the conversion to CO₂-bridged complexes that result from exposure to oxygen in DME/H₂O solutions, with the transformation of **8** being much slower than that of **1**. This difference appears to be due, in part, to the lower acidity of the intermediate metalcarboxylic acid, **6**, which slows the conversion of **8** to **10**. Although **6** can be observed in conversions of **8**, the bipyridyl analogue (**3**) is not observable in conversions of **1**.

Structural characterization of CO₂-bridged compound **11** confirms the binding mode of the carboxyl bridge as the μ₂-η²-type. The close relationship of the IR ν_{OCO} bands in **11** with those in CO₂-bridged compounds **10** and **4** (in the bipyridyl series) supports the formulation of those as the same type.

Experimental Section

General Procedures and Instrumentation. Reagent grade acetonitrile, dichloromethane, benzene, and diethyl ether were used as received without further purification. Dimethoxyethane was distilled under nitrogen from sodium/benzophenone. Methanol was distilled, under nitrogen, from magnesium turnings. Et₄NOH (aq, 20% w/w) was purchased from Aldrich. [Ru(phen)₂(CO)₂](PF₆)₂,⁸ [Ru(bpy)₂(CO)(H₂O)](PF₆)₂,¹⁰ and Et₄NBH₄¹³ were prepared according to literature methods. The ¹H and ¹³C NMR spectra were recorded on a Bruker AMX-500 spectrometer; chemical shifts were referenced to residual protons and carbons in the deuterated solvents. DRIFTS spectra were recorded on a Mattson RS-1 FTIR spectrometer using a Mini-Diff accessory (Graseby Specac Inc.). Melting points were measured on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Midwest Microlab, Indianapolis, IN.

Synthesis of [Ru(phen)₂(CO)COOH](PF₆) (6**).** [Ru(phen)₂(CO)₂](PF₆)₂ (0.50 g, 0.62 mmol) was dissolved in CH₃CN (20 mL). A saturated aqueous solution of Na₂CO₃ was then added. The color changed from pale yellow to bright yellow immediately. The mixture was stirred for 1 h, and then solvent was removed under vacuum. The residue was triturated with CH₃CN (20 mL), and the mixture was filtered. The

filtrate was evaporated under vacuum to yield a yellow solid, 0.39 g (94%), mp 170 °C, dec.

Anal. Calcd for $C_{26}H_{17}F_6N_4O_3PRu$: C, 45.95; H, 2.52. Found: C, 46.04; H, 2.60. IR (DRIFTS, KCl): ν_{CO} 1958; ν_{OCO} 1636 and 1009 cm^{-1} . 1H NMR (CD_3CN): δ 10.02 (m, 1, phen); 9.65 (m, 1, phen); 7.45–9.65 (m, 14, phen). ^{13}C NMR (CD_3CN): δ 207.53 (COOH), 202.52 (CO), 156.74–126.31 (23 resonances for 24 carbons).

Synthesis of $[Ru(phen)_2(CO)(COOMe)(PF_6)]$ (7). $[Ru(phen)_2(CO)_2](PF_6)_2$ (0.10 g, 0.13 mmol) was placed in a flask with CH_3OH (40 mL). $NaOCH_3$ (freshly prepared from Na (0.01 g) in CH_3OH (2.5 mL)) was added. A change in color from pale to bright yellow was observed as the mixture was stirred for 30 min. The resulting mixture was evaporated to dryness under vacuum. The solid was triturated with CH_2Cl_2 (40 mL), and the mixture was filtered. Solvent was removed under vacuum to yield a yellow solid, 0.08 g (89%), mp 160 °C, dec.

Anal. Calcd For $C_{27}H_{19}F_6N_4O_3PRu \cdot H_2O$: C, 45.57; H, 2.97. Found: C, 45.47; H, 2.80. IR (DRIFTS, KCl): ν_{CO} 1959 cm^{-1} ; ν_{OCO} 1616 and 1047 cm^{-1} . 1H NMR (CD_3CN): δ 9.92 (m, 1, phen); 9.64 (m, 1, phen); 8.85–7.46 (m, 14, phen); 3.26 (s, 3, CH_3). ^{13}C NMR (CD_3CN): δ 203.04 (COOMe), 202.78 (CO), 156.80–126.25 (24 resonances for 24 carbons), 49.96 (CH_3).

Synthesis of $[Ru(phen)_2(CO)(CHO)(PF_6)]$ (8). $[Ru(phen)_2(CO)_2](PF_6)_2$ (0.35 g, 0.43 mmol) was placed in a 100 mL flask and cooled to 0 °C. Then, methanol (30 mL) was added. Et_4NBH_4 (0.15 g, 2 equiv) was added, and the mixture was stirred for 30 min. A yellow solid separated and was collected by filtration, washed with H_2O , and dried under vacuum, 0.23 g (80%); it decomposes gradually, starting at 164 °C.

Anal. Calcd for $C_{26}H_{17}F_6N_4O_2PRu$: C, 47.06; H, 2.58. Found: C, 46.61; H, 2.58. IR (DRIFTS, KCl): ν_{CO} 1950 cm^{-1} ; $\nu_{C=O}$ 1611 cm^{-1} . 1H NMR (CD_3CN): δ 13.93 (s, 1, CHO); 9.72 (m, 1, phen); 9.66 (m, 1, phen); 7.47–9.72 (m, 14, phen). ^{13}C NMR (CD_3CN): δ 263.55 (CHO), 202.44 (CO), 139.80–126.12 (24 resonances for 24 carbons).

Synthesis of $[Ru(phen)_2(CO)(CO_2) \cdot 3H_2O]$ (9). $[Ru(phen)_2(CO)_2](PF_6)_2$ (0.32 g, 0.36 mmol) was dissolved in CH_3CN (10 mL), and Et_4NOH (aq., 20% w/w, 0.56 mL, 0.80 mmol) was added. The mixture was stirred for 30 min; after this time a red solid separated and was collected by filtration, washed with CH_3CN , and dried under vacuum, affording 0.21 g (93% yield), mp 110 °C, dec. The number of water molecules was confirmed by 1H NMR spectroscopy using an internal standard.

Anal. Calcd for $C_{26}H_{16}N_4O_3Ru \cdot 3H_2O$: C, 53.15; H, 3.77. Found: C, 53.19; H, 3.81. IR (DRIFTS, KCl): ν_{CO} , 1913 cm^{-1} ; ν_{OCO} , 1424 and 1245 cm^{-1} . 1H NMR (CD_3OD): δ 10.45 (m, 1, phen); 9.78 (m, 1, phen); 8.83–7.43 (m, 14, phen). ^{13}C NMR (CD_3OD): δ 209.76, 204.16 (CO and CO_2); 158.31–126.10 (24 resonances due to 24 carbons, phen).

Synthesis of $[Ru(phen)_2(CO)(CO_2)Ru(phen)_2(CO)](PF_6)_2$ (10). $[Ru(phen)_2(CO)(CHO)]PF_6$ (0.100 g, 0.151 mmol) was dissolved in DME/ H_2O (20:1, 21 mL) under O_2 . The mixture was stirred for 4 days and then solvent was removed under vacuum. The residue was recrystallized twice from CH_3CN /ether to yield yellow-orange crystals, 0.08 g (83% yield), mp 255 °C, dec.

Anal. Calcd for $C_{51}H_{32}F_{12}N_8O_4P_2Ru_2$: C, 46.65; H, 2.46. Found: C, 46.77; H, 2.56. IR (DRIFTS, KCl): ν_{CO} , 1954 cm^{-1} ; ν_{OCO} , 1500 and 1174 cm^{-1} . 1H NMR (CD_3CN): δ 10.41 (m, 1, phen); 9.62 (m, 1, phen); 9.45 (m, 1, phen); 8.83–6.88 (m, 29, phen). ^{13}C NMR (CD_3CN): δ 204.29, 204.24, 202.92 (CO and CO_2); 158.57–124.78 (46 resonances due to 48 carbons, phen).

Synthesis of $[Ru(phen)_2(CO)(CO_2)Ru(bpy)_2(CO)](PF_6)_2$ (11). $[Ru(bpy)_2(CO)(H_2O)](PF_6)_2$ (0.33 g, 0.44 mmol) and $[Ru(phen)_2(CO)(CO_2) \cdot 3H_2O]$ (0.26 g, 0.44 mmol) were dissolved in H_2O (40 mL). The pH value of the mixture was adjusted to 8–9 using NaOH (aq, 1 M). The mixture was stirred overnight. A yellow-orange solid was collected by filtration, washed with H_2O , and recrystallized from CH_3CN /ether. The

solid then was recrystallized from CH_3CN /benzene to yield orange crystals, 0.44 g (80%), mp >250 °C.

Anal. Calcd for $C_{47}H_{32}F_{12}N_8O_4P_2Ru_2$: C, 44.63; H, 2.55. Found: C, 44.21; H, 2.48. IR (DRIFTS, KCl): ν_{CO} , 1967 and 1952 cm^{-1} ; ν_{OCO} , 1499 and 1183 cm^{-1} . 1H NMR (CD_3CN): δ 10.33 (m, 1); 9.51 (m, 1); 9.26 (m, 1); 8.77 (m, 1); 8.43–6.66 (m, 28). ^{13}C NMR (CD_3CN): δ 204.22, 203.82, 202.42 (CO and CO_2); 158.28–123.69 (43 resonances due to 44 carbons).

Reactions of $[Ru(phen)_2(CO)(CHO)](PF_6)$ (8) in CH_3OH . (a) Compound **8** (0.10 g, 0.15 mmol) was placed in a Schlenk flask under N_2 . Then CH_3OH (50 mL) was added, and the mixture was stirred for 7 h under laboratory fluorescent lights. Solvent was removed under vacuum, and the residue was dissolved in CH_3CN/CH_3OH (5:1, 10 mL). Diethyl ether was diffused over this solution to yield **7** as a yellow crystalline solid (0.09 g, 81% yield). When this reaction was attempted in the dark, under nitrogen, no reaction was observed.

(b) An additional reaction of **8** was conducted as in method a, but the mixture was irradiated beside a 450 W Hg arc lamp contained in a water-cooled Pyrex immersion well. It was complete after 20 min and afforded ester **7** as the only product.

Reaction of $[Ru(bpy)_2(CO)(CHO)](PF_6)$ (1) with $[Ru(phen)_2(CO)(COOH)](PF_6)$ (6). $[Ru(bpy)_2(CO)(CHO)](PF_6)$ (0.054 g, 0.09 mmol) and $[Ru(phen)_2(CO)(COOH)](PF_6)$ (0.06 g, 0.09 mmol) were combined in a flask under O_2 . DME (20 mL) and H_2O (1 mL) were added and the mixture was stirred for 1 h, and then solvent was removed under vacuum. 1H NMR (CD_3CN) analysis showed that the product mixture consisted of unreacted *cis*- $[Ru(phen)_2(CO)(COOH)](PF_6)$, *cis,cis*- $[Ru(bpy)_2(CO)(CO_2)Ru(bpy)_2(CO)](PF_6)_2$ (**4**), and small amount of *cis,cis*- $[Ru(phen)_2(CO)(CO_2)Ru(bpy)_2(CO)](PF_6)_2$ (**11**); no unreacted formyl complex remained, and there was no evidence for acid **3**.

X-ray Crystallographic Analyses. A yellow crystal of **6**, $[Ru(phen)_2(CO)(COOH)](PF_6) \cdot 3/4(C_2H_5)_2O$, grown by diffusing diethyl ether over a CH_3CN solution of the compound, was mounted on a glass fiber with epoxy cement. Data were collected on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator. Crystal data, data collection, and refinement parameters are listed in Table 1. The structure was solved by direct methods. Three-quarter equivalent of diethyl ether was found in the lattice. The PF_6^- anion is disordered; each fluorine atom was located at two positions. One was refined with anisotropic thermal parameters at 66.7% occupancy; the other was refined with isotropic thermal parameters at 33.3% occupancy. All other non-hydrogen atoms were refined with anisotropic thermal parameters. An empirical correction for absorption (ψ -scans) was applied. The hydrogen atoms were located by difference maps and included as fixed contributions ($B = 1.2B$ of attached atom). The final R index of 0.043 with $R_w = 0.055$ was obtained for 439 variables. All calculations were performed using the teXsan package (Molecular Structure Corporation).¹³ An orange crystal of **11**, $[Ru(phen)_2(CO)(CO_2)Ru(bpy)_2CO](PF_6)_2 \cdot 2.08CH_3CN \cdot 0.4C_6H_6$, was grown by slow diffusion of benzene into an acetonitrile solution of the title compound. The crystal was mounted on a glass fiber with epoxy cement. Data were collected at a temperature of –80 °C on an Enraf-Nonius CAD-4 diffractometer using the ω - 2θ scan technique. Crystallographic data are summarized in Table 1. The structure, solved by direct methods (SIR92), contains no disorder in the cation; however, there are numerous sites of disorder involving the two isotropically refined hexafluorophosphate anions and several fractional solvates (see further comments in the Supporting Information). All non-hydrogen atoms of the cation were refined with anisotropic thermal parameters. An empirical correction for absorption (ψ -scans) was applied. The hydrogen atoms were located by difference maps and included

(13) Gibson, D. H.; Ahmed, F. U.; Phillips, K. R. *J. Organomet. Chem.* **1981**, *218*, 325.

as fixed contributions ($B = 1.2 \times$ attached atom). The discrepancy indices are $R = 0.069$ and $R_w = 0.078$ for 7628 unique, observed reflections with $I > 3\sigma(I)$ and 758 parameters. All calculations were performed using the teXsan package (Molecular Structure Corporation).¹⁴

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(14) *teXsan*. Single-Crystal Structure Analysis Software, Version 1.6; Molecular Structure Corp.: The Woodlands, TX 77381, 1993.

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Supporting Information Available: Tables of bond lengths, bond distances, positional and isotropic thermal parameters, and general displacement parameters for **6** and **11** are provided (36 pages). Ordering information is given on any current masthead page.

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