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Facile Decarboxylation of Propiolic Acid on a Ruthenium Center and Related Chemistry

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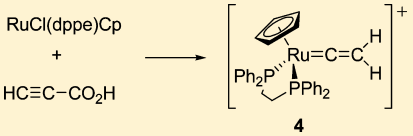
Supporting Information

ABSTRACT: Spontaneous decarboxylation of RC≡CCO_2H (R = H, Ph) occurs in reactions with RuCl(PP)Cp (PP = $(PPh_3)_2$, dppe) to give [Ru(=C=CHR)(PP)Cp]$^+$. Computational studies (DFT) of possible decarboxylation mechanisms suggest that the reaction that leads to extrusion of CO_2 and formation of [Ru(=C=CH_2)(dppe)Cp]$^+$ most likely occurs by initial interaction of the anion HC≡CCO_2^- with RuCl(dppe)Cp by coordination of carboxylate to Ru, followed by formation of an η^2-alkyne intermediate which rearranges to the η^1-ethynyl species with loss of CO_2. Protonation of the ethynyl group affords the parent vinylidene. In contrast, reactions of HC≡CCO_2R (R = Me, Et) with RuCl(PP)Cp and $[NH_4]PF_6$ in MeOH have given [Ru{=C(OMe)$CH_2(CO_2R)$}(PP)Cp]$^+$, formed by attack of MeOH at C_α of the intermediate vinylidenes [Ru{=C=$CH(CO_2R)$}(PP)Cp]$^+$. Deprotonation of the carbenes affords Ru{C(OMe)=$CH(CO_2R)$}(PP)Cp as mixtures of cis and trans isomers. The vinylidenes, which are obtained directly from RuCl(PP)Cp and HC≡CCO_2R in the presence of $[NH_4]PF_6$ in Bu^tOH, can be deprotonated (Na/Pr^iOH) to the corresponding alkynyls. Attempted deprotonation of [Ru(=C=CH_2)(dppe)Cp]$^+$ with LiBu gave the binuclear cyclobutenylidinium complex [{Ru(dppe)Cp}$_2$(μ-C_4H_3)]$^+$. The X-ray diffraction molecular structures of [{Ru(dppe)Cp}$_2$(μ-C_4H_3)]PF_6 (**11**), [Ru{=C(OMe)$CH_2(CO_2Me)$}(dppe)Cp]PF_6 (**13**), Ru{C(OMe)=$CH(CO_2R)$}(dppe)Cp (R = Me (**15**), Et (**16**)) and Ru(C≡CCO_2R)(dppe)Cp (R = Me (**21**), Et (**22**)) are described.



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INTRODUCTION

Fixation of CO_2 by organic molecules to give carboxylates is a useful synthetic method, since CO_2 is a readily available starting material that is nontoxic and is a C_1 moiety.[1] In the context of alkyne chemistry, carboxylation is usually carried out with metalated (Li, Mg) terminal alkynes reacting with CO_2 directly.[2] Also known is the Cu-catalyzed coupling of alkynes with CO_2, especially in the presence of alkyl bromides.[3] Initially, this reaction was reported to require elevated temperatures (100 °C) in polar solvents, although later studies used more reactive Cu/diamine,[4] Cu/NHC,[5] or Cu/phosphine[6] or, in one case, ligand-free Ag[7] systems.

The reverse reaction, decarboxylation of metal carboxylates, has long been used as a route to organometallic compounds. Originally described in 1901, the Pesci reaction uses thermal decarboxylation of the metal carboxylate formed from a metal salt and the carboxylic acid, often involving copper.[8] Many examples of its use both in the condensed phase[9] and, more recently, in the gas phase, have been reported.[10] It is of use in organic synthesis, potentially in metal-catalyzed syntheses.[11]

Relatively few examples of decarboxylations at lower temperatures are known. While decarboxylation of a variety of organic substrates in the presence of transition-metal compounds, particularly those of copper, is a well-established transformation,[9] such reactions generally require heating or free-radical initiation. Under the mild conditions described above, such reactions are rare and appear to be confined to polyfluorinated systems. Thus, the reaction between RhCl(CO)$(PPh_3)_2$ and $TlO_2CC_6F_5$ affords Rh(C_6F_5)(CO)$(PPh_3)_2$ directly,[12] while similar reactions with $PtCl_2$(dppx)$_2$ (x = e, p, b) in the presence of pyridine proceed at room temperature to give $PtCl_n(C_6F_5)_{2-n}$(dppx) (n = 0, 1).[13] Optimum yields in the second reaction are obtained in refluxing pyridine, however. A similar preparation of $AgCH(CF_3)_2$ from $(CF_3)_2CHCO_2Ag$ in pyridine is known,[14] while the reactions between $Hg(OAc)_2$ and $ArCO_2H$ (Ar = $(MeO)_nC_6H_{5-n}(OMe)_n$, n = 2 (2,6), 3 (2,3,4; 2,4,6)) in aqueous MeOH are reported to give $HgAr_2$ via Hg(OAc)Ar.[15] The proposed mechanism for the latter

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reaction resembles that of electrophilic aromatic substitution. Decarboxylation of $TlO_2CC_6F_5$ to give C_6F_5H has also been described.[13,16]

The closest example to the present work is the reaction of $Hg(OAc)_2$ with phenylpropiolic acid to give $Hg(C{\equiv}CPh)_2$, which occurs between 0 °C and room temperature.[17] Several mechanisms have been invoked to explain the decarboxylation reactions, most involving the formation of carbanions or free radicals.[9]

Elegant studies by O'Hair and his co-workers have extended the decarboxylation to the gas phase, studying particularly the formation of a variety of organocuprate species by multistage mass spectrometry experiments.[18] The minima and transition states relevant to fragmentation of ions $[Cu(O_2CR)_2]^-$ (R = Me, Et, CF_3) have been examined by DFT methods.[19]

Recently, we have been interested in examining the reactions of alkynecarboxylic acids and their esters with ruthenium complexes Ru(PP)Cp (PP = $(PPh_3)_2$, dppe). As previously described, the esters afford vinylidene and derived vinyl complexes;[20,21] we take this opportunity here to record relevant X-ray structural and spectroscopic data. The reactions with propiolic acids were originally carried out as a possible route, in the event unsuccessful, to 3-oxopropadienylidene (C_3O) derivatives, by analogy with the well-established route to allenylidenes:[22]

$$\mathrm{RuCl(PP)Cp' + HC{\equiv}CCR_2(OH)} \rightarrow [\mathrm{Ru\{{=}C{=}CCHC(OH)R_2\}(PP)Cp'}]^+ \rightarrow [\mathrm{Ru({=}C{=}C{=}CR_2)(PP)Cp'}]^+$$

$$\mathrm{RuCl(PP)Cp' + HC{\equiv}CC(OH){=}O} \rightarrow [\mathrm{Ru\{{=}C{=}CHC(OH){=}O\}(PP)Cp'}]^+ \rightarrow [\mathrm{Ru({=}C{=}C{=}C{=}O)(PP)Cp'}]^+$$

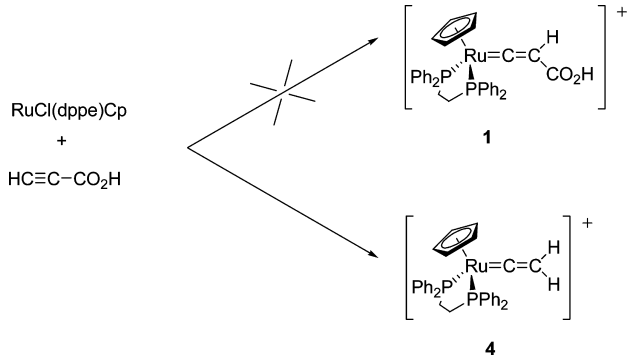
Only one substantiated example of a 3-oxopropadienylidene complex is known, namely $Cr(=C=C=C=O)(CO)_5$, obtained from a reaction between $[Cr(I)(CO)_5]^-$ and $AgC{\equiv}CCH(CO_2Na)$.[23]

Instead, the reaction resulted in facile decarboxylation reactions to give the parent vinylidenes, which can be deprotonated to the ethynyl–ruthenium complexes. This paper describes this chemistry and attempts to delineate possible mechanisms for this reaction.

RESULTS

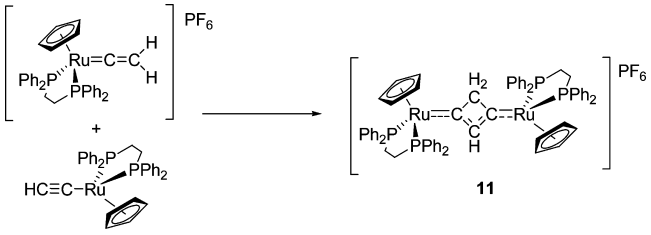
Reactions of Propiolic Acids or Their Salts. Attempted preparations of $[Ru\{=C=CH(CO_2H)\}(dppe)Cp]PF_6$ (**1**) from propiolic acid and RuCl(dppe)Cp under conditions similar to those used for preparation of the esters $[Ru\{=C=CH(CO_2R)\}(dppe)Cp]PF_6$ (R = Me (**2**), Et (**3**)) afforded instead the light yellow parent vinylidene $[Ru(=C=CH_2)(dppe)Cp]PF_6$ (**4**) (Scheme 1), identical with the material prepared in the conventional manner from RuCl(dppe)Cp and $HC{\equiv}CSiMe_3$ in Bu^tOH.[24] The same complex was isolated from a reaction between RuCl(dppe)Cp and $Ag[PF_6]$ (to generate $[Ru(thf)(dppe)Cp]PF_6$ in situ), followed by addition of propiolic acid. Finally, an attempt to intercept the propiolic vinylidene by carrying out the reaction in MeOH gave only $[Ru\{=CMe(OMe)\}(dppe)Cp]PF_6$ (**5**) as an off-white solid. This complex is a known product from the reaction of MeOH with vinylidene **4**.[20]

Scheme 1. Reaction of $HC{\equiv}CCO_2H$ with RuCl(dppe)Cp



Treatment of RuCl(PP)Cp′ with potassium propiolate in methanol also resulted in spontaneous elimination of CO_2 (most efficiently achieved by using refluxing MeOH) with formation of the neutral alkynyls $Ru(C{\equiv}CH)(PP)Cp^*$ ((PP)Cp′ = $(PPh_3)_2Cp$ (**6**), (dppe)Cp* (**7**)) in good to high yields (Scheme 2). In the presence of $[NH_4]PF_6$, the vinylidene

Scheme 2. Formation of a Cyclobutenylidinium–Ruthenium Complex



$[Ru(=C=CH_2)(PPh_3)_2Cp]PF_6$ (**8**) was obtained from the former precursor. With $PhC{\equiv}CCO_2K$, $RuCl(PPh_3)_2Cp$ gave $Ru(C{\equiv}CPh)(PPh_3)_2Cp$ (**9**). Attempted formation of a binuclear μ-C_2 complex by using $C_2(CO_2K)_2$ was thwarted, only RuH(PP)Cp′ being isolated. A similar reaction of $RuCl(PPh_3)_2Cp$, $(HO_2C)C{\equiv}C(CO_2K)$, and $[NH_4]PF_6$ in refluxing MeOH gave the carbene complex $[Ru\{=CMe(OMe)\}(PPh_3)_2Cp]PF_6$ (**10**), probably formed by a double decarboxylation and protonation of **6** so formed by $[NH_4]^+$, followed by addition of MeOH to the resulting vinylidene **8**.

Formation of a Cyclobutenylidinium Complex. In studies of the deprotonation of the parent vinylidene $[Ru(=C=CH_2)(dppe)Cp]PF_6$ with LiBu, we found that the reaction was accompanied by the formation of an orange material, which was successfully isolated and characterized by mass spectrometry and an X-ray structural determination as the binuclear cyclobutenylidinium complex $[\{Ru(dppe)Cp\}_2(\mu\text{-}C_4H_3)]PF_6$ (**11**) (Scheme 2). Once its identity had been established, a logical synthesis by reaction of equivalent amounts of $[Ru(=C=CH_2)(dppe)Cp]PF_6$ with $Ru(C{\equiv}CH)(dppe)Cp$ at room temperature for 2 h was carried out. Workup by filtration of a dichloromethane extract of the dried reaction mixture into diethyl ether afforded pure **11** as a yellow-brown solid in 86% yield.

Complex **11** was characterized by microanalysis, spectroscopy, and a single-crystal X-ray structure determination. In addition to signals from the $Ru(PPh_3)_2Cp$ group, a cumulenylidene ν(CC) band was found at 1980 cm^{-1}. In the ^1H NMR spectrum, triplets at δ 2.83 (CH_2) and 5.3 (CH) in a

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2/1 ratio were assigned to the C_4H_3 protons. The ^{13}C NMR spectrum contains resonances at δ 54.9 (CH_2), 174.1 (CH), and 262.1 (t, Ru−C), assigned to three of the four carbons of the bridging C_4 ligand. In the ES-MS, the molecular cation is at m/z 1181, with related ions at m/z 565 ($[Ru(dppe)Cp]^+$) and 606 ($[Ru(NCMe)(dppe)Cp]^+$; from solutions containing MeCN).

Figure 1 shows the binuclear cation in $[\{Ru(dppe)Cp\}_2(\mu\text{-}C_4H_3)]PF_6$ (**11**). Two Ru(dppe)Cp groups, with Ru−P = 2.2449−2.2696(9) Å and Ru−C(cp) = 2.26 Å (average), are attached at the 1,3-positions of a four-membered ring. Three hydrogen atoms were located on the C_4 ring, one on C(2) and two on C(4). The bridging ligand is thus the parent cyclobutenylidinium group, substituted examples of which have earlier been crystallographically substantiated in $(OC)_5Cr\text{-}\{\mu\text{-}C_4H_2(CO_2Me)\}Fe(CO)_2Cp$[25] and $[\{Ru(dppe)Cp^*\}_2\{\mu\text{-}C{\equiv}CC_4H_2(SiMe_3)C{\equiv}C\}]PF_6$.[26] In agreement with this assignment, there are two long (C(1,3)−C(2) = 1.542, 1.547(5) Å) and two short C−C distances (C(1,3)−C(4) = 1.402, 1.403(4) Å), suggesting that the positive charge is delocalized over atoms C(1,4,3) as well as the two Ru atoms, which are attached to C(1,3) by short Ru−C multiple bonds (1.971, 1.968(3) Å), as indicated in the structural diagram of the cation. The C_4 group is planar (χ^2 = 32), Ru(1,2) deviations being 0.125(7) and 0.053(7) Å (to the same side). There are pronounced asymmetries in the C(1,3)−Ru−P angles at each metal.

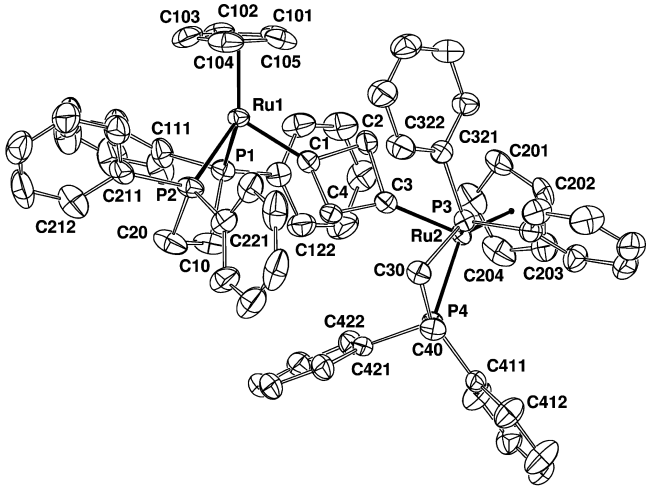
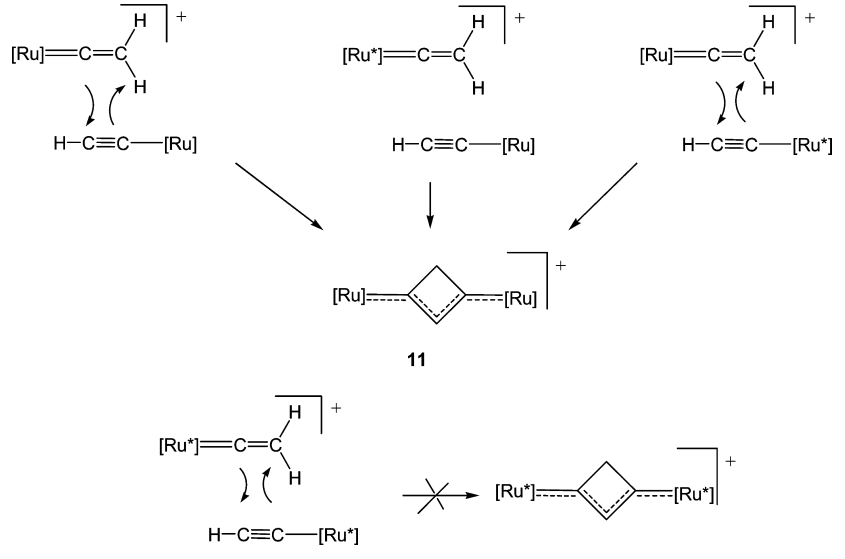


Figure 1. Plot of the cation in $[\{Ru(dppe)Cp\}_2(\mu\text{-}C_4H_3)]PF_6$ (**11**).

Following this synthesis, we attempted to obtain the mixed complex $[\{Cp(dppe)Ru\}(\mu\text{-}C_4H_3)\{Ru(dppe)Cp^*\}]PF_6$ (**12**) from reactions between equimolar amounts of Ru(C≡CH)(dppe)Cp and $[Ru(=C=CH_2)(dppe)Cp^*]PF_6$, or from the reverse addition of $[Ru(=C=CH_2)(dppe)Cp]PF_6$ to Ru(C≡CH)(dppe)Cp*, both in thf at room temperature. However, the only complex that could be isolated from either reaction was **11**. Neither the mixed analogue nor $[\{Ru(dppe)Cp^*\}_2(\mu\text{-}C_4H_3)]^+$ was formed.

Reactions between equimolar amounts of (i) Ru(C≡CH)(dppe)Cp and $[Ru(=C=CH_2)(dppe)Cp]PF_6$, (ii) Ru(C≡CH)(dppe)Cp* and $[Ru(=C=CH_2)(dppe)Cp^*]PF_6$, (iii) Ru(C≡CH)(dppe)Cp and $[Ru(=C=CH_2)(dppe)Cp^*]PF_6$, and (iv) Ru(C≡CH)(dppe)Cp* and $[Ru(=C=CH_2)(dppe)Cp]PF_6$ dissolved in d_6-acetone were monitored by ^{31}P NMR. For reaction i, the C_4H_3 complex $[\{Ru(dppe)Cp\}_2(\mu\text{-}C_4H_3)]PF_6$ (**11**) forms in less than 25 min, the color of the solution changing from yellow to orange. No reaction occurred between the two Cp* complexes in reaction ii. In reactions iii and iv, equilibria between all four possible components were set up, with proton transfer from the vinylidene to the more basic Cp* derivative being favored. Consequently, the only cyclobutenylidinium complex detected is the symmetrical complex $[\{Ru(dppe)Cp\}_2(\mu\text{-}C_4H_3)]PF_6$ (**11**), accompanied by an equimolar amount of $[Ru(=C=CH_2)(dppe)Cp]PF_6$ (**4**). These reactions are summarized in Scheme 3. The specificity found here is likely to be a consequence of the steric protection of C_α and C_β by the bulky Cp* ligands together with the dppe Ph groups. This reaction proceeds by attack of the electron-rich C_β upon the electron-

Scheme 3. Reactions between Ethynyl−Ruthenium and Vinylidene−Ruthenium Complexes[a]



[a][Ru] = Ru(dppe)Cp, [Ru*] = Ru(dppe)Cp*.

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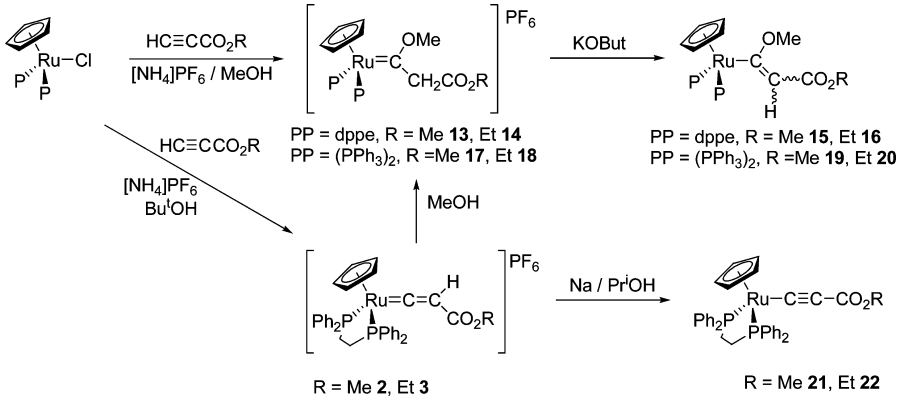
Scheme 4. Reactions of Ruthenium Complexes with Propiolic Acid and Esters



poor C_α of both reagents, resulting in a formal [2 + 2] cycloaddition reaction.

Reactions of HC≡CCO$_2$R (R = Me, Et). Reactions between RuCl(dppe)Cp and HC≡CCO$_2$R (R = Me, Et) were carried out in refluxing methanol in the presence of $[NH_4]PF_6$.[21] Conventional workup afforded pale yellow solids, which were characterized as the carbene complexes $[Ru\{=C(OMe)CH_2(CO_2R)\}(dppe)Cp]PF_6$ (R = Me (**13**), Et (**14**); Scheme 4) by elemental microanalyses (as for all complexes described herein) and spectroscopic methods, detailed in the Experimental Section. Only data relevant to the organic group will be discussed below. Thus, the IR spectra contained ester ν(CO) absorptions at ca. 1740 and 1250 cm^{-1}. The ^{1}H NMR spectra contained singlets at δ 2.9 (OMe, **13** and **14**) and 3.7 (for **13**, CO$_2$Me), or multiplets at δ 1.2, 3.8, and 4.1 (CO$_2$Et, for **14**). The ^{13}C NMR spectrum similarly contained resonances at δ 163.5 (ester CO) and 293.2 (Ru=C), with the Me/Et resonances at δ 14.0. The electrospray mass spectra (ES-MS) contained parent molecular cations at m/z 680 (**13**) and 694 (**14**), together with fragment ions at m/z 593 $[Ru(CO)(dppe)Cp]^+$ and 565 $[Ru(dppe)Cp]^+$.

Deprotonation of both **13** and **14** with metallic sodium or KOBu^t in MeOH solution resulted in the separation of pale yellow powders, which were characterized as the neutral vinyl complexes Ru{C(OMe)=CH(CO$_2$R)}(dppe)Cp (R = Me (**15**), Et (**16**), respectively). Their IR spectra contained strong ν(CO) absorptions at 1667, 1141, and 1048 cm^{-1}, together with a weaker ν(C=C) band at 1493 cm^{-1}. The NMR spectra of these complexes indicated that cis and trans isomers, each in the ratio 4/1, were present. Thus, characteristic Cp resonances were found for **15** at δ_H 4.6 (major)/4.5 (minor) and δ_C 85.1/86.2. Similarly, the OMe groups resonated at δ_H 2.2/2.7 and δ_C 49.5/49.2, the CO$_2$Me groups at δ_H 3.5/3.4 and δ_C 53.9/62.1, and the CH groups at δ_H 4.9/5.3 and δ_C 100.6/103.0. The ester CO carbons were found at δ_C 170.5/160.4, while the RuC signals overlapped at δ_C 224.9. Similar resonances were found for the ethyl ester complex **16**. The ^{31}P resonances for the dppe ligands are at δ_P 93.0/96.5 and 92.7/96.1, respectively. In the ES-MS M^+ ions were found at m/z 680 and 695, respectively.

The analogous carbenes $[Ru\{=C(OMe)CH_2(CO_2R)\}(PPh_3)_2Cp]PF_6$ (R = Me (**17**), Et (**18**)) and the vinyl compounds *cis*- and *trans*-Ru{C(OMe)=CH(CO$_2$R)}(PPh$_3$)$_2$Cp (R = Me (**19**), Et (**20**)) were similarly prepared from RuCl(PPh$_3$)$_2$Cp.[27] As detailed in the Experimental Section, their spectroscopic properties were very similar to those of complexes **13**−**16**, with the exception of the anticipated differences resulting from replacement of the dppe ligand by two PPh$_3$ groups. As previously noted, for steric reasons it is likely that the major isomer is trans, although the NMR spectra are not a reliable guide to the stereochemistry.[27]

In these reactions, the carbene cations **10**, **13**, **14**, **17**, and **18** result from attack by MeOH on C_α of the initially formed vinylidene complexes $[Ru\{=C=CH(CO_2R)\}(PP)Cp]^+$.[28] However, if *tert*-butyl alcohol is used as solvent for the initial reaction between RuCl(dppe)Cp and HC≡CCO$_2$R (R = Me, Et), the orange vinylidenes $[Ru\{=C=CH(CO_2R)\}(dppe)Cp]PF_6$ (R = Me (**2**), Et (**3**)) are obtained, Bu^{t}OH being too bulky to attack at the C_α atoms, which are sterically protected by the Ph groups of the tertiary phosphine ligands. These two compounds were characterized particularly by the downfield triplet resonances of C_α at δ_C 198.8 and 200.5, respectively (J(CP) = 17 Hz for both). Other resonances could be assigned to the groups present, including OMe at δ_H 3.1 and δ_C 51.6, the CH at δ_H 4.1 (for both complexes, with J(CP) = 1 Hz), and the ester CO at δ_C 163.2 and 162.8. Both IR spectra contained ν(CO) at 1697 cm^{-1} and ν(C=C) at 1619 cm^{-1}. Molecular cations at m/z 649 and 663 were found in the ES-MS of **2** and **3**, respectively. Some sensitivity to oxidation (by adventitious air) and solvent used for the ES sample (MeCN) was evident from accompanying ions at m/z 593 ($[Ru(CO)(dppe)Cp]^+$) and 606 ($[Ru(NCMe)(dppe)Cp]^+$).

Deprotonation of vinylidenes **2** and **3** with sodium in Pr^{i}OH readily afforded the corresponding neutral alkynyls Ru(C≡CCO$_2$R)(dppe)Cp (R = Me (**21**), Et (**22**)) as light yellow solids. In their IR spectra, ν(C≡C) bands were found at 2039 and 2050 cm^{-1}, respectively, together with ν(CO) bands at 1658 and 1655 cm^{-1}. The ES-MS contained $[M + H]^+$ ions at m/z 649 and 663, respectively; again, the operating conditions resulted in the presence of the carbonyl and acetonitrile cations found in the spectra of precursors **2** and **3**, no doubt as a result of ready protonation occurring in solution.

Molecular structures. The structures of complexes **13**, **15**, **16**, **21**, and **22** have been confirmed by single-crystal X-ray diffraction studies. The cation of **13** and single molecules of **15** and **21** are portrayed in Figures 2−4; the similar molecules of **16** and **22** are shown in Figures S1 and S2 (Supporting Information), while selected bond parameters of all molecules are collected in Table S1 (Supporting Information). All complexes contain the ruthenium atoms pseudo-octahedrally coordinated by the Cp, two P atoms, and the carbon atom of the unsaturated ligand, with P(1)−Ru−P(2) and P(1,2)−Ru−C(1) angles in the ranges 83.31(3)−84.82(2) and 80.65(4)−93.17(9)°, respectively. For the neutral complexes, the Ru−P

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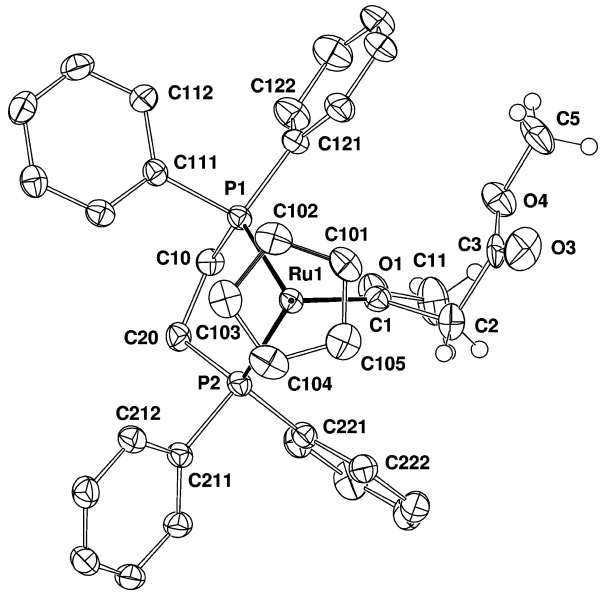

Figure 2. Plot of the cation in $[Ru\{=C(OMe)CH_2(CO_2Me)\}(dppe)Cp]PF_6$ (**13**). Only one component of the disordered carbene ligand is shown.

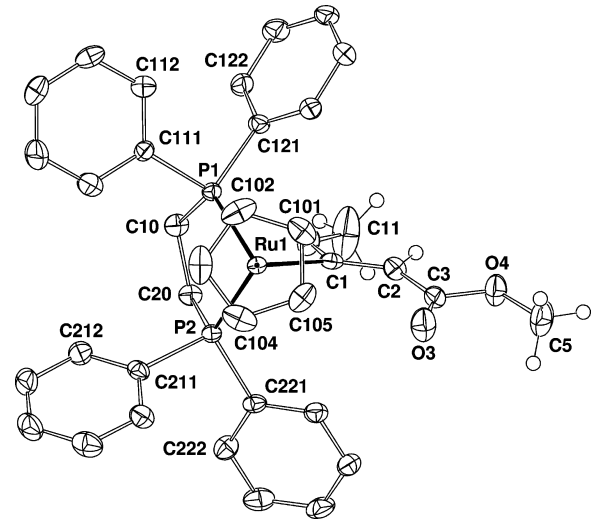

Figure 3. Plot of a molecule of $Ru\{C(OMe)=CH(CO_2Me)\}(dppe)Cp$ (**15**).

distances range between 2.2450(4) and 2.2709(6) Å, while the Ru−C(cp) separations average 2.239−2.267 Å. These parameters do not differ significantly from those found in many other analogous complexes with similar structures. The longer Ru−P distances (2.2890, 2.3043(10) Å) and increased Ru−C(cp) separations (2.267(11) Å (average)) in the cation of **13** reflect the reduced back-bonding into the Ru−P MOs.

The most interesting features relate to the unsaturated ligands derived from the alkynes. In carbene **13**, the Ru−C(1) distance of 1.933(4) Å is consistent with a degree of multiple bonding expected for the Ru=C interaction and may be compared with the longer values of 1.989(2), 2.008(2) Å (alkynyl; Ru−C(sp)) and 2.070(2), 2.083(3) Å (vinyl; Ru−$C(sp^2)$) found in the neutral complexes. Similarly, the C(1)−C(2) distances in **15** and **16** (1.365(4), 1.372(3) Å) and in **21** and **22** (1.221(3), 1.184(2) Å) are consistent with the presence of C=C double and C≡C triple bonds, respectively. Angles at

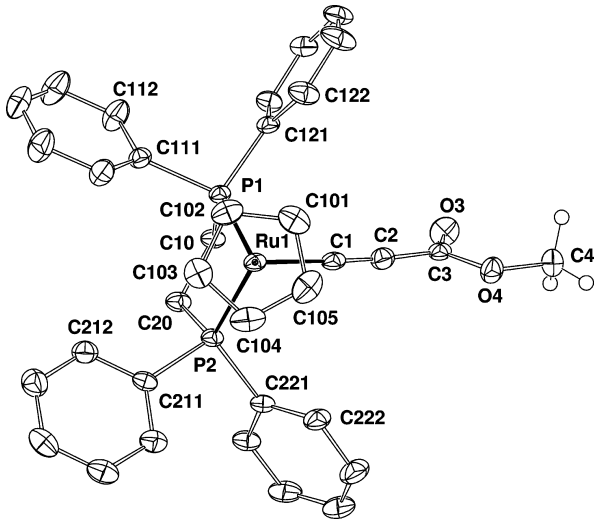

Figure 4. Plot of a molecule of $Ru(C{\equiv}CCO_2Me)(dppe)Cp$ (**21**).

C(1) in **13** and at C(1) and C(2) in **15** and **16** indicate the sp^2 hybridization of this atom, whereas the angles at C(1) and C(2) in alkynyls **21** and **22** (177.8(2), 177.80(14)°) are close to linear, as expected for C(sp) atoms. Within the ester groups, parameters associated with the various C−O bonds are within the usual ranges.

DISCUSSION

The syntheses of complexes described above parallel the well-known alkyne-to-vinylidene conversion by means of a 1,2-H shift, followed by characteristic reactions involving nucleophilic addition of MeOH to C_α of the resulting vinylidenes to give the corresponding alkoxycarbene complexes. Deprotonation of the vinylidenes or carbenes gives neutral alkynyls and alkoxyvinyls, respectively.[27,28]

The unusual decarboxylation of propiolic acids $RC{\equiv}CCO_2H$ or their potassium salts under mild conditions in the presence of complexes containing the Ru(PP)Cp′ moieties may proceed via initial formation of the expected vinylidene $[Ru\{=C{=}CR(CO_2H)\}(PP)Cp']^+$, but this could not be intercepted before decarboxylation occurred. Instead, this reaction provides a useful synthetic approach to the parent vinylidenes which does not use either ethyne or ethynyltrimethylsilane.

To gain more insight into the low-temperature decarboxylation reaction that results in the formation of the parent vinylidene $[Ru(=C{=}CH_2)(dppe)Cp]^+$ (**4**), DFT calculations were used to explore various reaction pathways and to provide information about the intermediate and transition state structures involved. Currently accepted mechanisms for the formation of vinylidene complexes from 1-alkynes include an approach of the metal center to the terminal carbon (C_α) with concomitant 1,2-migration of the proton over the alkyne to C_β[29−31] or formation of the η^2-alkyne complex, followed by oxidative addition of the C−H bond to the metal center and a concerted 1,3-shift of H to C_β.[32] The latter route has been demonstrated experimentally for Rh complexes[32] and, rarely, for Ru.[33] The latter mechanism appears to be more difficult for a $d^6 \rightarrow d^4$ change ($Ru^{II} \rightarrow Ru^{IV}$) than for a $d^8 \rightarrow d^6$ change ($Rh^{I} \rightarrow Rh^{III}$).

In performing the present calculations, two scenarios were considered: one looking at the interaction of $HC{\equiv}CCO_2H$ with RuCl(dmpe)Cp and the other similarly involving the

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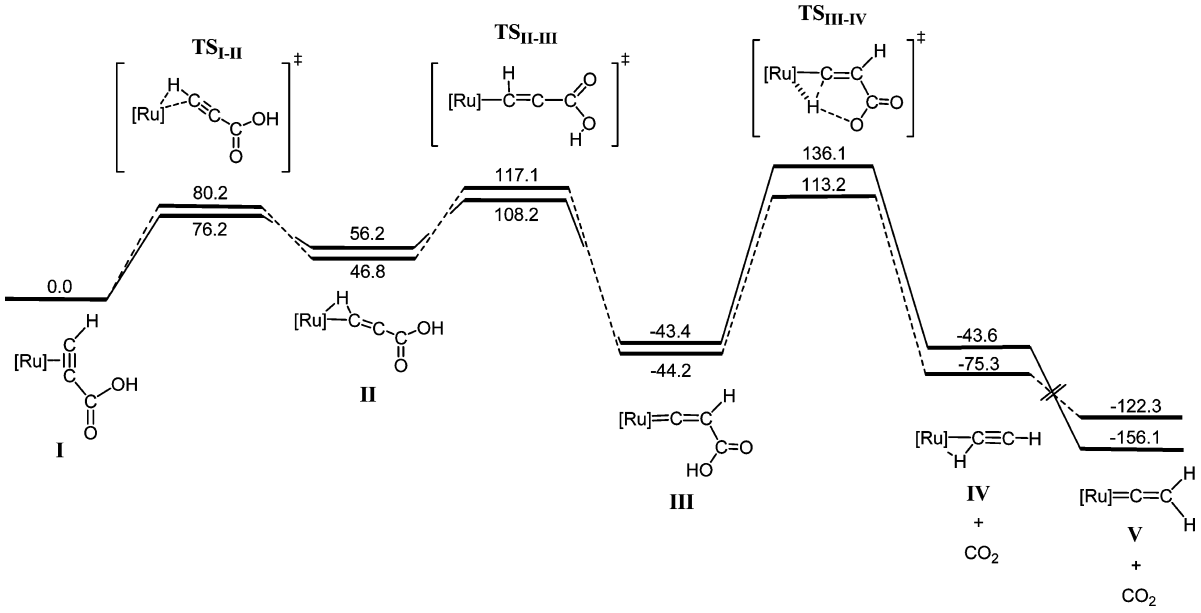

Figure 5. Calculated decomposition route of Ru−propiolic acid complex **I**. [Ru] = Ru(dmpe)Cp. In this and the following figures, energies are given in kJ mol^{-1}.

propiolate ion [HC≡CCO$_2$]$^-$. For the former, three reaction pathways were determined overall, with the starting point for all of them involving the initial formation of an η^2-alkyne intermediate. For the latter scenario, only one reaction pathway was computed, commencing with the formation of an intermediate containing a coordinated carboxylate group.[34,35]

Figure 5 presents one of the three reaction pathways determined for the decarboxylation reaction occurring after the interaction of HC≡CCO$_2$H with RuCl(dmpe)Cp. As shown, the first step of this pathway results in formation of the initial η^2-alkyne−Ru intermediate **I**, which is followed by intramolecular attack on the Ru center by the C−H bond of HC≡CCO$_2$H. This gives reaction intermediate **II** by formation of Ru−C and Ru−H bonds. Transition state **TS$_{I-II}$** is determined to be 76.2 kJ mol^{-1} higher in energy than structure **I** (80.2 kJ mol^{-1} when Bu^{t}OH solvation is taken into account). This is the lowest energetic barrier determined for all reaction pathways involving the interaction of HC≡CCO$_2$H with RuCl(dmpe)Cp (two alternative pathways involving this interaction but with higher energies are given in the Supporting Information). After the formation of **II**, the proton bridging the Ru and C$_\beta$ migrates to C$_\alpha$ via transition state **TS$_{II-III}$**, leading to the formation of the carboxyvinylidene intermediate **III**, which is the global minimum on the potential energy surface of the [Cp(dmpe)Ru]$^+$−HC≡CCO$_2$H interaction. Formation of **III** is then followed by proton transfer from the CO$_2$H group to C$_\alpha$ with concomitant extrusion of CO$_2$ and formation of a [Ru(C$_2$H$_2$)(dmpe)Cp]$^+$ isomer (**IV**). This isomer would be expected to rearrange to the parent vinylidene [Ru(=C=CH$_2$)(dmpe)Cp]$^+$ (**V**), as shown earlier by studies of the alkyne to vinylidene isomerizations occurring in [Ru(HC≡CR)(PMe$_3$)$_2$Cp]$^+$ (R = H, Me)[31] and [Ru(HC≡CCO$_2$Me)(dippe)Cp*]$^+$.[33] Despite the low initial energetic barrier associated with this reaction pathway, the barrier related to the proton transfer from the CO$_2$H group to C$_\alpha$ is 179.5 kJ mol^{-1} (157.4 kJ mol^{-1} with the Bu^{t}OH solvation correction) relative to structure **III**. We regard this as being too large for the decarboxylation reaction to proceed via this mechanism under mild conditions. Hence, as all three reaction pathways possess large energetic barriers associated with the CO$_2$H proton transfer process, it would appear that likely mechanisms for the decarboxylation reaction which involve an initial Ru−(η^2-HC≡CCO$_2$H) intermediate are not viable.

A reaction sequence involving oxidative addition of HC≡CCO$_2$H to the Ru center to give a hydrido−Ru(IV) intermediate is detailed in the Supporting Information (Figure S5 and discussion therein). Although the initial step has a satisfyingly low energy barrier, subsequent processes involve much higher energies and we conclude that this route is improbable.

We then considered an alternative approach involving interaction of the propiolate anion with the Ru center (Figure 6). Initial formation of the coordinated carboxylate intermediate **VI** leads to the formation of the η^2-alkynecarboxylate intermediate **VII** via transition state **TS$_{VI-VII}$**. This is followed by concomitant shortening of the Ru−C$_\alpha$ bond, lengthening of the Ru−C$_\beta$ bond, and cleavage of the C−CO$_2^-$ bond to yield

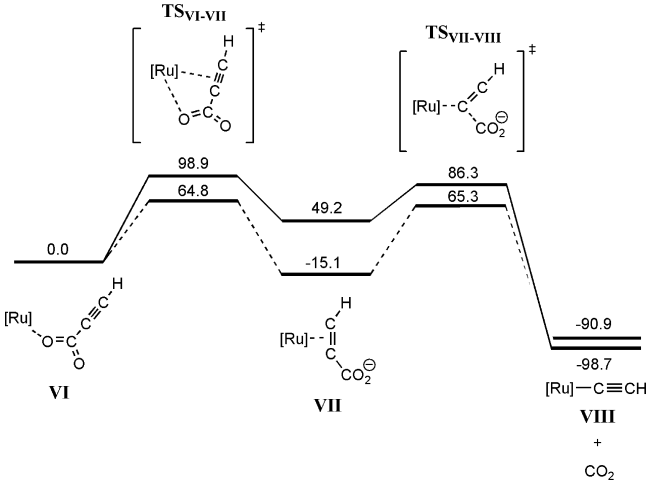

Figure 6. Calculated pathway for decomposition of Ru−propiolate complex **VI**. [Ru] = Ru(dmpe)Cp.

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the parent ethynyl Ru(C≡CH)(dmpe)Cp **VIII** with spontaneous emission of CO_2. Finally, protonation of **VIII** at the C_β atom and rearrangement occurs to give $[Ru(=C=CH_2)(dmpe)Cp]^+$ (**V**). Closer inspection of transition state $\mathbf{TS_{VI\text{-}VII}}$ shows that it is 98.9 kJ mol^{-1} higher in energy than **VI** (64.8 kJ mol^{-1} with the Bu^{t}OH solvation correction). Furthermore, transition state $\mathbf{TS_{VII\text{-}VIII}}$ is 37.1 kJ mol^{-1} higher in energy than **VII** (80.4 kJ mol^{-1} with the Bu^{t}OH solvation correction). Despite the initially encountered barrier being of energy similar to that calculated in the reaction pathway shown in Figure 5, the subsequent energetic barrier for the liberation of CO_2 is significantly lower in energy than any of the barriers encountered in the three reaction pathways which start from propiolic acid itself (relative to gas-phase energetics). Hence, we suggest that the facile decarboxylation reaction that leads to $[Ru(=C=CH_2)(dmpe)Cp]^+$ with extrusion of CO_2 most likely occurs via initial coordination of $HC{\equiv}CCO_2^-$ to the Ru center obtained from the precursor RuCl(dmpe)Cp. This conclusion is also supported by the same decarboxylation reaction occurring with the salt $HC{\equiv}CCO_2K$.

Coupling of Ethynyl and Vinylidene To Form Cyclobutenylidinium. Deprotonation of vinylidene to alkynyl is a well-established reaction, and its reverse is often the reaction of choice for the preparation of vinylidene complexes.[28] However, in the case of the present complexes, while deprotonation of the ester derivatives affords the expected alkynyl or alkoxyvinyl derivatives, when applied to the parent vinylidene, rapid coupling of the ethynyl complex with remaining vinylidene occurred to give the binuclear cyclobutenylidinium complex **11**. Formation of this type of complex has been described on several occasions. The first mentioned treatment of FpC≡CPh (Fp = Fe(CO)$_2$Cp) with $HBF_4{\cdot}OMe_2$ or FSO_3Me to give $[Fp_2(\mu\text{-}C_4RPh_2)]^+$ (R = H, Me).[36−38] Thermolysis of $[Ru(=C=CHMe)(PMe_3)_2Cp][M(CO)_3Cp]$ (M = Cr, Mo, W) in MeCN afforded a mixture of $[Ru(NCMe)(PMe_3)_2Cp]^+$ and $[\{Ru(PMe_3)_2Cp\}_2(\mu\text{-}C_4HMe_2)]^+$.[39] More recently, Fischer and co-workers have described the addition of FpC≡CR (R = Me, Bu, Ph, $C_6H_4NO_2$-4, CO_2Me) to $Cr(=C=CMe_2)(CO)_5$ to give the neutral heterobimetallic analogues $\{(OC)_5Cr\}(\mu\text{-}C_4Me_2R)\{Fp\}$; several related complexes were also prepared, with extensions to butadiynyl complexes such as FpC≡CC≡CR (R = SiMe$_3$, Bu, Ph) affording $\{(OC)_5Cr\}\{\mu\text{-}C_4(C{\equiv}CR)Me_2\}\{Fp\}$ and hence some trimetallic derivatives.[25] Similar chemistry of $Ru(C{\equiv}CC{\equiv}CSiMe_3)(dppe)Cp^*$ afforded $\{Ru(dppe)Cp^*\}_2\{\mu\text{-}C{\equiv}CC_4H_2(SiMe_3)C{\equiv}C\}$ as one product.[26] With the HOMO of alkynyl−metal complexes being localized on C_β,[40,41] electrophilic attack by the vinylidene thereupon readily leads to the bimetallic C_4R_3 compounds (Scheme 2).

Formation of Complexes from $HC{\equiv}CCO_2R$ (R = Me, Et). The syntheses of complexes described above parallel the well-known alkyne-to-vinylidene conversion by means of a 1,2-H shift,[29,30] followed by characteristic reactions involving nucleophilic addition of MeOH to C_α of the resulting vinylidenes to give the corresponding alkoxycarbene complexes. Deprotonation of the vinylidenes or carbenes gives neutral alkynyls and alkoxyvinyls, respectively.[27,28,42]

CONCLUSIONS

Spontaneous decarboxylation of propiolic acids or their potassium salts in similar reactions is attributed to the stability of the parent vinylidene complex, which theoretical studies have already shown to resist the insertion of CO_2. Computational studies of possible reaction mechanisms suggest that the lowest energy pathway derives from an initial structure involving η^2 coordination of $O_2CC{\equiv}C^-$ to the Ru center. Addition of ethynyl−ruthenium to cationic vinylidene−ruthenium moieties afforded a further example of a binuclear cyclobutenylidinium complex by (C_α + C_β) coupling. The formation of several alkynyl, vinylidene, and carbene complexes from $HC{\equiv}CCO_2R$ (R = H, Me, Et) and RuCl(PP)Cp (PP = $(PPh_3)_2$, dppe) is also described, together with single-crystal XRD structure determinations of some of the complexes, these studies supplementing earlier reports.[20,21]

EXPERIMENTAL SECTION

General Considerations. All reactions were carried out under dry nitrogen, although normally no special precautions to exclude air were taken during subsequent workup. Common solvents were dried, distilled under nitrogen, and degassed before use. Separations were carried out by preparative thin-layer chromatography on glass plates (20 × 20 cm^2) coated with silica gel (Merck, 0.5 mm thick).

Instruments. IR spectra were obtained on a Bruker IFS28 FT-IR spectrometer. Spectra in CH_2Cl_2 were obtained using a 0.5 mm path length solution cell with NaCl windows. Nujol mull spectra were obtained from samples mounted between NaCl disks. NMR spectra were recorded on a Varian 2000 instrument (^{1}H at 300.13 MHz, ^{13}C at 75.47 MHz, ^{31}P at 121.503 MHz). Unless otherwise stated, samples were dissolved in $CDCl_3$ contained in 5 mm sample tubes. Chemical shifts are given in ppm relative to internal tetramethylsilane for ^{1}H and ^{13}C NMR spectra and external H_3PO_4 for ^{31}P NMR spectra. Electrospray mass spectra (ES-MS, positive ion mode) were obtained from samples dissolved in MeOH unless otherwise indicated; if necessary, NaOMe was added as an aid to ionization.[43] Solutions were injected into a Fisons VG Platform II spectrometer via a 10 mL injection loop. Nitrogen was used as the drying and nebulizing gas. Ions listed are the most intense in the respective ion clusters. Elemental analyses were carried out by CMAS, Belmont, Victoria, Australia.

Reagents. The complexes RuCl(PP)Cp (PP = $(PPh_3)_2$,[44] dppe[45]), $Ru(C{\equiv}CH)(PP)Cp$,[20,46] and $[Ru(=C=CH_2)(PP)Cp]PF_6$[20,46] were obtained as previously described. $HC{\equiv}CCO_2H$, $HC{\equiv}CCO_2K$, $PhC{\equiv}CCO_2K$, and $(HO_2C)C{\equiv}C(CO_2K)$ were purchased from Aldrich and used as received; methyl and ethyl propiolates were prepared from $HC{\equiv}CCO_2H$.

Decarboxylation of Propiolic Acids. *Reactions of Propiolic Acid.* Propiolic acid (77 mg, 1.10 mmol) was added to a suspension of RuCl(dppe)Cp (302 mg, 0.502 mmol) and $[NH_4]PF_6$ (82 mg, 0.499 mmol) in dry degassed *t*-BuOH (5 mL). The mixture was refluxed for 2 h to give a light yellow precipitate. Hot solvent was removed by cannula, and the light yellow precipitate was washed with Et_2O (2 × 4 mL) to remove traces of *t*-BuOH and dried under vacuum to give $[Ru(=C=CH_2)(dppe)Cp]PF_6$ (**4**).

$Ag[PF_6]$ (42 mg, 0.166 mmol) was added to a solution of RuCl(dppe)Cp (100 mg, 0.166 mmol) in degassed thf (15 mL) and stirred at room temperature for 15 min. The solution immediately changed to red-orange with the precipitation of AgCl. After filtration, propiolic acid (23 mg, 0.333 mmol) was added to the filtrate and the mixture stirred at room temperature for 2 h to give a yellow-orange solution. Solvent was removed under vacuum, the residue was extracted with CH_2Cl_2 (3 mL), and the solution was filtered into rapidly stirred Et_2O (30 mL) to give a light brown precipitate. Filtration, washing with Et_2O (3 mL), and drying under vacuum gave $[Ru(CO)(dppe)Cp]PF_6$.

Propiolic acid (48 mg, 0.68 mmol) was added to a suspension of RuCl(dppe)Cp (203 mg, 0.338 mmol) and $[NH_4]PF_6$ (55 mg, 0.338 mmol) in degassed MeOH (10 mL). The reaction mixture was stirred at the reflux point for 2 h to give an off-white precipitate. This was isolated by filtration, washed with MeOH (2 mL), and dried under high vacuum to give $[Ru\{=CMe(OMe)\}(dppe)Cp]PF_6$ (**5**; 49 mg, 19%).

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Reactions of $KO_2CC{\equiv}CR$ (R = H, Ph). In general, reactions between powdered RuCl(PP)Cp′ ((PP)Cp′ = $(PPh_3)_2$Cp, (dppe)Cp*) and $KO_2CC{\equiv}CR$ (R = H, Ph) were carried out in refluxing MeOH for several hours, although they proceeded slowly at room temperature. Qualitatively, the reaction of $RuCl(PPh_3)_2Cp$ was faster than that of RuCl(dppe)Cp*.

A mixture of $RuCl(PPh_3)_2Cp$ (100 mg, 0.138 mmol) and $HC{\equiv}CCO_2K$ (22 mg, 0.207 mmol) in MeOH (5 mL) was heated at the reflux point for 3 h, after which time a yellow precipitate had separated. After cooling, the solid was collected and washed with MeOH (2 × 3 mL) and hexanes (4 mL) to give $Ru(C{\equiv}CH)(PPh_3)_2Cp$ (**6**; 66 mg, 67%). ^{1}H NMR: δ 2.02 (t, J(HP) = 3 Hz, 1H, ≡CH), 4.28 (s, 5H, Cp), 7.09−7.51 (m, 30H, Ph). ^{31}P NMR: δ 51.0 (s, PPh_3). The reaction between $RuCl(PPh_3)_2Cp$ and $HC{\equiv}CCO_2K$, carried out in the presence of $[NH_4]PF_6$, gave $[Ru(=C=CH_2)(PPh_3)_2Cp]PF_6$.

The product from RuCl(dppe)Cp* (150 mg, 0.223 mmol) and $HC{\equiv}CCO_2K$ (36 mg, 0.336 mmol) was yellow Ru(C≡CH)(dppe)Cp* **7** (97 mg, 66%). ^{1}H NMR (C_6D_6): δ 1.69 (s, 15H, Cp*), 2.06 (t, J(HP) = 3 Hz, 1H, HC≡), 2.00, 2.83 (2m, 2 × CH_2, CH_2P), 7.03−8.04 (m, 20H, Ph). ^{31}P NMR: δ 82.3 (s, dppe).

Similarly, $RuCl(PPh_3)_2Cp$ (100 mg, 0.138 mmol) and $KO_2CC{\equiv}CPh$ (32 mg, 0.152 mmol) in MeOH (5 mL) gave, after refluxing for 90 min, a yellow precipitate of $Ru(C{\equiv}CPh)(PPh_3)_2Cp$ (**9**; 95 mg, 87%). ^{1}H NMR: δ 4.33 (s, 5H, Cp), 7.07−7.53 (m, 35H, Ph). ^{31}P NMR: δ 51.5 (s, PPh_3).

Reactions of $KO_2CC{\equiv}CCO_2R$ (R = H, K). A mixture containing $RuCl(PPh_3)_2Cp$ (191 mg, 0.263 mmol), $(HO_2C)C{\equiv}C(CO_2K)$ (20 mg, 0.132 mmol), and $[NH_4]PF_6$ (23 mg, 0.138 mmol) in MeOH (8 mL) was heated at the reflux point for 6 h. After this time, unreacted $RuCl(PPh_3)_2Cp$ (81 mg, 42%) was removed by filtration. The filtrate was layered with Et_2O and kept at −10 °C for 24 h to give yellow $[Ru\{=CMe(OMe)\}(PPh_3)_2Cp]PF_6$ (**10**; 62 mg, 53%). ^{1}H NMR: δ 2.96 (s, 3H, Me), 3.21 (s, 3H, OMe), 4.69 (s, 5H, Cp), 6.89−7.38 (m, 30H, Ph). ^{13}C NMR δ 46.78 (Me), 61.00 (OMe), 91.58 (Cp), 128.28−136.28 (Ph), 308.78 (t, J(CP) = 13 Hz, Ru=C). ^{31}P NMR: δ 48.3 (PPh_3), −142.3 (sept, J(PF) = 708 Hz, PF_6). ES-MS (MeOH, m/z): 429, $[Ru(PPh_3)Cp]^+$.

Addition of $RuCl(PPh_3)_2Cp$ (191 mg, 0.263 mg) to a mixture of $(HO_2C)C{\equiv}C(CO_2K)$ (20 mg, 0.132 mmol) and K_2CO_3 (18 mg, 0.132 mmol) in MeOH (8 mL) and heating at the reflux point for 2.5 h afforded a yellow precipitate of $RuH(PPh_3)_2Cp$ (119 mg, 65%).[47] ^{1}H NMR (C_6D_6): δ −11.09 (t, J(PH) = 34 Hz, 1H, RuH), 4.49 (s, 5H, Cp), 6.89−7.56 (m, 30H, Ph). ^{13}C NMR (C_6D_6): δ 82.39 (Cp), 127.59−142.43 (Ph). ^{31}P NMR (C_6D_6): δ 69.2 (PPh_3). ES-MS (MeOH, m/z): 690, $[M - H]^+$; 429 $[Ru(PPh_3)Cp]^+$.

Similarly, RuCl(dppe)Cp* (176 mg, 0.263 mmol), $(HO_2C)C{\equiv}C(CO_2K)$ (20 mg, 0.132 mmol), and K_2CO_3 (18 mg, 0.32 mmol) in refluxing MeOH (8 mL) after 18 h afforded RuH(dppe)Cp* (92 mg, 55%).[48] ^{1}H NMR (C_6D_6): δ −13.50 (t, J(PH) = 34 Hz, 1H, RuH), 1.76 (s, 15H, Cp*), 1.89, 1.94 (2s (br), 2 × 2H, dppe), 7.10−7.82 (m, 20H, Ph). ^{31}P NMR (C_6D_6): δ 69.2 (PPh_2). ES-MS (MeOH, m/z): 635, $[M - H]^+$.

Cyclobutenylidinium Complex. *Synthesis of $[\{Ru(dppe)Cp\}_2(\mu\text{-}C_4H_3)]PF_6$ (**11**).* *n*-BuLi (0.16 mL, 1.74 M, 0.28 mmol) was added to a solution of $[Ru(=C=CH_2)(dppe)Cp]PF_6$ (103 mg, 0.139 mmol) in dry degassed thf (20 mL) at −78 °C. The reaction mixture was stirred at −78 °C for 15 min before being warmed to room temperature for 15 min, at which time the color had changed to orange-yellow. After the mixture was cooled to −78 °C, $SiClMe_3$ (0.026 mL, 0.208 mmol) was added to remove excess *n*-BuLi and the mixture was stirred for 30 min. After a further 30 min at room temperature, solvent was removed under vacuum to give a yellow-brown solid, which was recrystallized from acetone/hexane to give brown needles of $[\{Ru(dppe)Cp\}_2(\mu\text{-}C_4H_3)]PF_6$ (**11**; 118 mg, 86%).

A solution containing $[Ru(=C=CH_2)(dppe)Cp]PF_6$ (75.8 mg, 0.103 mmol) and [Ru(C≡CH)(dppe)Cp] (60.8 mg, 0.103 mmol) in degassed thf (25 mL) was stirred at room temperature for 2 h, after which time the yellow solution had changed to yellow-brown. After removal of solvent, a CH_2Cl_2 extract of the residue was filtered into Et_2O (30 mL), precipitating a yellow-brown solid. Filtration and washing with Et_2O (5 mL) gave **11**, which was dried under vacuum. Anal. Calcd for $C_{66}H_{57}F_6P_5Ru_2$: C, 60.00; H, 4.35; *M* (cation), 1321. Found: C, 60.01; H, 4.42. IR (Nujol, cm^{-1}): 1980 s ν(CCC), 839 vs ν(PF). ^{1}H NMR (d_6-acetone): δ 7.6−7.2 (m, 40H, Ph), 5.3 (1H, CH), 4.9 (10H, Cp), 2.87 (8H, PCH_2), 2.83 (t, 2H, CH_2). ^{13}C NMR (d_6-acetone): δ 262.1 (m, Ru−C), 174.1 (CH), 141.2−129.0 (m, Ph), 87.6 (Cp), 54.9 (s, CH_2), 27.3 (t, PCH_2). ^{31}P NMR (d_6-acetone): δ 86.1 (dppe), −142.7 (sep, J(PF) = 708 Hz, PF_6). ES-MS (MeOH−MeCN, m/z): 565, $[Ru(dppe)Cp]^+$; 606, $[Ru(MeCN)(dppe)Cp]^+$; 1180, $[\{Ru(dppe)Cp\}_2(C_4H_3)]^+$.

*Attempts To Prepare $[\{Ru(dppe)Cp\}(\mu\text{-}C_4H_3)\{Ru(dppe)Cp^*\}]PF_6$ (**12**).* A solution of $[Ru(=C=CH_2)(dppe)Cp^*]PF_6$ (49 mg, 0.061 mmol) and Ru(C≡CH)(dppe)Cp (36 mg, 0.061 mmol) in degassed thf (20 mL) was stirred at room temperature for 2 h. The yellow solution changed to yellow-brown. After removal of solvent, the residue was extracted with CH_2Cl_2 and filtered into Et_2O (30 mL), precipitating yellow-brown $[\{Ru(dppe)Cp\}_2(\mu\text{-}C_4H_3)]PF_6$ (**11**). This was isolated by filtration, washed with Et_2O (5 mL), and dried under vacuum.

A solution containing $[Ru(=C=CH_2)(dppe)Cp]PF_6$ (93 mg, 0.127 mmol) and Ru(C≡CH)(dppe)Cp*] (84 mg, 0.127 mmol) in degassed thf (20 mL) similarly gave yellow-brown **11**.

Reactions of Propiolic Esters with Chloro−Ruthenium Complexes. *$[Ru\{=C(OMe)CH_2(CO_2R)\}(dppe)Cp]PF_6$ (R = Me (**13**), Et (**14**)).* $HC{\equiv}CCO_2R$ (61 mg for **13** (R = Me), 71 mg for **14** (R = Et); 0.722 mmol) was added to a suspension of RuCl(dppe)Cp (203 mg, 0.337 mmol) and $[NH_4]PF_6$ (55 mg, 0.338 mmol) in degassed MeOH (20 mL). The reaction mixture was stirred at the reflux point for 1 h. After removal of solvent, the residue was extracted with CH_2Cl_2 and the extract filtered into Et_2O (30 mL), precipitating a light yellow solid. This was isolated by filtration, washed with Et_2O (2 mL), and dried under vacuum. The precipitate was recrystallized from CH_2Cl_2/MeOH under nitrogen.

R = Me (**13**; 223 mg, 0.270 mmol, 80%). ^{1}H NMR: δ 7.6−7.1 (m, 20H, Ph), 5.1 (5H, Cp), 3.8 (2H, CH_2), 3.7 (3H, OMe), 3.0 (m, 2H, PCH_2), 2.9 (3H, Me), 2.7 (m, 2H, PCH_2). ^{13}C NMR: δ 293.4 (t, J(CP) = 13 Hz, Ru=C), 163.7 (CO_2), 133.3−128.7 (Ph), 90.8 (Cp), 61.3, 60.1, 52.9, 28.2 (t, CH_2CH_2). ^{31}P NMR: δ 89.5 (dppe), −142.8 (sep, J(PF) = 708 Hz, PF_6). ES-MS (m/z): 564, $[Ru(dppe)Cp]^+$; 592, $[Ru(CO)(dppe)Cp]^+$; 680, $[Ru\{C(OMe)CH_2(CO_2Me)\}(dppe)Cp]^+$. IR (KBr, cm^{-1}): 1737 s ν(ester CO), 1247 s ν(CO), 839 vs ν(PF). Anal. Calcd for $C_{36}H_{37}F_6O_3P_3Ru$: C, 52.37; H, 4.52; *M* (cation), 825. Found: C, 52.28; H, 4.54.

R = Et (**14**; 192 mg, 0.229 mmol, 68%). ^{1}H NMR: δ 7.6−7.1 (m, 20H, Ph), 5.1 (5H, Cp), 4.1 (q, 2H, CH_2), 3.8 (2H, CH_2), 3.0 (m, 2H, PCH_2), 2.9 (3H, OMe), 2.7 (m, 2H, PCH_2), 1.2 (t, 3H, Me). ^{13}C NMR: δ 293.1 (t, J(CP) = 13 Hz, Ru=C), 163.3 (CO_2), 139.0−128.7 (Ph), 90.8 (Cp), 61.9, 61.1, 60.3, 28.0 (t, CH_2CH_2), 14.0 (Me). ^{31}P NMR: δ 89.6 (dppe), −142.8 (sep, J(PF) = 708 Hz, PF_6). ES-MS (m/z): 565, $[Ru(dppe)Cp]^+$; 595, $[Ru(CO)(dppe)Cp]^+$; 695, $[Ru\{C(OMe)CH_2(CO_2Et)\}(dppe)Cp]^+$. IR (KBr, cm^{-1}): 1725 s ν(ester CO), 1275 s ν(CO), 839 vs ν(PF). Anal. Calcd for $C_{37}H_{39}F_6O_3P_3Ru$: C, 52.92; H, 4.68; *M* (cation), 840. Found: C, 52.95; H, 3.49.

*$Ru\{C(OMe)=CH(CO_2R)\}(dppe)Cp$ (R = Me (**15**), Et (**16**)).* Sodium (4.17 mg, 0.181 mmol) was added to a solution of $[Ru\{=C(OMe)CH_2(CO_2R)\}(dppe)Cp]PF_6$ (150 mg for **15** (R = Me), 153 mg for **16** (R = Et); 0.181 mmol) in MeOH (20 mL). As sodium slowly dissolved in solution, a light yellow precipitate separated. The reaction mixture was stirred at room temperature for 15 min. The precipitate was isolated by filtration, washed with MeOH (2 mL), dried under vacuum, and recrystallized from CH_2Cl_2/hexane.

R = Me (**15**; 71 mg, 0.104 mmol, 58%). This complex is obtained as a 4/1 isomeric mixture. ^{1}H NMR: major isomer, δ 4.9 (1H, CH), 4.6 (5H, Cp), 3.5 (3H, CO_2Me), 2.2 (3H, OMe); minor isomer, δ 5.3 (1H, CH), 4.5 (5H, Cp), 3.4 (3H, CO_2Me), 2.7 (3H, OMe); common resonances, δ 7.8−7.1 (m, 20H, Ph), 2.7, 2.6 (2m, 2 × 2H, PCH_2). ^{13}C NMR: major isomer, δ 170.5 (CO_2), 100.6 (CH), 85.1 (Cp), 53.9, 49.5, 29.7 (t, CH_2CH_2); minor isomer, δ 160.4 (CO_2), 103.0 (CH), 86.2 (Cp), 62.1, 49.2, 29.2 (t, CH_2CH_2); common resonances, δ 224.9 (t, J(CP) = 15 Hz, Ru−C), 144.8−127.2 (m, Ph). ^{31}P NMR: δ 96.5

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(minor isomer), 93.0 (major isomer). ES-MS (m/z): 681, [Ru(C(OMe)CHCO$_2$Me)(dppe)Cp]$^+$. IR (KBr, cm^{-1}): 1667 m ν(CO), 1493 s ν(C=C), 1141 s ν(CO), 1048 s ν(CO). Anal. Calcd for $C_{36}H_{36}O_3P_2Ru$: C, 63.62; H, 5.34; *M*, 680 Found: C, 63.60; H, 5.27.

R = Et (**16**; 89 mg, 0.104 mmol, 77%). This complex is obtained as a 4/1 isomeric mixture. ^{1}H NMR: major isomer, δ 4.9 (1H, CH), 4.6 (5H, Cp), 4.0 (q, 2H, CH$_2$), 2.2 (3H, OMe), 1.2 (t, CH$_3$); minor isomer, δ 5.3 (1H, CH), 4.6 (5H, Cp), 3.8 (q, 2H, CH$_2$), 2.6 (3H, OMe), 1.1 (t, Me); common resonances, δ 7.8−7.1 (m, 20H, Ph), 2.7 (m, 2H, PCH$_2$), 2.5 (m, 2H, PCH$_2$). ^{13}C NMR: major isomer, δ 224.3 (t, *J*(CP) = 15 Hz, Ru−C), 170.4 (CO$_2$, major), 101.3 (CH), 85.4 (Cp), 57.5, 54.1, 29.8 (t, CH$_2$CH$_2$), 15.1 (Me); minor isomer, δ 229.2 (t, *J*(CP) = 15 Hz, Ru−C), 160.2 (CO$_2$), 104.1 (CH), 86.3 (Cp), 62.3, 53.9, 29.3 (t, CH$_2$CH$_2$), 15.0 (Me); common resonances, δ 144.8−127.4 (m, Ph). ^{31}P NMR: δ: 96.1 (minor isomer), 92.7 (major isomer). ES-MS (m/z): 565, [Ru(dppe)Cp]$^+$; 593, [Ru(CO)(dppe)Cp]$^+$; 695, [Ru{C(OMe)CH(CO$_2$Et)}(dppe)Cp]$^+$. IR (KBr, cm^{-1}): 1667 m ν(CO), 1493 s ν(C=C), 1141 s ν(CO), 1046 s ν(CO). Anal. Calcd for $C_{37}H_{38}O_3P_2Ru$: C, 64.06; H, 5.52; *M*, 694. Found: C, 63.96; H, 5.64.

*[Ru{=C(OMe)CH$_2$(CO$_2$R)}(PPh$_3$)$_2$Cp]PF$_6$ (R = Me (**17**), Et (**18**)).* HC≡CCO$_2$R (61 mg for **17** (R = Me), 71 mg for **18** (R = Et); 0.722 mmol) was added to a suspension of RuCl(PPh$_3$)$_2$Cp (245 mg, 0.337 mmol) and [NH$_4$]PF$_6$ (55 mg, 0.338 mmol) in degassed MeOH (20 mL). The reaction mixture was stirred at reflux for 1 h. After removal of solvents, the residue was extracted with CH$_2$Cl$_2$ and filtered into Et$_2$O (30 mL), precipitating a light orange solid. This was isolated by filtration, washed with Et$_2$O (2 mL), dried under vacuum, and recrystallized from CH$_2$Cl$_2$/MeOH under nitrogen.

R = Me (**17**; 263 mg, 0.276 mmol, 82%). ^{1}H NMR: δ 7.7−6.9 (m, 30H, Ph), 4.8 (5H, Cp), 4.5 (2H, CH$_2$), 3.8 (3H, OMe), 3.4 (3H, CO$_2$Me). ^{13}C NMR: δ 297.9 (m, Ru=C), 164.9 (CO$_2$), 135.5−128.2 (Ph), 91.9 (Cp), 90.6, 61.9, 52.2. ^{31}P NMR: δ 46.2 (PPh$_3$), −142.8 (sep, *J*(PF) = 708 Hz, PF$_6$). ES-MS (m/z): 719, [Ru(CO)(PPh$_3$)$_2$Cp]$^+$; 807, [Ru{C(OMe)CH$_2$(CO$_2$Me)}(PPh$_3$)$_2$Cp]$^+$. IR (KBr, cm^{-1}): 1731 s ν(ester CO), 1264 s ν(CO), 839 vs ν(PF). Anal. Calcd for $C_{46}H_{43}F_6O_3P_3Ru$: C, 58.05; H, 4.55; *M* (cation), 952. Found: C, 57.94; H, 4.54.

R = Et (**18**; 234 mg, 0.242 mmol, 72%). ^{1}H NMR: δ 7.7−6.9 (m, 30H, Ph), 4.8 (5H, Cp), 4.5 (2H, CH$_2$), 4.2 (q, 2H, CH$_2$), 3.4 (3H, OMe), 1.3 (t, 3H, CH$_3$). ^{13}C NMR: δ 298.4 (t, *J*(CP) = 13 Hz, Ru=C), 164.5 (CO$_2$), 135.6−128.2 (Ph), 91.9 (Cp), 90.7, 65.8, 62.2, 13.9. ^{31}P NMR: δ 46.1 (PPh$_3$), −142.8 (sep, *J*(PF) = 708 Hz, PF$_6$). ES-MS (m/z): 719, [Ru(CO)(PPh$_3$)$_2$Cp]$^+$; 821, [Ru{C(OMe)CH$_2$(CO$_2$Et)}(PPh$_3$)$_2$Cp]$^+$. IR (KBr, cm^{-1}): 1725 s ν(ester C−O), 1264 s ν(CO), 839 vs ν(PF). Anal. Calcd for $C_{47}H_{45}F_6O_3P_3Ru$: C, 58.45; H, 4.70; *M* (cation), 966. Found: C, 58.33; H, 4.76.

*Ru{C(OMe)=CH(CO$_2$R)}(PPh$_3$)$_2$Cp (R = Me (**19**), Et (**20**)).* Sodium (4 mg, 0.18 mmol) was added to a solution of [Ru{=C(OMe)CH$_2$(CO$_2$R)}(PPh$_3$)$_2$Cp]PF$_6$ (172 mg for **19** (R = Me), 175 mg for **20** (R = Et); 0.181 mmol) in MeOH (20 mL). As the sodium slowly dissolved, a light yellow precipitate formed. The reaction mixture was stirred at room temperature for 15 min. The precipitate was isolated by filtration, washed with MeOH (2 mL), dried under vacuum, and recrystallized from CHCl$_2$/hexane.

t-BuOK (37 mg, 0.332 mmol) was added to a solution of [Ru{=C(OMe)CH$_2$(CO$_2$Me)}(PPh$_3$)$_2$Cp]PF$_6$ (105 mg, 0.110 mmol) in dry thf (30 mL). The reaction mixture immediately changed color from light orange to red-orange. After the mixture was stirred at room temperature for 15 min, solvent was removed under vacuum and the residue was recrystallized from benzene/hexane, yielding yellow crystals.

R = Me (**19**; 95 mg, 0.117 mmol, 65%). The product was obtained as a 7/3 isomeric mixture. ^{1}H NMR: major isomer, δ 5.4 (1H, CH), 4.4 (5H, Cp), 3.7 (3H, CO$_2$Me), 2.5 (3H, OMe); minor isomer, δ 5.8 (1H, CH), 4.3 (5H, Cp), 3.5 (3H, CO$_2$Me), 3.1 (3H, OMe); common resonances, δ 7.3−7.1 (m, 30H, Ph). ^{13}C NMR: major isomer, δ 170.9 (CO$_2$), 102.1 (CH), 85.8 (Cp), 58.2, 49.8; minor isomer, δ 160.8 (CO$_2$), 103.9 (CH), 87.3 (Cp) 62.6, 52.0; common resonances, δ 222.9 (t, *J*(CP) = 16 Hz, Ru−C), 140.1−127.2 (Ph). ^{31}P NMR (CDCl$_3$): δ 51.9 (major), 51.0 (minor). ES-MS (m/z): 806, [Ru{C(OMe)CH(CO$_2$Me)}(PPh$_3$)$_2$Cp]$^+$. IR (KBr, cm^{-1}): 1686 m ν(CO), 1493 s ν(C=C), 1149 s ν(CO), 1046 s ν(CO). Anal. Calcd for $C_{46}H_{42}O_3P_2Ru$: C, 68.56; H, 5.25; *M*, 806. Found: C, 68.58; H, 5.23.

R = Et (**20**; 89 mg, 0.108 mmol, 60%). This complex was obtained as a 65/35 isomeric mixture. ^{1}H NMR: major isomer, δ 5.4 (1H, CH), 4.4 (5H, Cp), 4.2 (2H, CH$_2$), 2.5 (3H, OMe), 1.3 (3H, Me); minor isomer, δ 5.8 (1H, CH), 4.3 (5H, Cp), 4.0 (2H, CH$_2$), 3.1 (3H, OMe), 1.2 (3H, Me); common resonances, δ 7.4−7.2 (m, 30H, Ph). ^{13}C NMR: major isomer, δ 170.5 (CO$_2$), 102.6 (CH), 85.8 (Cp), 57.8, 58.1, 14.9; minor isomer, δ 160.5 (CO$_2$), 104.4 (CH), 87.2 (Cp), 62.6, 57.6, 14.3; common resonances, δ 222.1 (t, *J*(CP) = 16 Hz, Ru−C), 140.2−127.0 (Ph). ^{31}P NMR: δ 51.9 (major), 51.0 (minor). ES-MS (m/z): 820, [Ru{C(OMe)CH(CO$_2$Et)}(PPh$_3$)$_2$Cp]$^+$. IR (KBr, cm^{-1}): 1681 m ν(CO), 1493 s ν(C=C), 1144 s ν(CO), 1048 s ν(CO). Anal. Calcd for $C_{47}H_{44}O_3P_2Ru$: C, 68.85; H, 5.41; *M*, 820. Found: C, 68.73; H, 5.29.

*[Ru{=C=CH(CO$_2$R)}(dppe)Cp]PF$_6$ (R = Me (**2**), Et (**3**)).* HC≡CCO$_2$R (62 mg for **2** (R = Me), 73 mg for **3** (R = Et); 0.741 mmol) was added to a suspension of RuCl(dppe)Cp (204 mg, 0.339 mmol) and [NH$_4$]PF$_6$ (55 mg, 0.338 mmol) in degassed *t*-BuOH (5 mL). The reaction mixture was stirred at the reflux point for 2 h, generating an orange precipitate. After removal of the hot solvent by cannula filtration, the orange precipitate was washed with Et$_2$O (2 × 4 mL) to remove traces of *t*-BuOH and dried under vacuum.

R = Me (**2**; 213 mg, 0.268 mmol, 79%). ^{1}H NMR: δ 7.9−7.1 (m, 20H, Ph), 5.5 (5H, Cp), 4.1 (t, 1H, CH), 3.1 (3H, Me), 3.0 (m, 4H, PCH$_2$). ^{13}C NMR: δ 198.8 (t, *J*(CP) = 16 Hz, Ru=C), 163.2 (CO$_2$), 135.8−129.0 (Ph), 110.2 (CH), 88.1 (Cp), 51.6 (Me), 29.0 (t, PCH$_2$). ^{31}P NMR: δ 76.1 (dppe), −142.8 (sept, J(PF) = 709 Hz, PF$_6$). ES-MS (m/z): 565, [Ru(dppe)Cp]$^+$; 593, [Ru(CO)(dppe)Cp]$^+$; 606, [Ru(MeCN)(dppe)Cp]$^+$; 649, [Ru(CCHCO$_2$Me)(dppe)Cp]$^+$. IR (KBr, cm^{-1}): 1697 s ν(CO), 1619 s ν(C=C), 839 vs ν(PF). Anal. Calcd for $C_{35}H_{33}F_6O_2P_3Ru$: C, 52.97; H, 4.19; *M* (cation), 749. Found: C, 52.85; H, 4.18.

R = Et (**3**; 208 mg, 0.257 mmol, 76%). ^{1}H NMR: δ 7.6−7.2 (m, 20H, Ph), 5.5 (5H, Cp), 4.1 (t, 1H, CH), 3.68 (q, 2H, CH$_2$), 3.0 (m, 4H, PCH$_2$), 0.9 (t, 3H, Me). ^{13}C NMR: δ 200.5 (t, *J*(CP)=17 Hz, Ru=C), 162.8 (CO$_2$), 134.8−127.9 (Ph), 110.5 (CH), 88.1 (Cp), 60.5 (CH$_2$), 27.7 (t, PCH$_2$), 14.1 (Me). ^{31}P NMR: δ 75.9 (dppe), −142.7 (sept, *J*(PF) = 708 Hz, PF$_6$). ES-MS (m/z): 565, [Ru(dppe)Cp]$^+$; 593, [Ru(CO)(dppe)Cp]$^+$; 606, [Ru(MeCN)(dppe)Cp]$^+$; 663, [Ru(CCHCO$_2$Et)(dppe)Cp]$^+$. IR (KBr, cm^{-1}): 1689 s ν(CO), 1613 s ν(C=C), 833 vs ν(PF). Anal. Calcd for $C_{36}H_{35}F_6O_2P_3Ru$: C, 53.54; H, 4.37; *M* (cation), 808. Found: C, 53.57; H, 4.25.

*Ru(C≡CCO$_2$R)(dppe)Cp (R = Me (**21**), Et (**22**)).* Sodium (18 mg, 0.80 mmol) was added to a solution of [Ru{=C=CH(CO$_2$R)}(dppe)Cp]PF$_6$ (159 mg for **21** (R = Me), 162 mg for **22** (R = Et); 0.20 mmol) in Pr^{i}OH (10 mL). The reaction mixture was stirred at room temperature for 2 days, giving a light yellow precipitate. Solvent was removed by cannula filtration, and the residue was dried under vacuum.

R = Me (**21**; 65 mg, 0.100 mmol, 50%). ^{1}H NMR: δ 7.8−7.2 (m, 20H, Ph), 4.8 (5H, Cp), 3.4 (3H, Me), 2.8 (m, 2H, PCH$_2$), 2.3 (m, 2H, PCH$_2$). ^{13}C NMR: δ 152.8 (CO$_2$), 141.2−127.6 (m, Ph), 104.8 (Ru−C), 88.0 (C), 83.4 (Cp), 51.0 (Me), 27.9 (t, PCH$_2$). ^{31}P NMR: δ 85.6 (dppe). ES-MS (m/z): 565, [Ru(dppe)Cp]$^+$; 593, [Ru(CO)(dppe)Cp]$^+$; 606, [Ru(MeCN)(dppe)Cp]$^+$; 649, [Ru(C$_2$CO$_2$Me)(dppe)CpH]$^+$. IR (KBr, cm^{-1}): 2039 s ν(C≡C), 1658 s ν(CO). Anal. Calcd for $C_{35}H_{32}O_2P_2Ru$: C, 64.91; H, 4.98; *M*, 648. Found: C, 64.92; H, 4.90.

R = Et (**22**; 71 mg, 0.108 mmol, 54%). ^{1}H NMR: δ 7.8−7.2 (m, 20H, Ph), 4.8 (5H, Cp), 3.8 (q, 2H, CH$_2$), 2.8 (m, 2H, PCH$_2$), 2.3 (m, 2H, PCH$_2$), 1.1 (t, 3H, Me). ^{13}C NMR: δ 152.7 (CO$_2$), 141.5−127.6 (m, Ph), 105.3 (Ru−C), 83.3 (Cp), 79.6 (C), 59.7 (CH$_2$), 27.9 (t, PCH$_2$), 14.5 (Me). ^{31}P NMR: δ 85.9. ES-MS (m/z): 565, [Ru(dppe)Cp]$^+$; 606, [Ru(MeCN)(dppe)Cp]$^+$; 663, [Ru(C$_2$CO$_2$Et)(dppe)Cp]$^+$. IR (KBr, cm^{-1}): 2050 s ν(C≡C), 1655 s ν(CO) cm^{-1}.

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Table 1. Crystal Data and Refinement Details

	11	13	15	16	21	22
formula	$C_{66}H_{61}F_6P_4Ru_2{\cdot}F_6P.2C_3H_6O$	$C_{36}H_{37}O_3P_2Ru{\cdot}F_6P$	$C_{36}H_{36}O_3P_2Ru$	$C_{37}H_{38}O_3P_2Ru$	$C_{35}H_{32}O_2P_2Ru{\cdot}CH_2Cl_2$	$C_{36}H_{34}O_2P_2Ru$
MW	1441.29	825.64	679.66	693.68	732.54	661.64
cryst syst	monoclinic	monoclinic	orthorhombic	orthorhombic	triclinic	monoclinic
space group	$C2/c$	$P2_1/n$	$Pna2_1$	$Pna2_1$	$P\bar{1}$	$P2_1/c$
a/Å	46.357(3)	16.548(2)	17.869(2)	18.276(2)	8.8398(14)	9.4256(7)
b/Å	11.9083(8)	11.4212(14)	10.5412(10)	10.6795(10)	12.126(2)	16.0155(11)
c/Å	24.695(2)	18.348(2)	16.1841(15)	16.1890(15)	16.502(3)	20.5021(14)
α/deg					80.644(3)	
β/deg	107.864(1)	95.738(2)			80.180(3)	101.760(1)
γ/deg					73.254(3)	
V/Å^3	12975	3450	3049	3160	1657	3030
ρ_c/g cm^{-3}	1.47_6	1.58_9	1.48_1	1.45_8	1.46_8	1.45_0
Z	8	4	4	4	2	4
$2\theta_{max}$/deg	60	58	58	58	60	67
μ(Mo Kα)/mm^{-1}	0.65	0.66	0.66	0.63	0.76	0.66
$T_{min/max}$	0.85	0.80	0.88	0.92	0.79	0.86
cryst dimens/mm^3	0.50 × 0.23 × 0.15	0.32 × 0.28 × 0.16	0.45 × 0.20 × 0.16	0.55 × 0.40 × 0.23	0.55 × 0.24 × 0.10	0.48 × 0.40 × 0.32
N_{tot}	91 596	10 650	27 906	28 867	22 965	43 203
N (R_{int})	18 060 (0.061)	8678 (0.056)	7567 (0.024)	7801 (0.015)	9545 (0.046)	11 526 (0.020)
N_o	12254	6843	7233	7705	8324	9598
R1	0.048	0.059	0.029	0.020	0.037	0.031
wR2 (a, b)	0.14 (0.071, 13.7)	0.116 (0.098, 3.1)	0.065 (0.030, 23)	0.051 (0.026, 1.37)	0.111 (0.082, 0.18)	0.080 (0.035, 2.1)

Anal. Calcd for $C_{36}H_{34}O_2P_2Ru$: C, 65.35; H, 5.18; *M*, 662. Found: C, 65.30; H, 5.07.

Structure Determinations. Full spheres of diffraction data were measured at ca. 153 K using a Bruker AXS CCD area-detector instrument. N_{tot} reflections were merged to N_{unique} (R_{int} cited) after "empirical"/multiscan absorption correction (proprietary software), all reflections being used in the full-matrix least-squares refinements on F^2; N_o values with $F > 4\sigma(F)$ were considered "observed". All data were measured using monochromatic Mo Kα radiation (λ = 0.710 73 Å). Anisotropic displacement parameter forms were refined for the non-hydrogen atoms; hydrogen atoms were treated with a riding model. Reflection weights were $(\sigma^2(F_o^2) + (aP)^2 + bP)^{-1}$ ($P = (F_o^2 + 2F_c^2)/3$). Neutral atom complex scattering factors were used; computation used the SHELXL-97 program.[49] Pertinent results are given in the figures (which show non-hydrogen atoms with 50% probability amplitude displacement ellipsoids) and in Table 1 and Table S1 (Supporting Information).

Variata. **11**·C_3H_6O: the two independent PF_6 groups are disposed about a crystallographic 2 axis and an inversion center, respectively. The central C_4H_3 group was assigned as such from refinement behavior and difference map evidence.

13: the ligand string was modeled as disordered over two sets of sites from C(2) onward, site occupancies being set at 0.5 after trial refinement. The PF_6 was also modeled as disordered about the F(1)−P−F(2) axis, component occupancies refining to 0.867(10) and complement (minor component adp form isotropic).

15 and **16**: these complexes are isomorphous, the specimens chosen being of opposite chiralities (x_{abs} = −0.04(2), −0.015(15), respectively).

21: the solvent molecule was modeled with the Cl atoms disordered over two sets of sites, occupancies refining to 0.808(8) and complement.

Computational Methods. All calculations were carried out using the Gaussian03 suite of programs.[50] All geometry optimizations were performed using the B3LYP[51−53] density functional and the LANL2DZ/6-31+G(d,p) compound basis set (LANL2DZ[54,55] on the ruthenium atom and the 6-31+G(d,p)[56−59] basis set on the remaining atoms), with pure d functions (5D) used throughout. In order to minimize computational resources, all calculations were performed with dmpe (1,2-bis(dimethylphosphino)ethane) in place of dppe (1,2-bis(diphenylphosphino)ethane) used experimentally. Excellent agreement between the real and simplified systems has been found in previous studies.[60]

Upon attaining all optimized structures, harmonic vibrational frequency calculations at the same level of theory were subsequently performed to ascertain whether they were local minima (zero imaginary frequencies) or local transition state maxima (one imaginary frequency). Wave function stability tests (Stable=Opt) were also performed in order to ensure that there were no instabilities in the optimized electronic wave functions. Once the characteristics of all individual stationary points was determined and their wave function stabilities verified, various reaction pathways (Figures 5 and 6 and Figures S3−S5 (Supporting Information)) were explored by visually linking specific transition-state structures to minimum structures and confirmed using intrinsic reaction coordinate (IRC) calculations.

In order to account for the effects of solvation upon the energetics of the reaction pathways, single-point energy corrections were calculated by means of a polarizable continuum model (IEP-PCM)[61−63] using radii based on the united atom topological model (RADII = UAHF). To simulate experimental conditions in Bu^{t}OH, the values for the static dielectric constant (ε = EPS), dynamic dielectric constant (ε_{inf} = EPSINF), solvent density (ρ = DENSITY), and solvent radius (r = RSOLV) were set to 12.47, 1.92, 0.0063 particles/Å^3, and 2.70 Å, respectively. The EPS and DENSITY values were generated from readily available data,[64] while the remaining values were not readily available and were calculated using the square of the refractive index of Bu^{t}OH for the EPSINF value[65] and the Stearn−Eyring equation for the RSOLV value.[66]

In each of the reaction pathways presented, the relative gas-phase Gibbs free energies of all minima and transition states are represented by solid lines. The relative Bu^{t}OH solvation-corrected Gibbs free energies are represented by dashed lines. All relative energy values discussed and displayed throughout the computational section of this paper are in kJ mol^{-1} and were calculated at 298 K unless otherwise specified.

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■ ASSOCIATED CONTENT

Supporting Information

Figures S1 and S2 (plots of Ru{C(OMe)=CH(CO_2Et)}(dppe)Cp (**16**) and Ru(C≡CCO_2Et)(dppe)Cp (**22**), tables giving selected bond parameters for **11**, **13**, **15**, **16**, **21**, and **22**, text giving full details and Figures S3−S5 relating to computational studies of three alternative pathways for the decarboxylation reaction of propiolic acid on the Ru(dppe)Cp center, text giving the full citation for ref 50, and CIF files giving crystallographic data for the compounds studied by X-ray diffraction. This material is available free of charge via the Internet at http://pubs.acs.org. Full details of the structure determinations (except structure factors) have also been deposited with the Cambridge Crystallographic Data Centre as CCDC 662444−662449. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, + 44 1223 336 033; e-mail, deposit@ccdc.cam.ac.uk; web, http://www.ccdc.cam.ac.uk).

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Notes

The authors declare no competing financial interest.

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(34) An alternative reaction pathway leading to the formation of the carboxyvinylidene global minimum **III** via an oxidative-addition process was also computed (see the Supporting Information). However, this pathway was also found to involve much higher energetic barriers prior to the formation of **III**.

(35) As the mechanism for the spontaneous emission of CO_2 is the main focus of this computational work, no further calculations were performed on the possible mechanisms of the ethyne−vinylidene rearrangements on the Ru(dmpe)Cp centre. Earlier work[29−33] is relevant to this process.

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