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Selective Diphosphine Ligand Chelation and π Bond Coordination in $CoRu(CO)_7(\mu\text{-}PPh_2)$: Kinetics and X-ray Structure of $CoRu(CO)_4(\mu\text{-bma})(\mu\text{-}PPh_2)$

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Thermolysis of $CoRu(CO)_7(\mu\text{-}PPh_2)$ (**1**) in refluxing 1,2-dichloroethane in the presence of the diphosphine ligands 2,3-bis(diphenylphosphino)maleic anhydride (bma) and 4,5-bis(diphenylphosphino)-4-cyclopenten-1,3-dione (bpcd) furnishes the new mixed-metal complexes $CoRu(CO)_4(\mu\text{-P−P})(\mu\text{-}PPh_2)$ [where P−P = bma (**3a**), bpcd (**3b**)] along with trace amounts of the known complex $CoRu(CO)_6(PPh_3)(\mu\text{-}PPh_2)$ (**4**). The requisite pentacarbonyl intermediates $CoRu(CO)_5(\mu\text{-P−P})(\mu\text{-}PPh_2)$ [where P−P = bma (**2a**), bpcd (**2b**)] have been prepared by separate routes (mild thermolysis and Me_3NO activation) and studied for their conversion to $CoRu(CO)_4(\mu\text{-P−P})(\mu\text{-}PPh_2)$. The penta- and tetracarbonyl complexes have been isolated and fully characterized in solution by IR and NMR spectroscopy. The kinetics for the conversion of **2a** → **3a** and of **2b** → **3b** were measured by IR spectroscopy in chlorobenzene solvent. On the basis of the first-order rate constants, CO inhibition, and the activation parameters (**2a** → **3a**, $\Delta H^\ddagger = 29.2 \pm 1.4$ kcal mol^{-1} and $\Delta S^\ddagger = 8.2 \pm 3.8$ eu; **2b** → **3b**, $\Delta H^\ddagger = 27.7 \pm 0.6$ kcal mol^{-1} and $\Delta S^\ddagger = 1.4 \pm 1.6$ eu), a mechanism involving dissociative CO loss as the rate-limiting step is proposed. The solid-state structure of $CoRu(CO)_4(\mu\text{-bma})(\mu\text{-}PPh_2)$ (**3a**), as determined by X-ray crystallography, reveals that the two PPh_2 groups are bound to the ruthenium center while the maleic anhydride π bond is coordinated to the cobalt atom.

Introduction

The reactivity and physical properties of mononuclear transition-metal complexes containing the diphosphine ligands 2,3-bis(diphenylphosphino)maleic anhydride (bma) and 4,5-bis(diphenylphosphino)-4-cyclopenten-1,3-dione (bpcd) have been extensively studied over the last two decades.[1,2] The presence of a readily accessible π^* LUMO on the unsaturated diphosphine ligand has been shown to be instrumental in stabilizing electron counts in excess of 18 electrons. The chemistry of such $18 + \delta$ complexes has been thoroughly investigated by Tyler and Rieger.[3−6]

Our initial interest in the bma and bpcd ligand systems stemmed from the absence of any reported chemistry of these ligands with polynuclear metal complexes. In earlier reports we provided evidence showing the ease by which these ligands undergo P−C bond cleavage reactions when tethered to dimetal and trimetal clusters (eq 1).[7,8,9] While far from unequivocal at this point, it is our thinking that any type of diphosphine ligand activation occurs after the coordination of the π bond of the carbocyclic ring to a metal center(s). The driving force in our P−C bond activations is presumably facilitated by the electron-withdrawing behavior of the ancillary maleic anhydride or dione rings.[10]

While our previous studies have involved homometallic systems, we wished to extend our substitution and reactivity studies using the bma and bpcd ligands with heterometallic complexes. This would allow us the opportunity to explore any site selectivity that might be associated with the initial coordination and subsequent activation of the diphosphine ligand. Herein

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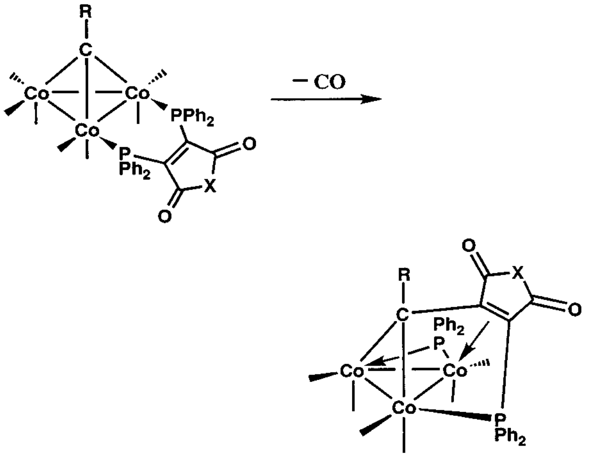

(1)

R = Ph, Fc; X = O, CH$_2$

we report our data on the substitution chemistry and structural characterization of the products formed from the reaction between the ligands bma and bpcd and the phosphido-bridged complex CoRu(CO)$_7$(μ-PPh$_2$). This particular heterometallic dimer was chosen, in part, due to the well-documented behavior of CoRu(CO)$_7$(μ-PPh$_2$) toward a variety of two-electron donor ligands,[11] coupled with the possibility of the ruthenium center in promoting the oxidative cleavage of a P−Ph bond as opposed to the cleavage of the P−C bond belonging to the redox-active carbocyclic ring. This latter bond activation process has been, to date, the predominant mode of ligand activation found by us.

Experimental Section

General Methods. (p-cymene)RuCl$_2$(PPh$_2$H) used in the synthesis of CoRu(CO)$_7$(μ-PPh$_2$)[12] was prepared from hydrated RuCl$_3$ according to the published procedures.[13] The chemicals Co$_2$(CO)$_8$ and α-phellandrene were purchased from Strem Chemical Co. and Lancaster Chemicals, respectively, and were used as received. The ligands bma and bpcd were prepared according to published procedures.[1a,5b] All solvents were distilled from an appropriate drying agent under argon and were transferred to Schlenk storage vessels using inert-atmosphere techniques.[14] All combustion analyses were performed by Atlantic Microlabs, Norcross, GA.

Infrared spectra were recorded on a Nicolet 20 SXB FT-IR spectrometer in 0.1 mm NaCl cells, using PC control and OMNIC software. The ^{1}H NMR and ^{31}P spectra were recorded at 300 and 121 MHz, respectively, on a Varian 300-VXR spectrometer. Positive ^{31}P chemical shifts are to low field of external H$_3$PO$_4$, whose chemical shift is taken to have $\delta = 0$.

Synthesis of CoRu(CO)$_5$(μ-bma)(μ-PPh$_2$) (2a). To a Schlenk tube containing 0.40 g (0.74 mmol) of CoRu(CO)$_7$(μ-PPh$_2$) and 0.40 g (0.86 mmol) of bma was added 35 mL of 1,2-dichloroethane by syringe, after which the solution was heated overnight at 65−70 °C. IR analysis at this point showed that the major product was CoRu(CO)$_5$(μ-bma)(μ-PPh$_2$) (~80%). Since **2a** decomposes extensively upon chromatography over silica gel, the desired product was isolated by an extraction procedure. The solvent was removed under vacuum, and the residue was dissolved in a minimum amount of CH$_2$Cl$_2$, followed by treatment with 100 mL of petroleum ether. This initial precipitate was separated from the mother liquor by filtration and discarded, as it contained unreacted **1** and minor amounts of **2a** and **3a**. The CH$_2$Cl$_2$/petroleum ether solution was concentrated to 20 mL and then cooled to 0 °C for 0.5−1.0 h. The resulting precipitate was collected and dried under vacuum. Analytically pure CoRu(CO)$_5$(μ-bma)(μ-PPh$_2$) was obtained after recrystallization from a mixture of CH$_2$Cl$_2$/hexane (2:8). Yield: 0.45 g (64%). IR (CH$_2$Cl$_2$): ν(CO) 2043 (w), 1993 (vs), 1933 (m), 1844 (w, asymm bma C=O), 1776 (m, symm bma C=O) cm^{-1}. ^{1}H NMR (CDCl$_3$, 298 K): δ 7.15−8.00 (m, phenyl groups). ^{31}P NMR (THF, 273 K): δ 171.4 (d, phosphido, $J_{\text{P-P}} = 124$ Hz), 58.0 (d, PPh$_2$, $J_{\text{P-P}} = 124$ Hz), 54.5 (s, PPh$_2$). Anal. Calcd (found) for C$_{45}$H$_{30}$CoO$_8$P$_3$Ru: C, 56.80 (56.76); H 3.18 (3.21).

Synthesis of CoRu(CO)$_5$(μ-bpcd)(μ-PPh$_2$) (2b). A 0.40 g (0.74 mmol) amount of CoRu(CO)$_7$(μ-PPh$_2$) and 0.41 g (0.80 mmol) of bpcd were charged to a large Schlenk flask under argon, after which 35 mL of 1,2-dichloroethane was added. The solution was stirred overnight, maintaining the reaction temperature from 65 to 70 °C. Both IR and TLC analyses revealed that **2b** was present as the major product (>85%). The solvent was removed under vacuum, and the crude material was purified by chromatography over silica gel using CH$_2$Cl$_2$/petroleum ether (1:1) as the eluent. Recrystallization of **2b** from CH$_2$Cl$_2$/hexane (1:1) afforded 0.45 g of red-brown **2b** (yield: 64%). IR (CH$_2$Cl$_2$): ν(CO) 2047 (w), 1987 (vs), 1925 (m), 1750 (w, asymm bpcd C=O), 1719 (m, symm bpcd C=O) cm^{-1}. ^{1}H NMR (CDCl$_3$, 298 K): δ 6.70−7.80 (m, phenyl groups), 3.63 (s, 2H, methylene group). ^{31}P NMR (THF, 273 K): δ 167.2 (d, phosphido, $J_{\text{P-P}} = 124$ Hz), 56.5 (d, PPh$_2$, $J_{\text{P-P}} = 124$ Hz), 51.2 (s, PPh$_2$). Anal. Calcd (found) for C$_{46}$H$_{32}$CoO$_8$P$_3$Ru: C, 58.20 (57.93); H 3.40 (3.45).

Synthesis of CoRu(CO)$_4$(μ-bma)(μ-PPh$_2$) (3a). A 1,2-dichloroethane solution containing 0.20 g (0.37 mmol) of CoRu(CO)$_7$(μ-PPh$_2$) and 0.18 g (0.39 mmol) of bma was heated overnight at reflux under an argon atmosphere. The solution was cooled to room temperature and examined by IR and TLC analyses, both of which revealed the presence of two new compounds, in addition to some unreacted starting material. The solvent was removed under vacuum, and purification was effected by column chromatography over silica gel. Unreacted **1** (<5%) was obtained as the first eluted band when an 8:2 mixture of petroleum ether/CH$_2$Cl$_2$ was employed as the eluent, while changing the solvent system to a 1:1 mixture of petroleum ether/CH$_2$Cl$_2$ afforded a minor amount of the known compound CoRu(CO)$_6$(PPh$_3$)(μ-PPh$_2$) (0.05 g) (yield: 17%). The tetracarbonyl complex **3a** was obtained from the column as the third band when CH$_2$Cl$_2$ was used as the eluting solvent. The analytical sample and single crystals suitable for X-ray diffraction analysis were from a CH$_2$Cl$_2$ solution of **3a** that had been layered with heptane. Yield: 0.17 g (48%). IR (CH$_2$Cl$_2$): ν(CO) 2043 (m), 2017 (vs), 1993 (s), 1953 (s), 1789 (m, asymm bma C=O), 1738 (m, symm bma C=O) cm^{-1}. ^{1}H NMR (CDCl$_3$, 298 K): δ 6.90−7.85 (m, phenyl groups). ^{31}P NMR (THF, 273 K): δ 168.0 (s, phosphido), 31.2 (s, PPh$_2$), 30.6 (s, PPh$_2$). Anal. Calcd (found) for C$_{44}$H$_{30}$CoO$_7$P$_3$Ru: C, 57.16 (57.06); H 3.25 (3.33).

Synthesis of CoRu(CO)$_4$(μ-bpcd)(μ-PPh$_2$) (3b). The procedure used to synthesize **3b** was identical to that used with **3a** and will not be described in detail. The compound was isolated by chromatography, which yielded a trace amount of starting material (<2% of **1**) and 0.04 g of CoRu(CO)$_6$(PPh$_3$)(μ-PPh$_2$) (yield: 14%). CoRu(CO)$_4$(μ-bpcd)(μ-PPh$_2$) was isolated as the third eluted band from the column using CH$_2$Cl$_2$ and was recrystallized from a 1:1 mixture of CH$_2$Cl$_2$/heptane to give 0.20 g (yield: 59%). IR (CH$_2$Cl$_2$): ν(CO) 2035 (s), 2009 (vs), 1981 (s), 1948 (s), 1708 (m, asymm bpcd C=O), 1675 (m, symm bpcd C=O) cm^{-1}. ^{1}H NMR (CDCl$_3$, 298 K): δ 6.70−7.80 (m, phenyl groups), 3.66 (2H, AB quartet, $J_{\text{H-H}} = 22$ Hz). ^{31}P NMR (THF, 273 K): δ 169.4 (s, phosphido), 33.1 (s, PPh$_2$), 32.8 (s, PPh$_2$). Anal. Calcd (found) for C$_{45}$H$_{32}$CoO$_8$P$_3$Ru: C, 58.62 (58.33); H 3.50 (3.95).

X-ray Diffraction Structure of CoRu(CO)$_4$(μ-bma)(μ-PPh$_2$) (3a). Single crystals of CoRu(CO)$_4$(μ-bma)(μ-PPh$_2$) suitable for X-ray diffraction analysis were grown from a CH$_2$Cl$_2$ solution containing CoRu(CO)$_4$(μ-bma)(μ-PPh$_2$) that had been layered with heptane. A

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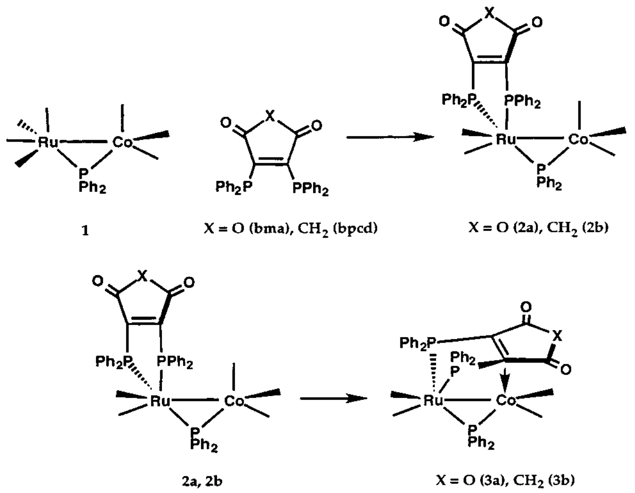
Scheme 1



black crystal of dimensions 0.07 × 0.09 × 0.44 mm^3 was selected and sealed inside a Lindemann capillary tube, followed by mounting on the goniometer of an Enraf-Nonius CAD-4 diffractometer. The Mo Kα radiation used was monochromatized by a crystal of graphite. Cell constants were obtained from a least-squares refinement of 25 reflections with $2\theta > 30°$. Intensity data in the range of $2.0 < \theta < 44.0°$ were collected at 298 K using the ω-scan technique in the variable-scan speed mode. The crystal structure was solved by using SHELX-86, and all of the non-hydrogen atoms were located with difference Fourier maps and refined by using full-matrix least-squares methods. Excluding the carbon atoms, all non-hydrogen atoms were refined anisotropically. Refinement converged at $R = 0.0633$ and $R_w = 0.0768$ for 2320 unique reflections with $I > 3\sigma(I)$.

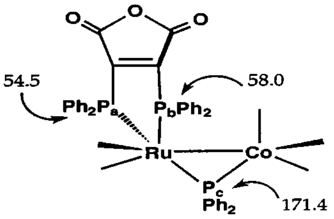
Results and Discussion

Synthesis and Spectral Characterization. The reaction between CoRu(CO)$_7$(μ-PPh$_2$) (**1**) and the diphosphine ligands bma and bpcd proceeds readily over the temperature range of 65−70 °C in 1,2-dichloroethane to afford the disubstituted complexes CoRu(CO)$_5$(μ-bma)(μ-PPh$_2$) (**2a**) and CoRu(CO)$_5$(μ-bpcd)(μ-PPh$_2$) (**2b**) as the major product in each reaction. The minor byproducts found were unreacted **1** and small amounts of **3a,b** (vide infra). Scheme 1 depicts the course of reactivity between 1 and the diphosphine ligands bma and bpcd. In compounds **2a,b** the diphosphine ligands are bound at the ruthenium center in a chelating fashion as verified by ^{31}P NMR spectroscopy. The site of bma and bpcd ligand substitution in compounds **2a,b** is analogous to the reaction of CoRu(CO)$_7$(μ-PPh$_2$) with dppm.[11c,e] The only major difference between our results and those of Dixneuf and Carty is the absence of any sign of a bridged-bma or -bpcd isomer. In the case of the reaction with dppm, both the chelating and bridging isomers of CoRu(CO)$_5$(dppm)(μ-PPh$_2$) were observed depending upon the reaction conditions.

Compound CoRu(CO)$_5$(μ-bpcd)(μ-PPh$_2$) (**2b**) could be obtained free of CoRu(CO)$_4$(μ-bpcd)(μ-PPh$_2$) (**3b**) when the reaction between CoRu(CO)$_7$(μ-PPh$_2$) and bpcd was carried out at room temperature using the oxidative−decarbonylation reagent Me$_3$NO.[15] The ligand substitution was rapid and the only product found was **2b**. Treatment of CoRu(CO)$_7$(μ-PPh$_2$) and bma with Me$_3$NO also led to an immediate reaction and the production of **2a**, as ascertained by IR analysis; however, under these conditions compound **2a** decomposed almost as quickly as it was formed presumably by attack of the liberated Me$_3$N on the anhydride ring of the ligand. Given the higher yields of **2a** by the thermolysis route, the reaction using Me$_3$NO was abandoned.

Both **2a** and **2b** were subsequently isolated and characterized in solution by IR and NMR spectroscopy. Attempted chromatography of **2a** over silica gel led to extensive decomposition, as observed by us in other bma-substituted complexes.[16] Here the pendant anhydride ring of the ligand is readily hydrolyzed on the adsorbent. Changing the chromatographic support to either alumina or Florisil or carrying out the separation at low-temperature did little to improve the situation. Accordingly, compound **2a** was isolated via an extraction/recrystallization sequence, as outlined in the Experimental Section. Compound **2b** with its 1,3-dione ring is stable to silica gel and was purified by column chromatography.

Both **2a** and **2b** exhibit three terminal carbonyl bands [2043 (w), 1993 (vs), 1933 (m) cm^{-1} for **2a**; 2047 (w), 1987 (vs), 1925 (m) cm^{-1} for **2b**] and two ν(CO) bands that are assigned to the anhydride ring and the 1,3-dione ring of **2a,b**, respectively. The ^{31}P{^{1}H} NMR spectrum of CoRu(CO)$_5$(μ-bma)(μ-PPh$_2$) (**2a**) at 273 K reveals the presence of the expected low-field μ-phosphido moiety at δ 171.4.[17,18] Coupling of the μ-PPh$_2$ ligand to a trans PPh$_2$ group associated with the bma ligand leads to the observed phosphido doublet with $^2J_{P-P} = 124$ Hz. The bma ligand exhibits two inequivalent PPh$_2$ groups because of their differing orientations relative to the bridging phosphido moiety, as depicted in the structure of CoRu(CO)$_5$(μ-bma)(μ-PPh$_2$) shown below. Assuming a distorted octahedral geometry at the ruthenium center, the PPh$_2$ singlet found at δ 54.5 and the doublet resonance at δ 58.0 are assigned to P$_a$ and P$_b$, respectively, on the basis of their cis and trans relationship to the μ-PPh$_2$ group. The bpcd-substituted complex **2b** shows an analogous pattern for the ^{31}P chemical shifts and indicates that compounds **2a,b** possess identical structures.



Thermolysis of CoRu(CO)$_7$(μ-PPh$_2$) with added bma or bpcd in refluxing 1,2-dichloroethane affords the new compounds CoRu(CO)$_4$(μ-bma)(μ-PPh$_2$) (**3a**) and CoRu(CO)$_4$(μ-bpcd)(μ-PPh$_2$) (**3b**) in moderate to high yields. Besides the tetracarbonyl compounds, we observed the presence of the pentacarbonyl precursors **2a,b** (for the appropriate ligand), in addition to production of the known PPh$_3$-substituted compound CoRu(CO)$_6$(PPh$_3$)(μ-PPh$_2$) (**4**).[11c,19]Compound **4** was routinely isolated in yields of ca. 15% and was unequivocally characterized in solution by IR and ^{31}P NMR spectroscopy and by comparison to independently prepared samples of CoRu(CO)$_6$(PPh$_3$)(μ-

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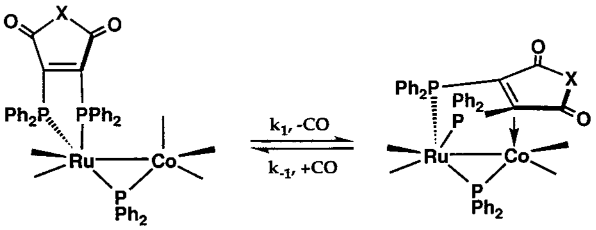
Table 1. Experimental Rate Constants for the Transformation of **2a** → **3a** and **2b** → **3b**[a]

entry no.	T, °C	10^4k_{obsd}, s^{-1}
	2a → **3a**	
1	77.2	2.37 ± 0.11
2	83.0	7.30 ± 0.68
3	88.0	10.14 ± 0.59
4	88.0	0.32 ± 0.02[b]
5	93.2	20.35 ± 1.41
6	98.1	30.29 ± 0.91
	2b → **3b**	
7	83.3	1.53 ± 0.05
8	88.3	2.60 ± 0.10
9	88.3	1.66 ± 0.07[b]
10	93.3	4.04 ± 0.24
11	98.2	8.35 ± 0.34
12	103.3	12.07 ± 0.49

[a] From ca. 10^{-2} M CoRu(CO)$_5$(μ-bma)(μ-PPh$_2$) (**2a**) and CoRu(CO)$_5$(μ-bpcd)(μ-PPh$_2$) (**2b**) in chlorobenzene solvent by following the disappearance of the ν(CO) band at 1775 and 1718 cm^{-1}, respectively. [b] In the presence of 1 atm of CO.

PPh$_2$). The path by which CoRu(CO)$_6$(PPh$_3$)(μ-PPh$_2$) arises is not known, but it is clear that a formal transfer of a phenyl group to a PPh$_2$ ligand has taken place. The source of the PPh$_3$ group in **4** could be either the phosphido moiety or a PPh$_2$ group from the bma or bpcd ligands.

Proof of the involvement of **2a** → **3a** and **2b** → **3b** was established by conducting independent experiments using isolated samples of **2a,b** at temperatures in excess of 75 °C, as shown in eq 2. The expected tetracarbonyl complex was formed in each as the major product, along with small amounts of CoRu(CO)$_6$(PPh$_3$)(μ-PPh$_2$) (**4**) (vide supra).



(2)

2a, 2b

X = O (3a), CH$_2$ (3b)

The identities of **3a,b** were ascertained by spectroscopic methods and X-ray diffraction analysis in the case of CoRu(CO)$_4$(μ-bma)(μ-PPh$_2$) (**3a**). Coordination of the π bond to the cobalt center causes enough of an angular distortion between the phosphido group and P$_b$ so that all three phosphorus centers appear as singlets in the ^{31}P NMR spectrum of **3a,b**. This fact is also supported by the X-ray data on **3a** (vide infra). In the case of **3b**, the methylene group in the dione ring appears as an AB quartet centered at δ 3.66 due to the diastereotopic nature of these protons.

The kinetics for the conversion of **2a** → **3a** and **2b** → **3b** were measured in order to establish whether product formation proceeded via a dissociative CO loss scheme or an associative attack of the ancillary π bond on the cobalt center, coupled with simultaneous CO expulsion. Each reaction was studied by IR spectroscopy in chlorobenzene solution over the temperature range of ca. 77−103 °C. All reactions followed first-order kinetics over a period of at least 3 half-lives, as evidenced by linear plots of ln($A_t - A_\infty$) vs time. The slopes of such plots afforded the reported first-order rate constants given in Table 1. The quoted rate constants were obtained by monitoring the decrease in the absorbance of the bma and bpcd bands at 1775 and 1718 cm^{-1}, respectively. The effect of added CO on the reaction of **2a** → **3b** and **2b** → **3b** is shown by entries 4 and 9, respectively, in Table 1. In the case of the reaction of **2a** → **3b** the presence of 1 atm of CO leads to a significant drop in the reaction rate by a factor of ca. 32. While the effect of added CO on the reaction of **2b** → **3b** is less dramatic than in the bma derivative, a rate retardation of ca. 1.6 was found for the conversion of **2b** to **3b**. The activation parameters for **2a** → **3a** ($\Delta H^\ddagger = 29.2 \pm 1.4$ kcal mol^{-1} and $\Delta S^\ddagger = 8.2 \pm 3.8$ eu) and **2b** → **3b** ($\Delta H^\ddagger = 27.7 \pm 0.6$ kcal mol^{-1} and $\Delta S^\ddagger = 1.4 \pm 1.6$ eu),[20] coupled with the rate retardation in the presence of added CO, support a unimolecular process involving CO loss as the rate-limiting step and which obeys the following general rate law:[21,22]

$$\text{rate} = \frac{k_1k_2[\mathrm{RuCo(CO)_5(P{-}P)(PPh_2)}]}{k_{-1}[\mathrm{CO}] + k_2}$$

Finally, the presence of minor amounts of CoRu(CO)$_6$(PPh$_3$)(μ-PPh$_2$) was verified in all kinetic experiments by TLC analysis. What may be concluded at this time is that the observed byproduct **4** does not originate from the chelated diphosphine compounds CoRu(CO)$_4$(μ-bma)(μ-PPh$_2$) (**2b**) and CoRu(CO)$_4$(μ-bpcd)(μ-PPh$_2$) (**3b**). No evidence (TLC and IR) was obtained for the formation of CoRu(CO)$_6$(PPh$_3$)(μ-PPh$_2$) when independent theromlysis reactions were carried out with isolated samples of **2b** and **3b** at 85 °C overnight. Under these conditions only the slow decomposition of **2b** and **3b** was observed.

X-ray Diffraction Data. The structure of CoRu(CO)$_4$(μ-bma)(μ-PPh$_2$) (**3a**) was determined by single-crystal X-ray diffraction analysis in order to establish the coordination mode exhibited by the ancillary bma ligand. Single crystals of CoRu(CO)$_4$(μ-bma)(μ-PPh$_2$) were grown (see Experimental Section for the exact conditions), and CoRu(CO)$_4$(μ-bma)(μ-PPh$_2$) was found to exist in the unit cell with no unusually short inter- or intramolecular contacts. The X-ray data collection and processing parameters for CoRu(CO)$_4$(μ-bma)(μ-PPh$_2$) are given in Table 2 with selected bond distances and angles listed in Table 3.

The ORTEP diagram presented in Figure 1 shows the molecular structure of CoRu(CO)$_4$(μ-bma)(μ-PPh$_2$) and establishes the chelation of both of the maleic anhydride PPh$_2$ groups to ruthenium center and coordination of the maleic anhydride π bond to the cobalt atom. Both the ruthenium and cobalt centers in **3a** may be described as having distorted octahedral geometries, assuming that the cobalt-bound π bond is counted as a two-coordinate ligand. The Ru−Co bond length of 2.674(3) Å is consistent with its single-bond designation[12,23] and is only

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(20) For examples of rate-limiting dissociative CO loss in mono- and polynuclear compounds exhibiting large, positive values of $\Delta H^\ddagger$ (25−30 kcal/mol) and low, positive values of $\Delta S^\ddagger$ (0−10 eu), see: (a) Covey, W. D.; Brown, T. L. *Inorg. Chem.* **1973**, *12*, 2820. (b) Sonnenberger, D.; Atwood, J. D. *Inorg. Chem.* **1981**, *20*, 3243. (c) Payne, M. W.; Leussing, D. L.; Shore, S. G. *J. Am. Chem. Soc.* **1987**, *109*, 616.

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(22) The rate law in the absence of added CO ($k_2 > k_{-1}$[CO]) reduces to the simple first-order expression: rate = k_1[RuCo(CO)$_5$(P−P)(PPh$_2$)].

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Table 2. X-ray Crystallographic Data and Processing Parameters for $CoRu(CO)_4(\mu\text{-bma})(\mu\text{-}PPh_2)$ (**3a**)

space group	$P2_1/c$, monoclinic
a, Å	21.318(3)
b, Å	9.3693(9)
c, Å	20.352(2)
β, deg	91.88(1)
V, Å^3	4062.8(8)
mol formula	$C_{44}H_{30}CoO_7P_3Ru$
fw	923.65
formula units/cell (Z)	4
ρ, g·cm^{-3}	1.510
λ(Mo Kα), Å	0.710 73
collcn range, deg	$2.0 \leq \theta \leq 44.0$
tot. no. of data collcd	5446
no. of indep data, $I > 3\sigma(I)$	2320
R[a]	0.0633
R_w[b]	0.0768
GOF[c]	0.82
weights	$[0.04F^2 + (\sigma(F))^2]^{-1}$

[a] $R = \Sigma||F_o| - |F_c||\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. [c] $GOF = \Sigma w(|F_o| - |F_c|^2/N - NP$.

Table 3. Selected Bond Distances (Å) and Angles (deg) in $CoRu(CO)_4(\mu\text{-bma})(\mu\text{-}PPh_2)$ (**3a**)[a]

Bond Distances			
Ru−Co	2.674(3)	Ru−P(1)	2.354(5)
Ru−P(2)	2.366(5)	Ru−P(3)	2.318(5)
Co−P(3)	2.229(5)	Co−C(11)	2.05(2)
Co−C(15)	2.04(2)	P(1)−C(11)	1.81(2)
P(2)−C(15)	1.81(2)	O(12)−C(12)	1.19(2)
O(13)−C(12)	1.37(2)	O(13)−C(14)	1.39(2)
O(14)−C(14)	1.19(2)	C(11)−C(12)	1.47(2)
C(11)−C(15)	1.45(2)	C(14)−C(15)	1.47(3)

Bond Angles			
Co−Ru−P(1)	70.3(1)	Co−Ru−P(2)	75.5(1)
Co−Ru−P(3)	52.5(1)	Co−Ru−C(1)	167.4(6)
Co−Ru−C(2)	96.2(5)	P(1)−Ru−P(2)	80.4(2)
P(1)−Ru−P(3)	122.5(2)	P(1)−Ru−C(1)	116.0(6)
P(1)−Ru−C(2)	90.3(5)	P(2)−Ru−P(3)	89.4(2)
P(2)−Ru−C(1)	94.3(6)	P(2)−Ru−C(2)	169.2(5)
P(3)−Ru−C(1)	121.2(6)	P(3)−Ru−C(2)	90.9(5)
C(1)−Ru−C(2)	94.8(8)	Ru−Co−C(3)	99.3(6)
Ru−Co−C(4)	157.0(6)	Ru−Co−C(11)	80.3(4)
Ru−Co−C(15)	78.2(5)	P(3)−Co−C(3)	97.4(6)
P(3)−Co−C(4)	103.8(7)	C(11)−Co−C(15)	41.3(6)
Ru−P(3)−Co	72.0(1)		

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

slightly shorter than the 2.7858(7) Å (chelating) and 2.7580(9) Å (bridging) Ru−Co bond distances reported in the isomeric $RuCo(CO)_5(dppm)(\mu\text{-}PPh_2)$ complexes.[11e] The Ru−P(1) and Ru−P(2) distances of 2.354(5) and 2.366(5) Å are not significantly different unlike the two metal−phosphorus bond distances associated with the phosphido moiety. The Ru−P(3) distance of 2.318(5) and the Co−P(3) bond distance of 2.229(5) Å show the asymmetric bonding of the three-electron donating PPh_2 group to the Ru−Co vector, a feature that has been observed in other phosphido-bridged metal−metal bonds.[24]

The near trans diaxial arrangement of P(1) and the phosphido group P(3) is clearly seen in the ORTEP diagram, and the loss of P−P coupling in the ^{31}P NMR spectrum of **3a** (vide supra) is reflected by the P(1)−Ru−P(3) bond angle whose value is 122.5(2)°. This deviation from an idealized bond angle of 180° is due to the tethering of the maleic anhydride moiety to the cobalt atom in going from **2a** to **3a**. Here the substantial diminution in the P(1)−Ru−P(3) bond angle from the idealized 180° bond angle at an octahedral center approaches the cis relationship exhibited by P(2)−Ru−P(3) [89.4(2)°] and P(1)−Ru−P(2) [80.4(2)°] and is expected to show a negligible or zero phosphorus−phosphorus coupling.[25] The coordination of the maleic anhydride moiety to the cobalt center leads to a slight elongation of the carbon−carbon π bond. The C(11)−C(15) distance of 1.45(2) Å is ca. 0.11 Å longer than bma-substituted complexes having a noncomplexed π bond.[1b,7,8] The remaining bond distances and angles are unexceptional and require no comment.

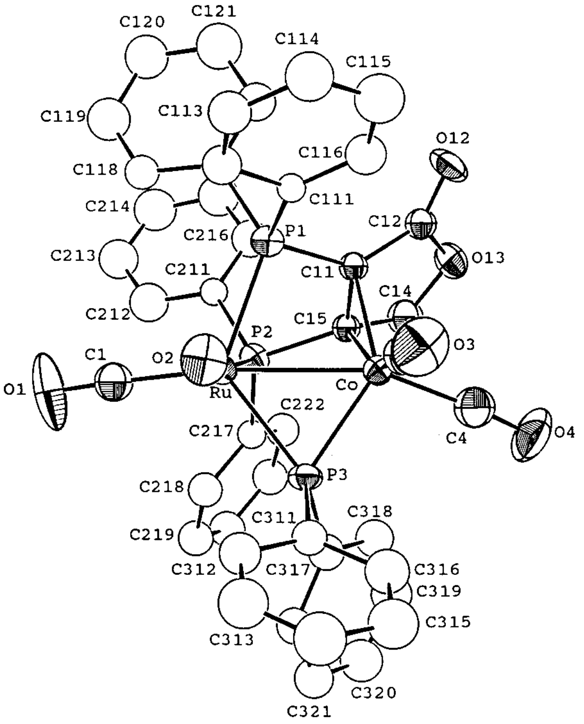

Figure 1. ORTEP drawing of the non-hydrogen atoms of $CoRu(CO)_4(\mu\text{-bma})(\mu\text{-}PPh_2)$ (**3a**) showing the thermal ellipsoids at the 50% probability level.

Conclusions

The bidentate ligands bma and bpcd react with $CoRu(CO)_7(\mu\text{-}PPh_2)$ under thermolysis conditions and Me_3NO activation initially at the ruthenium center to afford $CoRu(CO)_5$(diphosphine)(μ-PPh_2). Thermolysis of these pentacarbonyl complexes leads to the coordination of the π bond of the redox-active diphosphine ligand to the cobalt center. The activation parameters and CO inhibition found for the reaction of **2a** → **3b** and **2b** → **3b** support a rate-limiting step involving dissociative CO loss, followed by a rapid coordination of the maleic anhydride and 1,3-dione π bonds.

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Supporting Information Available: Tables and figures of X-ray crystallographic files that are not available in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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