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# Reaction of Acetylene with a Diruthenium(0) Complex: Easy Interconversion of Dimetallacyclobutene and Dimetallacyclopentenone Complexes

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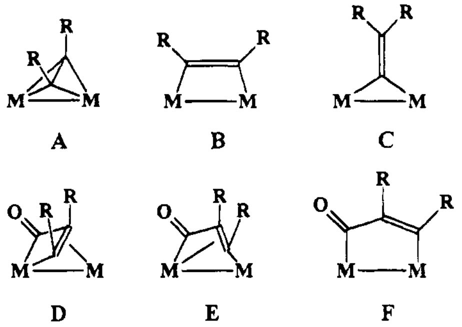
$[Ru_2(\mu\text{-}CO)(CO)_4(\mu\text{-dppm})_2]$, **1**, reacts with excess HC≡CH to give the dimetallacyclobutene $[Ru_2(\mu\text{-}CH{=}CH)(CO)_4(\mu\text{-dppm})_2]$, **2**, and CO as the products of kinetic control. If the reaction is carried out in a closed flask, a further reaction occurs by addition of CO to **2** to give the dimetallacyclopentenone $[Ru_2(\mu\text{-}CH{=}CHCO)(CO)_4(\mu\text{-dppm})_2]$, **3**. Complex **3** decomposes on heating to give **2** and CO. The nature of these reactions has been elucidated by using $^{13}C$ labeled reagents and monitoring the reactions by NMR. Complex **3** has been characterized by an X-ray structure determination [$\mathbf{3}{\cdot}2CH_2Cl_2$, monoclinic, space group *Cc*, $a = 19.500(2)$ Å, $b = 17.146(3)$ Å, $c = 17.349(2)$ Å, $\beta = 101.21(1)°$, $V = 5690(1)$ Å$^3$, $Z = 4$, $R = 0.0499$, $R_2 = 0.0520$].

## Introduction

The chemistry of alkynes with transition metal complexes continues to be of great interest, driven by academic interest in the rich organometallic chemistry and by potential applications in catalysis and the formation of materials with unusual properties.[1–3] Many catalytic reactions involve coupling of alkynes with carbon monoxide, and with binuclear transition metal catalysts, the initial steps are often proposed to occur by way of alkyne complexes of types **A** or **B** (a dimetallacyclobutene), vinylidene complexes of type **C** (only if R = H), and then metallacyclobutenone or dimetallacyclopentenone complexes of types **D**–**F**.[1–10]



Much of the recent research in this area has focused on diruthenium complexes, and a remarkably diverse chemistry has been discovered.[2,3] For example, Knox reported the reactions of eq 1 (Cp = $\eta$-$C_5H_5$), including the very easy, reversible cleavage of the CR—CO bond in the dimetallacyclopentenone product,[4] and Takats reported the similar reaction of eq 2 (PP = dppm = $Ph_2PCH_2PPh_2$).[5] Gladfelter showed that the dimetallacyclopentenone was formed before the dimetallacyclobutene in the reactions of equation 3 (R = $CO_2Me$, PP = dmpm = $Me_2PCH_2PMe_2$), which therefore involve initial addition of the alkyne without CO loss.[6] Very recently and strongly in contrast with eq 3, Haines reported that the reaction of eq 4 [PP = $(RO)_2PNEtP(OR)_2$] occurs after initial loss of CO; no dimetallacyclopentenone derivatives were observed.[7] The products appear to depend on the nature of the alkyne and, in the diphosphine bridged complexes, on both the

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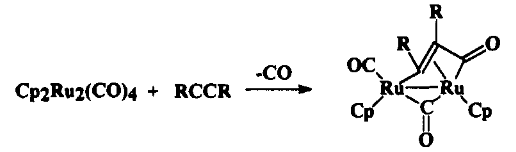
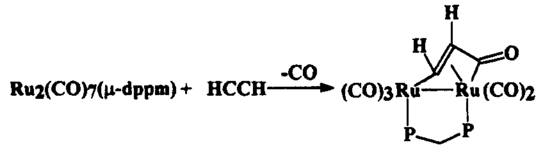
number and the nature of these bridging groups.[5-7] Since a simple route to the complex [$Ru_2(\mu\text{-}CO)(CO)_4(\mu\text{-}dppm)_2$], **1**, is now available,[11] it was of interest to compare its reactivity toward alkynes with the reactivities of the smaller diphosphine dmpm or of the more electron-withdrawing diphosphines $(RO)_2PNEtP(OR)_2$.[6,7,12,13] This paper reports the reactions of **1** with the simplest acetylene HC≡CH, which lead in sequence to a dimetallacyclobutene and a dimetallacyclopentenone derivative. Most previous examples of dimetallacyclopentenones have been of the type **E**,[1,4,5,8] with relatively few of type **F**.[6,9,10] Note that the $C_2R_2CO$ unit in **D** and **E** acts as a 4-electron ligand whereas in **F** it acts as a 2-electron ligand. The only examples of a type **F** complex with R = H of which we are aware are heterobimetallic complexes such as [$OsRu(CO)_8(\mu\text{-}CH{=}CHC({=}O))$], obtained from [$Os(CO)_4(HC{\equiv}CH)$] with metal carbonyls (eq 5).[10]



(1)



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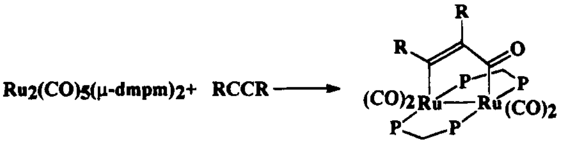

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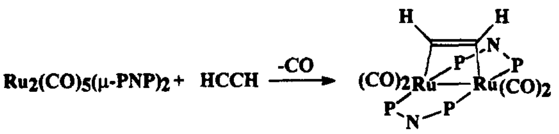

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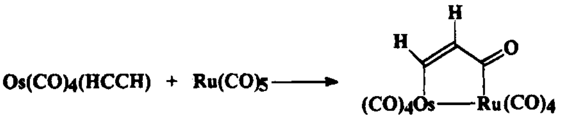
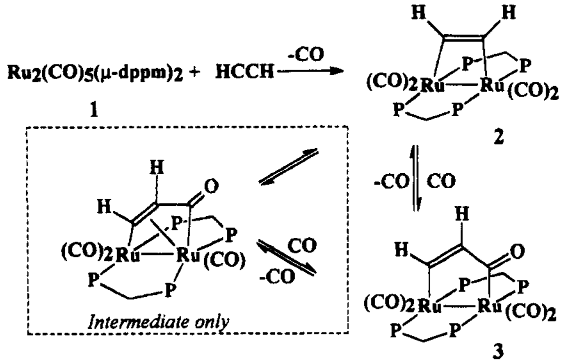


(5)

## Results and Discussion

The reaction of **1** with excess HC≡CH occurs in a stepwise fashion according to eq 6. The first step is complete in about 30 min at room temperature, and the dimetallacyclobutene product **2** can be isolated in pure form by evaporation of the solvent and excess acetylene at that stage. If the reaction is carried out in a closed flask and is allowed to proceed for about 1 day, a further reaction occurs to give the dimetallacyclopentenone product **3**. Further reactions occur on standing for longer periods, but these reactions lead to mixtures which it has not been possible to purify; the $^1H$ NMR spectra clearly indicate that vinylruthenium complexes are formed but complete characterization was not accomplished.



(6)

The reactions of eq 6 were monitored by NMR methods using either HC≡CH or $H^{13}C{\equiv}^{13}CH$ as the reagent in a closed NMR tube. These experiments clearly showed that, in the early stages of the reaction, complex **2** was the only product formed, with no **3** detectable and no $\mu$-vinylidene complex formed either. Complex **2** could be isolated and then treated with CO to give **3** in a separate reaction. When **2** was treated with excess $^{13}CO$, the labeled CO was detected mostly in the terminal carbonyl ligands of the product **3**, with a lower level of incorporation in the metallacycle. Complex **3** is evidently the thermodynamically stable product containing 1 equiv. of acetylene since a solution of **2** in the absence of excess CO slowly decomposed to give **3** as the major product; evidently, the extra carbon monoxide needed comes from general decomposition of **2** in this case. Heating **3** in the solid state caused a loss of CO with regeneration of **2**. This reaction was monitored by thermogravimetric analysis; a weight loss at 150 °C corresponding to loss of one carbonyl group was observed, and the product CO was confirmed by IR and by GC/MS, while **2** was identified by NMR. In solution, **3** reacted with $^{13}CO$ to undergo exchange of the terminal carbonyl ligands over a period of several hours but less exchange with the carbonyl group of the dimetallacyclopentene unit was detected. These observations are consistent with a mechanism of conversion of **3** to **2** in which a terminal carbonyl is lost from **3** and then, in a slower step, the carbonyl is eliminated from the dimetallacyclopentene group to take the place of the carbonyl ligand (eq 6). It follows that formation of **3** from **2** occurs by formation of the metallacyclopentenone ring by migratory insertion, thus creating a coordination site, followed by addition of a carbonyl ligand.

Both complexes **2** and **3** are air-stable yellow solids. Complex **3** can be stored for long periods without decomposition but **2** decomposes slowly, even in the solid state, with formation of **3** as the major product. The IR spectrum of **2** contains only terminal carbonyl bands. The $^{31}P$ NMR spectrum in $CD_2Cl_2$ solution shows only a sharp singlet resonance which remains unchanged at lower temperatures, indicating that all phosphorus atoms are equivalent and, from the chemical shift at $\delta$ = 29.5, that the dppm is coordinated in the bridging mode.[14] The $^1H$ NMR spectrum shows two multiplet resonances at $\delta$ = 3.55 and 4.65, assigned to the $CH_2P_2$ protons of the dppm ligand and consistent with an "A-

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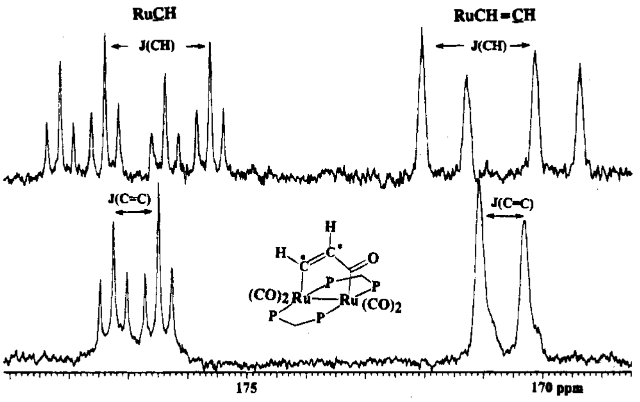

**Figure 1.** $^{13}C$ NMR spectra of **3** prepared from $^{13}C_2H_2$, showing only the RuCH=CH carbon resonances: below, the $^1H$ decoupled spectrum and, above, the $^1H$ coupled spectrum.

frame" structure.[14] The $Ru_2CH{=}CH$ ring in **2** is characterized by a well-resolved quintet resonance at $\delta$ = 7.80 with $J(PH)_{obs}$ = 1 Hz in the $^1H$ NMR spectrum and, in **2*** prepared from $H^{13}C{\equiv}^{13}CH$, by a singlet at $\delta$ = 136, $^1J(CH)$ = 130 Hz, in the $^1H$ coupled spectrum, and by a doublet at $\delta$ = 7.8, $^1J(CH)$ = 130 Hz, in the $^{13}C$ and $^1H$ NMR spectra, respectively. For comparison, the analogous complex with $(MeO)_2PNEtP(OMe)_2$ bridging ligands (eq 2) gave $\delta(^1H, C_2H_2)$ = 7.1 and $\delta(^{13}C, C_2H_2)$ = 121.[7] These NMR parameters support the formulation as a dimetallacyclobutene or dimetalated alkene ($CH_2{=}CH_2$ has $\delta$(C) = 123.3, $^1J(CH)$ = 156 Hz). The FAB-mass spectrum of this complex shows a parent ion peak for $Ru_2(CO)_4(HC{\equiv}CH)(dppm)_2^+$ at $m/z$ = 1110 and peaks at $m/z$ = 1082, 1054, 1026, and 998 attributed to ions formed by loss of one, two, three, and four CO groups, respectively.

The IR spectrum of **3** contains four terminal carbonyl bands and a strong band at 1534 $cm^{-1}$, which is assigned to the ketonic carbonyl group. The $\nu(C{=}O)$ frequency is particularly low, indicating strong back-bonding to this group. For comparison, $[OsRu(CO)_8(CH{=}CH{-}C({=}O))]$ has $\nu(C{=}O)$ = 1635 $cm^{-1}$ and the dimetallacyclopentenes of structure **E** have $\nu(C{=}O)$ = 1690–1750 $cm^{-1}$.[4,5,8,10] The $^{31}P$ NMR spectrum of **3** contains two multiplet resonances, typical of an AA′BB′ spin system, as expected for a complex with $C_s$ symmetry. The $^1H$ NMR of the complex gives resonances due to the $CH_2P_2$ groups at $\delta$ = 4.20 and 4.75. Two $^1H$ NMR resonances are expected for the dimetallacyclopentenone ring, but only one multiplet resonance was observed as a doublet of triplets at $\delta$ = 8.0 with $^3J(HH)$ = 9.8 Hz and $^4J(PH)$ = 3.1 Hz, assigned to the RuC*H* proton. The 2D(COSY) $^1H$ NMR spectrum clearly showed that the resonance due to the RuCOC*H* proton is hidden under the phenyl proton resonances at $\delta$ = 7.4. In $[OsRu(CO)_8(CH{=}CHCO)]$, the $^1H$ resonances are at $\delta$ = 8.17 and 7.46, and the latter resonance falls in the usual region for aryl resonances.[10] The $^{13}C$ NMR spectrum of **3***, prepared from $^{13}C_2H_2$, gives two multiplet resonances, as shown in Figure 1. The resonance at $\delta$ = 176.8 appears as a doublet of triplets due to the couplings $^1J(CC)$ = 57 Hz and $^2J(PC)$ = 17 Hz and is assigned to the RuCH atom; in the $^1H$ coupled spectrum (Figure 1) an extra doublet splitting is observed due to $^1J(CH)$ = 134 Hz. The resonance at $\delta$ = 170.8 is assigned to the RuCOCH carbon atom; it is a doublet due to $^1J(CC)$ = 57 Hz and gives a further doublet splitting in the $^1H$ coupled spectrum due to $^1J(CH)$ = 144 Hz. The values of $^1J(CC)$ and $^1J(CH)$ are similar to those for ethylene (68 and 156 Hz, respectively) and so support the presence of a localized C=C double bond in **3**. In the product **3****, prepared by reaction of **2** with $^{13}CO$, the carbonyl ligands were observed as triplet resonances at $\delta$ = 194.2, 194.8, 210.3, and 211.2, each with $^2J(PC)$ = 10 Hz. A much weaker resonance at $\delta$ = 264.9, $^2J(PC)$ = 11 Hz, is assigned to the carbonyl group of the metallacycle. The chemical shift can be compared to $\delta(^{13}C)$ = 236.3 in $[OsRu(CO)_8(CH{=}CHCO)]$, consistent with stronger back-bonding in **3**, and $\delta$(C) = 262.6 in $[Ru_2(\mu\text{-dmpm})_2(CO)_4(CR{=}CRCO)]$, R = $CO_2Me$.[6,10] The observation of five separate carbonyl resonances for **3*** clearly shows that the molecule is not fluxional.

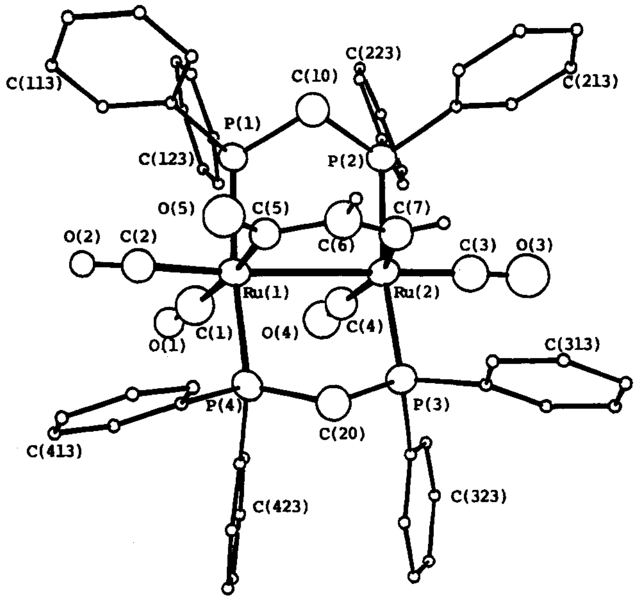

**Figure 2.** ORTEP view of the structure of **3**, showing 50% probability ellipsoids except for carbon atoms of the phenyl rings, which are assigned a small fixed radius. Only the H atoms of the dimetallacycle are shown.

The dimetallacyclopentenone **3** was further characterized by an X-ray structure determination. The structure is shown in Figure 2 and selected bond distances and angles are given in Table 1. The structure contains a *trans,trans*-$Ru_2(\mu\text{-dppm})_2$ core with the distance Ru–Ru = 2.988(1) Å, which is consistent with a single bond although at the long end of the usual range.[2–8,12,13] Each $Ru_2P_2C$ ring adopts an envelope conformation with the flap toward the dimetallacycle; thus all the phenyl substituents on this side of the molecule are equatorial and the steric repulsions are minimized.[14] The angles around each ruthenium center are close to those expected for octahedral coordination, with the angle C(4)–Ru(2)–C(7) at 159.7(6)° having a much greater deviation from linearity than the corresponding angle C(1)–Ru(1)–C(5) at 171.4(6)°. Since this is the first structure of a type **F** dimetallacyclopentenone with R = H to be reported, a discussion is justified. The dimetallacycle is essentially planar with the maximum displacement from the least-squares plane for the atoms Ru(1)Ru(2)C(5)O(5)C(6)C(7) being 0.021 Å for C(5). The bond distances within the ring are fully consistent with there being localized double bonds between C(5)O(5) and C(6)C(7). A comparison of bond distances and angles for the dimetallacycle with the two other reported structures of type **F** is given in

**Table 1. Selected Bond Distances (Å) and Angles (deg) for 3**

| | | | |
|---|---|---|---|
| Ru(1)—Ru(2) | 2.988(1) | Ru(1)—P(1) | 2.360(4) |
| Ru(1)—P(4) | 2.350(4) | Ru(2)—P(2) | 2.344(4) |
| Ru(2)—P(3) | 2.340(4) | Ru(1)—C(1) | 1.95(2) |
| Ru(1)—C(2) | 1.94(2) | Ru(2)—C(3) | 1.81(2) |
| Ru(2)—C(4) | 1.94(1) | Ru(1)—C(5) | 2.11(1) |
| Ru(2)—C(7) | 2.09(1) | C(1)—O(1) | 1.13(2) |
| C(2)—O(2) | 1.11(2) | C(3)—O(3) | 1.20(2) |
| C(4)—O(4) | 1.12(2) | C(5)—O(5) | 1.21(2) |
| C(5)—C(6) | 1.49(2) | C(6)—C(7) | 1.33(2) |

| | | | |
|---|---|---|---|
| P(1)—Ru(1)—Ru(2) | 88.1(1) | P(4)—Ru(1)—Ru(2) | 88.1(1) |
| P(4)—Ru(1)—P(1) | 170.2(1) | C(1)—Ru(1)—Ru(2) | 104.8(5) |
| C(1)—Ru(1)—P(1) | 96.1(5) | C(1)—Ru(1)—P(4) | 93.6(5) |
| C(2)—Ru(1)—Ru(2) | 171.3(4) | C(2)—Ru(1)—P(1) | 90.2(5) |
| C(2)—Ru(1)—P(4) | 92.2(5) | C(2)—Ru(1)—C(1) | 83.9(7) |
| C(5)—Ru(1)—Ru(2) | 83.8(4) | C(5)—Ru(1)—P(1) | 84.9(4) |
| C(5)—Ru(1)—P(4) | 85.7(4) | C(5)—Ru(1)—C(1) | 171.4(6) |
| C(5)—Ru(1)—C(2) | 87.5(6) | P(2)—Ru(2)—Ru(1) | 92.1(1) |
| P(3)—Ru(2)—Ru(1) | 91.5(1) | P(3)—Ru(2)—P(2) | 163.0(1) |
| C(3)—Ru(2)—Ru(1) | 176.7(5) | C(3)—Ru(2)—P(2) | 88.0(5) |
| C(3)—Ru(2)—P(3) | 89.3(6) | C(4)—Ru(2)—Ru(1) | 76.3(5) |
| C(4)—Ru(2)—P(2) | 97.5(5) | C(4)—Ru(2)—P(3) | 99.5(5) |
| C(4)—Ru(2)—C(3) | 100.4(7) | C(7)—Ru(2)—Ru(1) | 83.4(4) |
| C(7)—Ru(2)—P(2) | 82.3(4) | C(7)—Ru(2)—P(3) | 81.7(4) |
| C(7)—Ru(2)—C(3) | 99.9(6) | C(7)—Ru(2)—C(4) | 159.7(6) |
| O(2)—C(2)—Ru(1) | 178(1) | O(3)—C(3)—Ru(2) | 178(1) |
| O(4)—C(4)—Ru(2) | 175(1) | O(5)—C(5)—Ru(1) | 125(1) |
| C(6)—C(5)—Ru(1) | 121(1) | C(6)—C(5)—O(5) | 114(1) |
| C(7)—C(6)—C(5) | 126(1) | C(6)—C(7)—Ru(2) | 125(1) |

**Table 2. Comparison of Molecular Dimensions (Distances (Å) and Angles (deg)) in Dimetallacyclopentenones of Type F: 3, $[Ru_2(CO)_4(\mu\text{-dmpm})_2\{C(CO_2Me){=}C(CO_2Me)C({=}O)\}]$, 4, and $[Rh_2Cp_2(CO)_2\{C(CF_3){=}C(CF_3)C({=}O)\}]$, 5 (Nomenclature as in Figure 2)**

| | 3 | 4 | 5 |
|---|---|---|---|
| M(1)—M(2) | 2.988(1) | 2.936(1) | 2.680(1) |
| M(1)—C(5) | 2.11(1) | 2.132(3) | 2.021(6) |
| M(2)—C(7) | 2.09(1) | 2.156(3) | 2.056(5) |
| C(6)=C(7) | 1.33(2) | 1.340(4) | 1.336(5) |
| C(5)—C(6) | 1.49(2) | 1.496(4) | 1.499(8) |
| C(5)=O(5) | 1.21(2) | 1.23(3) | 1.213(8) |
| M(1)—M(2)—C(7) | 83.4(4) | 81.0(1) | 86.2(2) |
| M(2)—M(1)—C(5) | 83.8(4) | 83.7(1) | 84.1(2) |
| M(1)—C(5)—C(6) | 121(1) | 119.1(2) | 119.2(4) |
| M(2)—C(7)=C(6) | 125(1) | 126.5(2) | 122.9(4) |
| C(5)—C(6)=C(7) | 126(1) | 121.3(3) | 117.6(5) |

Table 2.[6,9] The dimensions are remarkably similar, with most differences in bond angles related to the differences in metal—metal distances. The rhodium complex appears most distorted from planarity with the carbonyl carbon atom displaced by 0.523(7) Å from the least-squares plane.[9]

It is significant that both ruthenacyclopentenone derivatives with structure **F** are based on the *trans,-trans*-Ru$_2$(diphosphinomethane)$_2$ skeleton,[6] while all others have structure **E**.[4,5,8] This is probably not a coincidence. The structure type **E** requires a twisting of the dimetallacyclopentenone structure to allow coordination of the alkene group, and the *trans,trans*-Ru$_2$(diphosphinomethane)$_2$ skeleton prevents this, perhaps partly by steric effects but also by leaving available only coordination sites in the plane perpendicular to the Ru$_2$P$_4$ atoms. A distortion to a *cis*-RuP$_2$ stereochemistry at one ruthenium center would be necessary to allow structure **E**. This may occur at intermediate stages to minimize the effects of coordinative unsaturation (see eq 6) but appears to be thermodynamically unfavorable in stable complexes. When only one dppm ligand is present, structure **E** is preferred.[5]

It is clear from this work that the sequence of reactions leading to the dimetallacyclopentenone can differ in closely related systems. Thus the reactions of eq 3 and 6 both involve $[Ru_2(CO)_5(\mu\text{-PCP})_2]$ complexes but the dimetallacyclopentenones are formed in very different ways. The ease of cleavage and formation of C—C bonds in these metallacycles is evident and is no doubt the basis of several catalytic reactions.[1-3]

## Experimental Section

General methods and the synthesis of complex **1** are given in ref 11.

**Synthesis of $[Ru_2(CO)_4(C_2H_2)(\mu\text{-dppm})_2]$, 2.** A slow stream of HC≡CH was passed through a solution of $[Ru_2(CO)_4(\mu\text{-CO})(\mu\text{-dppm})_2]$ (0.07 g) in $C_6H_6$ (20 mL) for 5 min. The inital green-yellow solution immediately turned bright yellow. The flask was sealed, and the solution was stirred for 0.5 h in an atmosphere of HC≡CH. The solvent was then evaporated under vacuum. The yellow solid so formed was washed with EtOH (5 mL) and dried under reduced pressure. Yield: 90%. Anal. Calc for $C_{56}H_{46}O_4P_4Ru_2{\cdot}4CH_2Cl_2$: C, 49.7; H, 3.7. Found: C, 49.4; H, 4.5. IR (Nujol): $\nu(CO) = 1995$ (s), 1943 (vs), 1925 (vs), 1879 (s) cm$^{-1}$. NMR ($CD_2Cl_2$): $\delta(^1H) = 3.55$ [m, 2H, $^2J(HH) = 12$ Hz, $J(PH)_{obs} = 5$ Hz, $CH_2P_2$], 4.65 [m, 2H, $^2J(HH) = 12$ Hz, $J(PH)_{obs} = 5$ Hz, $CH_2P_2$], 5.32 [s, $CH_2Cl_2$], 6.8–7.7 [m, 40H, Ph], 7.80 [quintet, 2H, $J(PH)_{obs} = 1$ Hz, $C_2H_2$]; $\delta(^{31}P) = 29.5$ [s, dppm]. FAB-MS: $m/z$ = 1110, 1082, 1054, 1026, 998 amu. A sample prepared similarly using H$^{13}$C≡$^{13}$CH gave $\delta(^{13}C) = 136.0$ [s, $^1J(CH) = 130$ Hz].

**Synthesis of $[Ru_2(CO)_4(H_2C_2CO)(\mu\text{-dppm})_2]$3.** A solution of $[Ru_2(CO)_4(\mu\text{-CO})(\mu\text{-dppm})_2]$ (0.3 g) in $CH_2Cl_2$ (20 mL) at 0 °C was stirred under an atmosphere of HCCH for 16 h. The volume of solvent was then reduced under vacuum to ca. 7 mL, and the solution was cooled overnight at −5 °C. The yellow microcrystalline solid so formed was filtered off, washed with EtOH (5 mL), and dried under vacuum. Yield: 75%. Anal. Calc for $C_{57}H_{46}O_5P_4Ru_2{\cdot}1.5CH_2Cl_2$: C, 55.5; H, 3.9. Found: C, 55.7; H, 4.2. IR (Nujol), cm$^{-1}$: $\nu(CO) = 1990$ (s), 1967 (vs), 1935 (vs), 1914 (vs), 1534 (s); $\nu(C{=}C) = 1587$ (vw), 1574 (vw). NMR ($CD_2Cl_2$): $\delta(^1H) = 4.20$ [m, 2H, $^2J(HH) = 12$ Hz, $J(PH)_{obs} = 5$ Hz, $CH_2P_2$], 4.75 [m, 2H, $^2J(HH) = 12$ Hz, $J(PH)_{obs} = 5$ Hz, $CH_2P_2$], 5.32 [s, $CH_2Cl_2$], 6.8–7.7 [m, 40H, Ph], 8.0 [dt, 1H, $^3J(HH) = 9.8$ Hz, $^4J(PH) = 3.1$ Hz, RuCH]; $\delta(^{31}P) = 27.7$ [m, dppm], 30.0 [m, dppm]. FAB-MS: $m/z$ = 1110, 1082, 1054, 1026, 998 amu. A $^{13}$C labeled derivative was prepared by reaction of $[Ru_2(CO)_4(\mu\text{-CO})(\mu\text{-dppm})_2]$ with $^{13}C_2H_2$ and was further characterized by $^{13}$C NMR: $\delta(^{13}C) = 176.8$ [ddt, $^1J(CC) = 57$ Hz, $^1J(CH) = 134$ Hz, $^2J(CP) = 17$ Hz, RuCH], 170.8 [dd, $^1J(CC) = 57$ Hz, $^1J(CH) = 144$ Hz, RuCHCH]. A $^{13}$CO labeled derivative prepared from **2** and $^{13}$CO gave $\delta(^{13}C) = 194.2$, 194.8, 210.3, 211.2 [each t, $^2J(PC) = 10$ Hz, terminal CO] and 264.9 [t, $^2J(PC) = 11$ Hz, RuC(=O)].

**X-ray Structure Determination of 3·2CH$_2$Cl$_2$.** Single crystals of 3·2CH$_2$Cl$_2$ were grown from a CH$_2$Cl$_2$/EtOH solution. The diffraction measurements were carried out by using an Enraf-Nonius CAD4F diffractometer at ambient temperature (295 K) using graphite monochromated Mo K$\alpha$ radiation. A yellow crystal (with dimensions 0.22 × 0.14 × 0.10 mm) was mounted at the end of a glass fiber with epoxy glue. Photo-indexing and automatic indexing routines, followed by least-squares fits of 21 reflections ($22.3 \le 2\theta \le 25.1°$) gave cell constants and orientation matrices.[15] The Niggli matrix suggested a monoclinic system with symmetry $2/m$ and this was confirmed from an inspection of equivalent reflections. The $C$ centering in the lattice was deduced from the systematic absences ($hkl$, $h + k = 2n + 1$). Intensity data were recorded in the $\omega$-$2\theta$ scan mode at variable scan speeds (1.27–4.12°/

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[15] *CAD4 Diffractometer Manual*; Enraf-Nonius: Delft, The Netherlands, 1988.

min), so chosen as to optimize counting statistics within a maximum time per datum of 60 s. Background measurements were made by extending the scan by 25% on each side. Three standard reflections (−2,0,0, 020, 1,1,−1) were monitored every 120 min of X-ray exposure time, and orientation checks were done for every 300 reflections measured. In total, 4710 reflections were collected in the $2\theta$ range 0−46° ($-21 \le h \le 21$, $-1 \le k \le 18$, $-1 \le l \le 19$). The data were processed using the NRCVAX crystal structure programs[16] running on a SUN 3/80 workstation. The data crystal had six faces with face indices {100}, (111), (1,−1,1), (1,1-1), and (1,−1,−1)). An empirical absorption correction was applied to the data on the basis of the $\psi$ scans of nine reflections with $\theta$ ranging from 3.2 to 14.7 ($\mu$ = 7.87 cm$^{-1}$). The maximum and minimum correction factors were 0.998 and 0.897, respectively. The cell parameters and the systematic absences indicated[17a] that the space group could be either *C*2/*c* (No. 15) or *Cc* (No. 9). The distribution of *E* suggested[18] an acentric space group. For $Z = 4$, therefore, the space group *Cc* was assumed and the correctness of the choice of the space group was confirmed by successful solution and refinement of the structure. The equivalent reflections were averaged ($R_{int}$ = 0.015), leaving 4552 unique reflections. The structure was solved using SHELXS-86 program[18] and subsequent difference Fourier techniques. The final full-matrix least-squares refinements on *F* were done using the SHELX-76 software.[19] Scattering factors for neutral non-hydrogen atoms were taken from ref 17b. The phenyl rings were treated as regular hexagons (with a C—C distance of 1.395 Å). Of the two $CH_2Cl_2$ solvate molecules, one was found to be disordered and a satisfactory model was found. The C—Cl bond lengths and Cl—C—Cl angles were fixed at 1.75 Å and 110°, respectively. The hydrogen atoms of the phenyl groups and one dichloromethane molecule were placed in the calculated positions (C—H = 0.95 Å), and they were included for the structure factor calculations only. A common thermal parameter was assigned and refined in the least-squares cycles. In the final least-squares refinement cycles, the data converged at $R = 0.0499$ and $R_w = 0.0520$ for 3423 observations with $I \ge 2.5\sigma(I)$ and 255 variables using the weighting scheme $w = k/\sigma^2F + gF^2$ where $g = 0.0005$ and $w = 1.9171$. In the final difference Fourier synthesis the electron density ranged from 1.11 to −0.61 e Å$^{-3}$; of these, the top peak (with electron density more than 1.0 e Å$^{-3}$) was associated with Ru(2) at a distance of 0.99 Å. The rest of the peaks have electron densities less than 0.76 e Å$^{-3}$. The maximum shift/esd in the final cycle was −0.035. The secondary extinction coefficient was refined to 0.05(22) × 10$^{-4}$. For the inverted model $R = 0.0506$ and $R_w = 0.0527$. The experimental details and crystal data are given in Table 3. The positional and thermal parameters, anisotropic thermal parameters, calculated hydrogen atom coordinates, selected weighted least-squares planes, and selected torsion angles have been included in the supplementary material.

**Table 3. Crystal Data and Experimental Details**

| | |
|---|---|
| compd, fw | $C_{59}H_{50}Cl_4O_5P_4Ru_2$, 1306.89 |
| cryst syst, space group | monoclinic, *Cc* |
| cell dimens | |
| *a*, Å | 19.500(2) |
| *b*, Å | 17.146(3) |
| *c*, Å | 17.349(2) |
| $\beta$, deg | 101.21(1) |
| temp, K | 295 |
| cell vol, Å$^3$; *Z* | 5690(1); 4 |
| density, g·cm$^{-3}$ (calcd) | 1.525 |
| diffractometer, monochromator | Enraf-Nonius CAD4F; graphite |
| radiation; wavelength, Å | Mo K$\alpha$; 0.71073 |
| abs coeff, cm$^{-1}$ | 7.87 |
| no. of observ, variables | 3423 ($I \ge 2.5\sigma(I)$), 255 |
| final model:[a] *R* and $R_w$ | 0.0499, 0.0520 |

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $R_w = [\Sigma w^{1/2}(||F_o| - |F_c||)^2/\Sigma w^{1/2}|F_o|]$.

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**Supplementary Material Available:** Table S1, listing fractional coordinates and $B_{iso}$, Table S2, giving bond distances and angles, Table S3, giving anisotropic thermal parameters, Table S4, listing calculated hydrogen atom positional parameters, Table S5, giving weighted least-squares planes, and Table S6, listing selected torsion angles (9 pages). Ordering information is given on any current masthead page.

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