Ruthenium Allenylidene/Alkenylcarbyne Complexes Triggering Keto−Enol Tautomerism: An Alternative Approach to γ-Keto Vinylidenes from Simple Ketones and 1,3-Dicarbonyl Compounds

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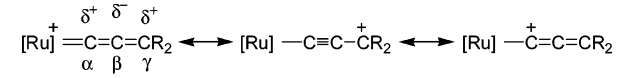
[Cp*Ru(=C=C=CHPh)(dippe)][BF_4] and [Cp*Ru(≡C−C=CHPh)(dippe)][BF_4]$_2$ complexes are reactive toward a variety of simple ketones (acetone, acetophenone, cyclopentanone) and 1,3-dicarbonyl compounds (acetylacetone, dimethylmalonate, malononitrile, ethyl acetoacetate) to give a series of alkylated vinylidene compounds [Cp*Ru{=C=CH−CH(L)Ph}(dippe)][BF_4] (dippe = 1,2-bis(diisopropylphosphino)ethane). Two cross-linked processes are operating simultaneously, creating two interconverting pairs of species: the allenylidene/carbyne complexes and the keto/enol tautomers of the ketones, producing the final vinylidene product, which is stable due to the formation of a new C−C bond. The protonation/deprotonation equilibrium produces the electrophilic alkenylcarbyne complex and enols as the nucleophilic reagent. Stoichiometric studies with deuterated reagents and NMR monitoring of the reaction have been carried out. The X-ray structure of [Cp*Ru{=C=CH−CH(CH_2COCH_3)Ph}(dippe)][BF_4] is also reported.

Introduction

The chemistry of allenylidene complexes[1] and especially that of allenylidene complexes of ruthenium,[2] [Ru]=C=C=CR_2, has been largely developed during the last two decades since Selegue's discovery of a general synthetic methodology by activation of propargyl alcohols.[3] Based on a large number of studies on stoichiometric allenylidene reactions, the main trends of allenylidene reactivity have been rapidly established, being also supported by theoretical calculations:[4] α- and γ-carbons are electrophilic centers, whereas the β-carbon exhibits a nucleophilic character. The electronic and steric properties of the metal fragment and the allenylidene substituents control the regioselectivity. This behavior is easily rationalized by the contribution of three resonance forms, namely, allenylidene, propargyl, and allenyl cation (Scheme 1). Owing to the unsaturated character of the cumulated double bonds, allenylidenes are excellent substrates for C−C and C−heteroatom couplings.

Useful applications are increasing from the field of homogeneous catalysis. The allenylidene [(*p*-cymene)RuCl(=C=C=CPh_2)(PCy_3)]$^+$ plays a decisive role as catalyst precursor to generate highly active catalysts for olefin metathesis.[5]

Scheme 1



Of particular relevance is the ruthenium-catalyzed propargylic substitution reaction of propargylic alcohols with a variety of heteroatom- and carbon-centered nucleophiles, recently developed by Nishibayashi et al (Scheme 2).[6,7] A nucleophilic attack on the electrophilic γ-carbon in allenylidene intermediates seems to be the key step. This innovative transformation represents a catalytic alternative to the Nicholas reaction, which requires a stoichiometric amount of cobalt complex to provide the

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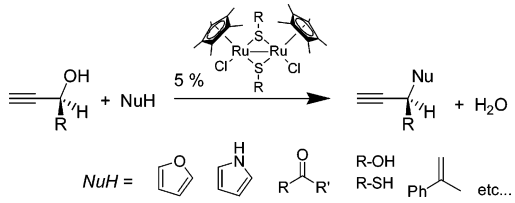
Scheme 2



stabilization of the propargyl cation intermediate.[8] Surprisingly, this reaction requires a thiolate-bridged diruthenium catalyst. With scarce exceptions,[9] most mononuclear ruthenium complexes are not active as catalysts for this reaction.

An analogous reaction with ketones, developed by Gimeno and co-workers, allows the stoichiometric, step-by-step preparation of alkylated compounds from propargyl alcohols via enolate addition to ruthenium allenylidene complexes (Scheme 3).[10]

However, the catalytic propargylic alkylation of propargyl alcohols with ketones proceeds smoothly under mild and neutral reaction conditions (without addition of base), and therefore the mechanism involved in this reaction still remains unknown.[7] So far, there is no example of a *direct* reaction of the allenylidene ligand with ketonic compounds.

In our laboratory, we have recently reported the activation of propargyl alcohol by [Cp*RuCl(dippe)] to give allenylidene complexes via 3-hydroxyalkynyl and 3-hydroxyvinylidene intermediates.[11] The particular combination of the electron-releasing bulky ligands η^5-C_5Me_5 (Cp*) and 1,2-bis(diisopropylphosphino)ethane (dippe) provided electron-rich allenylidene complexes, with an increased stability toward nucleophilic attack with regard to other more electrophilic allenylidenes. On the contrary, they exhibit a nucleophilic behavior. By protonation on the β-carbon, dicationic alkenylcarbyne complexes were isolated and fully characterized.[12] At that moment ruthenium alkenylcarbynes were very scarce, but during the last years some other examples have been reported.[5,13] From the X-ray structural data, the alkenyl carbyne moiety has a high contribution of the vinylidene canonical form with some carbocation character on the γ-carbon (Scheme 4).

This accounts for the reactivity of the parent allenylidene with weak nucleophiles such pyrrole or 2-methylfuran only under acidic conditions. The substituted vinylidene products resulted from the addition of Nu−H to the allenylidene Cβ−Cγ double bond, by a mechanism alternative to the well-known addition of anionic nucleophiles followed by alkynyl protonation (see Scheme 3b).

In this paper, we report the novel reactivity of our allenylidene/carbyne system toward a variety of ketones to give a series of alkylated vinylidene compounds. To the best of our knowledge, this kind of reactivity has not been reported so far. Stoichiometric studies with deuterated reagents and NMR monitoring have been carried out in order to elucidate the reaction mechanism.

Similarly to Nishibayashi's catalytic system, our complexes react smoothly with ketones and heterocycles regioselectively at the γ-carbon. This parallel reactivity is observed in both cases only for secondary propargyl alcohols. The reported stoichiometric version of the catalytic reaction offers an alternative mechanistic approach, which could probably serve as a model for a better understanding of the operating catalytic cycle.

Results and Discussion

Protonation on the β-carbon of vinylidene[14] or allenylidene[5,13] ligands is a known versatile entry to carbyne and alkenylcarbyne species, frequently employed during the last years to prepare, isolate, and characterize the formerly elusive ruthenium carbyne complexes. Not unexpectedly, these protonations can be easily reversed, and attempts to test the alkenylcarbyne reactivity and catalysis activity usually fail. Addition of very weak bases such as acetone or diethyl ether has been reported to lead to the regeneration of the allenylidene compounds.[13]

A similar effect was initially observed for the alkenylcarbyne complex $[Cp^*Ru(\equiv C-CH=CHPh)(dippe)]^{2+}$, which reverts partially to allenylidene in the presence of acetone.[12] However, when this complex is treated with acetone overnight even at room temperature, a novel reactivity has been observed for the first time in allenylidene chemistry.

The modification of the original preparative procedure from [Cp*RuCl(dippe)] (**1**) has allowed the synthesis of $[Cp^*Ru(=C=C=CHPh)(dippe)][BF_4]$ (**2**) and $[Cp^*Ru(\equiv C-CH=CHPh)(dippe)][BF_4]_2$ (**3**) complexes as $[BF_4]^-$ salts, in order to avoid $[BPh_4]^-$, unstable under acidic conditions. Whereas complex **2** is indefinitely stable in acetone, the distinctive dark red color of complex **3** slowly disappears when left overnight in acetone solution. After workup, the vinylidene complex $[Cp^*Ru\{=C=CH-CH(CH_2COCH_3)Ph\}(dippe)][BF_4]$ (**4**) was isolated as a light brown solid. Complex **4** formally corresponds to the product of acetone addition to the allenylidene terminal double bond.

An alternative and more straightforward method to prepare compound **4** involves the treatment of the chloro complex **1** with the corresponding alkynol HC≡CCH(OH)Ph and $NaBF_4$ in CH_2Cl_2. The spontaneous formation of the allenylidene **2** is followed by addition of an excess of HBF_4 to generate in situ the alkenyl carbyne **3**. Removal of the excess of acid is mandatory, by evaporation of the solvent and washing with Et_2O. Addition of acetone to the residue gives complex **4** after stirring at room temperature for 6 h (Scheme 5).

Complex **4** has been characterized by NMR, IR, elemental analysis, and particularly by the X-ray structure. Figure 1 shows an ORTEP view of the cation. As usual, the vinylidene moiety

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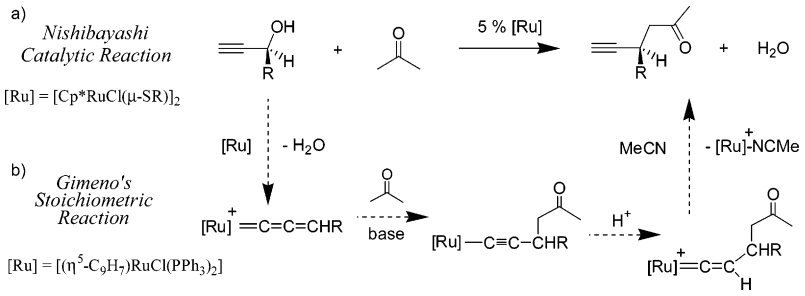
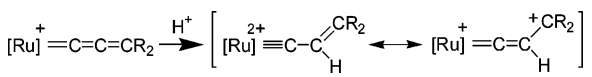
Scheme 3



Scheme 4



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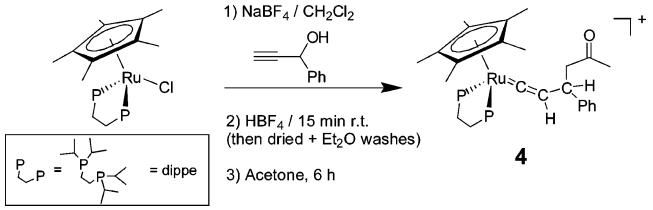
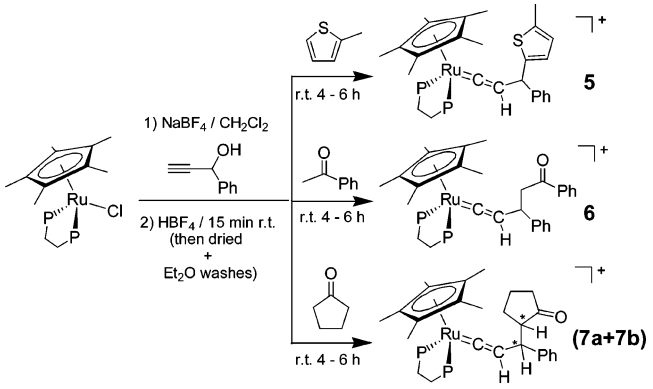


Scheme 6



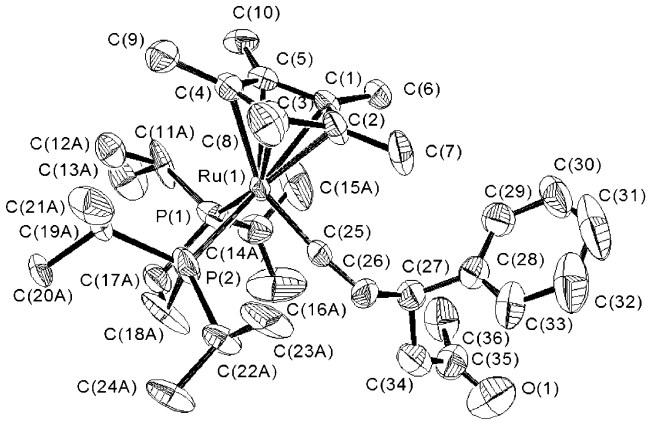


Figure 1. ORTEP view of the cation of the complex [Cp*Ru{=C=CH−CH(CH2COCH3)Ph}(dippe)][BF4] (**4**). Selected bond lengths (Å) and angles (deg): Ru(1)−P(1) 2.3222(16), Ru(1)−P(2) 2.3246(14), Ru(1)−C(25) 1.862(5), C(25)−C(26) 1.274(7), C(26)−C(27) 1.570(8), C(27)−C(34) 1.541(9); P(1)−Ru(1)−P(2) 81.65(7), Ru(1)−C(25)−C(26) 172.7(5), C(25)−C(26)−C(27) 127.0(5), C(26)−C(27)−C(28) 108.0(5), C(26)−C(27)−C(34) 111.8(5), C(27)−C(34)−C(35) 114.9(5).

is almost linear with the ruthenium atom (172.7°). The Ru−C_α (1.862 Å) and C_β−C_γ (1.274 Å) distances correspond to Ru−C and C−C double bonds, respectively, similar to those found in [Cp*Ru(=C=CH−COOMe)(dippe)][BPh4].[15] The angle $C_\alpha C_\beta C_\gamma$ of 127.0° indicates an sp^2 hybridation at C_β.

The formation of the vinylidene **4** is surprising, since acetone itself lacks nucleophilic carbon atoms. A more classical preparation would involve the enolate formation with a strong base to give the corresponding neutral γ-substituted alkynyl complex and subsequent protonation to vinylidene (see Scheme 3b).[10] In fact, compound **4** had already been obtained by this method in our laboratory.[12]

The reaction between the alkenyl carbyne and acetone has been monitored by $^{31}P\{^1H\}$ NMR. Addition of 100 μL of acetone to a $CDCl_2CDCl_2$ solution of complex **3** at room temperature produces the formation of a mixture of the complexes carbyne **3** (δ 86.1 ppm) and allenylidene **2** (δ 88.2 ppm). The conversion to vinylidene **4** is too slow at room temperature, but it occurs at appreciable rate at 60−70 °C. The two singlets for **2** and **3** gradually disappear as two doublets at δ 86.0 and 87.3 ppm arise, corresponding to the two diasterotopic phosphine groups on the vinylidene complex **4**, which contains a chiral center at the γ-carbon upon acetone addition.

Related γ-substituted vinylidene complexes were previously obtained by reaction of pyrrole or 2-methylfuran with the allenylidene **2** in acidic medium.[12] The reaction involves allenylidene protonation, followed by nucleophilic attack and ulterior deprotonation. In the case of 2-methylthiophene as well as with acetone, no reaction is observed under acidic conditions. However, the isolated alkenylcarbyne **3** reacts smoothly with 2-methylthiophene to give the vinylidene [Cp*Ru{=C=CH−CH(CH3−C4H3S)Ph}(dippe)][BF4] (**5**) (Scheme 6). Heterocycles and enols are structurally related since both species contain the X−C=C unit responsible for their nucleophilic character due to the heteroatom effect.

A series of ketones have been employed to test the generality of the reaction. The presence of an excess of acid inhibits the reaction, and it should be first removed by washing with Et_2O. Then, the vinylidene compounds [Cp*Ru{=C=CH−CH(L)Ph}(dippe)][BF4] (L = CH_2COPh (**6**), C_5H_7O (**7a**+**7b**)) were obtained similarly to compound **4** and characterized by NMR, IR, and elemental analysis (Scheme 6).

All vinylidene complexes exhibit the ν(C=C) band at 1630−1640 cm^{-1}, and those with ketone groups one ν(C=O) band at 1700−1716 cm^{-1}. The $^{31}P\{^1H\}$ NMR spectra always show an AB system due to the chiral center at the vinylidene γ-carbon, which renders the phosphine groups diasterotopic. This effect is often observed for other vinylidene compounds with different metal fragments.[11,16] Compound **7** exhibits two pairs of doublets in the $^{31}P\{^1H\}$ NMR, due to the formation of a second chiral center on the ketone α-carbon, generating two pairs of diaster-

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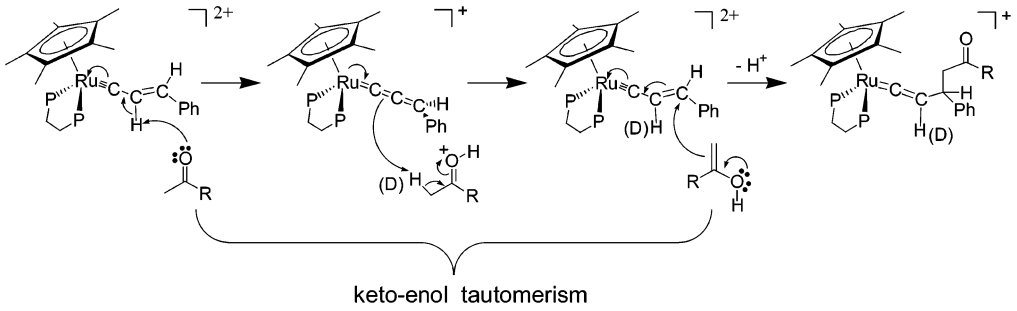
Scheme 7



oisomers (**7a** and **7b**). It is worth mentioning here that all complexes have been prepared from racemic propargyl alcohol. The most characteristic signal in the $^{13}C\{^1H\}$ NMR spectra is the low-shielded triplet corresponding to the carbenic carbon atom, observed at δ 336−339 ppm.

The ^1H NMR spectrum of compound **4** shows a characteristic pattern for the protons ═C═CHCH(Ph)CH_2− between δ 2.7−5.0 ppm. However, only one broad singlet at δ 4.14 ppm is observed when the carbyne **3** is reacted with deuterated acetone, corresponding to the hydrogen at C_γ. The C_β hydrogen atom, expected at δ 4.50 ppm, is not observed, in agreement with a ═C═CDCH(Ph)CD_2− structure.

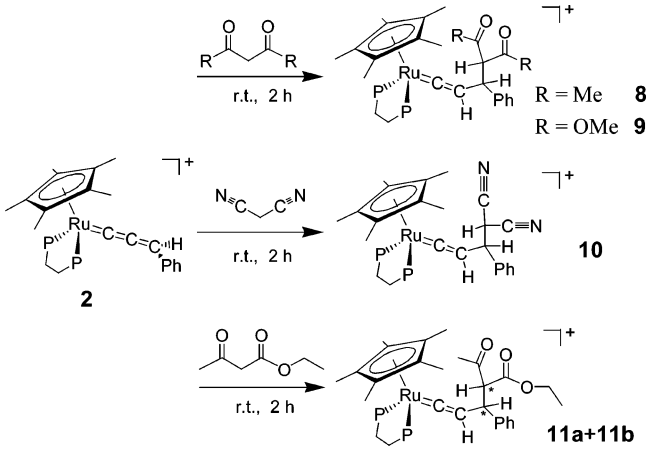
This is consistent with the mechanism proposed in Scheme 7. Acetone is basic enough to partially deprotonate the carbyne **3** at the β-carbon to give allenylidene **2**. This proton transfer makes carbyne **3** to behave as an acid catalyst for the keto−enol tautomerism of acetone. The acid-catalyzed enolization involves equilibrium protonation of the carbonyl, which acidifies the α-hydrogen, allowing an allenylidene molecule to act as a base and abstract the proton. The enol form of acetone would be responsible for the nucleophilic attack to the electrophilic γ-carbon of the alkenyl-carbyne **3**.

As previously observed, the allenylidene complex **2** reacts with nucleophiles bearing acidic protons such as thiophenol and pyrazole (i.e., thiophenol pK_a 6.6), without addition of acid.[12] Acetone, acetophenone, or cyclopentanone (as well as thiophene, furan, or pyrrole) are not acidic enough (i.e., acetone pK_a = 19); therefore a previous activation of the allenylidene by protonation is necessary, which simultaneously catalyzes the nucleophilic enol formation.

However, 1,3-dicarbonyl compounds are acidic compounds (p$K_a \approx 9-11$), which have large amounts of enol present at equilibrium, and therefore they should be able to react directly with the allenylidene complex **2** in agreement with the previous results and the mechanistic proposal. As predicted, acetylacetone reacts with the allenylidene **2** to give the corresponding substituted vinylidene complex [Cp*Ru{═C═CH−CH(Ph)CH-$(COCH_3)_2$}(dippe)][BF_4] (**8**). The reaction is faster than with simple ketones, and it is complete within 2 h at room temperature. Similarly, other acidic species such as dimethylmalonate, malononitrile, and ethyl acetoacetate are also reactive toward the allenylidene **2**, giving the substituted vinylidene complexes [Cp*Ru{═C═CH−CH(Ph)(R)}(dippe)][BF_4] (R = $CH(COOCH_3)_2$ (**9**), R = $CH(CN)_2$ (**10**), R = $CH(COCH_3)$(COOEt) (**11**)) (Scheme 8).

The ^1H NMR spectra of compounds **8**−**11** show a characteristic pattern for the protons ═C═CHCH(Ph)CHR_2. All $^{13}C\{^1H\}$ NMR spectra show the low-shielded triplet corresponding

Scheme 8



to the carbenic carbon atom in the range δ 334−338 ppm. As observed in the case of the cyclopentanone, ethyl acetoacetate generates a second chiral center when bonded to the vinylidene chain, giving a mixture of the diasteroisomers **11a** and **11b**. Two triplets at δ 336.9 and 337.8 are observed in the $^{13}C\{^1H\}$ NMR spectrum, as well as four doublets in the $^{31}P\{^1H\}$ NMR.

The reaction with acetylacetone was monitored by $^{31}P\{^1H\}$ NMR at room temperature. The initial signal corresponding to allenylidene **2** (δ 88.2 ppm) is rapidly replaced by two doublets (δ 87.6 and 85.0 ppm), characteristic of the γ-substituted vinylidene **8**. In this case, the signal of the alkenylcarbyne intermediate is not observed. Another test was carried out with the alkenylcarbyne **3** and acetylacetone. Similarly, the initial carbyne signal (δ 86.1 ppm) is directly replaced by the two mentioned doublets. Therefore, both the allenylidene and the alkenylcarbyne complexes are reactive against acetylacetone. In agreement with this, it seems plausible to propose a mechanism where the allenylidene is protonated in the first step by the acidic acetylacetone, generating the electrophilic carbyne intermediate, which immediately reacts with the already present nucleophilic enol tautomer.

The reactivity of alkenylcarbyne or allenylidene complexes with simple ketones or 1,3-dicarbonyl compounds, respectively, has not been described yet. The closest process is the catalytic propargylic alkylation of propargyl alcohols with ketones.[7] There are several parallelisms between both systems with regard to the propargylic substitution reaction: it works only for secondary propargyl alcohols; the reaction is regioselective at the propargyl position (γ-carbon); heterocycles and ketones are suitable substrates; no basic conditions are required; and both vinylidene and allenylidene species are proposed as intermediates.

At difference with Nishibayashi's system, an acidic activation of the allenylidene is necessary to generate enols from simple ketones. The catatytic reaction involves heating (60 °C, 4 h) the propargyl alcohol in acetone as solvent, in the presence of

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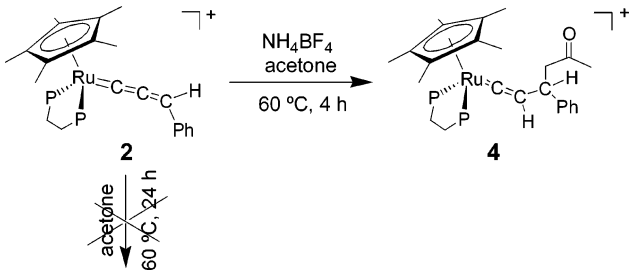
Scheme 9



the ruthenium catalyst and NH_4BF_4.[7] We have tested whether the NH_4^+ cation is acidic enough to trigger the keto−enol tautomerism to some extent. Allenylidene complex **2** was heated in acetone at 60 °C for 24 h without reaction. On the other hand, in the presence of NH_4BF_4, heating at 60 °C for 4 h gives a 1:3 mixture of allenylidene **2** and the γ-substituted vinylidene **4** (Scheme 9). This experiment confirms that even slightly acidic conditions are adequate to induce the enol formation and the ulterior nucleophilic attack. This stoichiometric reactivity of allenylidene complexes with ketonic compounds constitutes a unique precedent within allenylidene reactivity, and it supports the allenylidene intermediacy in the related catalytic process, thus explaining the nucleophilic reactivity of ketones, not yet established.

Unfortunately, attempts to release the vinylidene ligand by heating complex **4** in acetonitrile failed. $[Cp^*Ru(P)_2]^+$ fragments are not able to reproduce this reaction in catalytic conditions, likely because of the high energy difference of the π-alkyne/vinylidene isomers[17] and the lower stability of the coordinatively unsaturated mononuclear ruthenium system with regard to the binuclear one.[18] The reversible alkyne/vinylidene isomerization and smooth substitution of the product by another molecule of propargyl alcohol are key steps to initiate the catalytic cycle.

Concluding Remarks

In this paper we have reported for the first time that allenylidene and alkenyl carbyne complexes are reactive with a variety of ketones and 1,3-dicarbonyl compounds, respectively, to give a series of γ-substituted vinylidene complexes. This is the first example of a direct reaction of an allenylidene ligand with ketonic compounds. The mechanism involves a protonation/deprotonation equilibrium, which produces the electrophilic alkenylcarbyne complex and, at the same time, enols as the nucleophilic reagents. This new approach constitutes an alternative mechanistic pathway to the classical enolate addition, which requires drastic basic conditions. The outcome of this novel stoichiometric reactivity could serve as a model for a better understanding of the catalytic propargylic alkylation of propargyl alcohols with ketones. Ongoing studies focus on the allenylidene/carbyne reactivity against different C, N, and O nucleophiles and the expansion of the results to other ruthenium fragments.

Experimental Section

All synthetic operations were performed under a dry dinitrogen or argon atmosphere by following conventional Schlenk techniques. Tetrahydrofuran, diethyl ether, and petroleum ether (boiling point range 40−60 °C) were distilled from the appropriate drying agents. All solvents were deoxygenated immediately before use. IR spectra were recorded in Nujol mulls on a Perkin-Elmer FTIR Spectrum 1000 spectrophotometer. NMR spectra were taken on a Varian Inova 400 MHz or Varian Gemini 300 MHz equipment. Chemical shifts are given in parts per million from $SiMe_4$ (^1H and $^{13}C\{^1H\}$) or 85% H_3PO_4 ($^{31}P\{^1H\}$). Microanalysis was performed on a LECO CHNS-932 elemental analyzer at the Servicio Central de Ciencia y Tecnología, Universidad de Cádiz.

Preparation of the [Cp*Ru(=C=C=CHPh)(dippe)][BF4] (2). Compound **1** (300 mg, 0.56 mmol) was dissolved in 10 mL of CH_2Cl_2. An excess of $NaBF_4$ (100 mg, 0.91 mmol) and 1-phenyl-2-propyn-1-ol (73 μL, 0.60 mmol) were added immediately. After stirring for 4 h at room temperature, the solution was passed through an acidic alumina column (activity grade I, height of column 10 cm). The dark brown band was collected and taken to dryness under vacuum, giving a dark brown solid. Yield: 345 mg (89%). ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 0.92, 1.12 and 1.22 (m, 24 H, dippe-C*H*$_3$), 1.93 (s, 15 H, $C_5(CH_3)_5$), 2.06 and 2.28 (m, 8 H, dippe-C*H* and C*H*$_2$), 7.36 (t, 2 H, $^3J_{HH}$ = 7.4 Hz, *m*-C_6H_5), 7.64 (t, 1 H, $^3J_{HH}$ = 7.4 Hz, *p*-C_6H_5), 7.71 (t, 2 H, $^3J_{HH}$ = 7.4 Hz, *o*-C_6H_5), 9.17 (s, 1 H, C=C=C*H*Ph). $^{31}P\{^1H\}$ NMR (161.89 MHz, $CDCl_3$, 298 K): δ 88.9.

Preparation of the [Cp*Ru(≡CCH=CHPh)(dippe)][BF4]2 (3). Compound **1** (133 mg, 0.25 mmol) was dissolved in 5 mL of CH_2Cl_2. A slight excess of $NaBF_4$ (40 mg, 0.36 mmol) and 1-phenyl-2-propyn-1-ol (40 μL, 0.33 mmol) were immediately added, and the solution was stirred at room temperature for 2 h. Addition of 40 μL of HBF_4 (54 wt % solution in Et_2O, 0.30 mmol) rapidly produced a clear color change from brown to dark red. After stirring for 10 min at room temperature the solvent was evaporated under vacuum, and the residue was washed with 2 × 10 mL of Et_2O and dried, giving a dark red solid. Yield: 160 mg (81%). ^1H NMR (400 MHz, CD_2Cl_2, 298 K): δ 1.03 and 1.32 (m, 24 H, dippe-C*H*$_3$), 2.00 (s, 15 H, $C_5(CH_3)_5$), 2.25 and 2.57 (m, 8 H, dippe-C*H* and C*H*$_2$), 6.87 and 8.14 (both d, 1 H each, $^3J_{HH}$ = 15.8 Hz, C*H*=C*H*Ph), 7.45 (t, 2 H, $^3J_{HH}$ = 7.6 Hz, *m*-C_6H_5), 7.69 (t, 1 H, $^3J_{HH}$ = 7.6 Hz, *p*-C_6H_5), 7.86 (t, 2 H, $^3J_{HH}$ = 7.6 Hz, *o*-C_6H_5). $^{31}P\{^1H\}$ NMR (161.89 MHz, CD_2Cl_2, 298 K): δ 86.6.

Preparation of the [Cp*Ru{=C=CH−CH(L)Ph}(dippe)][BF4] (L = CH2COCH3 (4), CH3−C4H2S (5), CH2COPh (6), C5H7O (7)). The first step of the synthesis of compounds **4**−**7** was carried out as described for the preparation of compound **3**. The addition of 40 μL of HBF_4 (54 wt % solution in Et_2O, 0.30 mmol) rapidly produced the in-situ formation of the carbyne intermediate **3**, shown by the distinctive dark red color. After stirring for 10 min at room temperature the solvent was evaporated under vacuum. The residue was washed with 2 × 10 mL of Et_2O in order to remove the excess acid and then redissolved in 5 mL of CH_2Cl_2. An excess of 2-methylthiophene (50 μL, 0.50 mmol) or the corresponding ketone (0.5 mL) was added. The solution was stirred at room temperature until the complete disappearance of the characteristic carbyne dark red color (∼6 h). Then, the solution was concentrated to less than 1 mL at reduced pressure. Addition of 10 mL of a 1:1 mixture of Et_2O and petroleum ether caused the precipitation of a brown solid, which was filtered, washed with petroleum ether, and dried under vacuum. Yields, microanalyses, and selected spectral data are as follows:

Compound 4. Yield: 152 mg (80%). Anal. Calcd for $C_{36}H_{59}BF_4OP_2Ru$: C, 57.1; H, 7.85. Found: C, 57.0; H, 7.91. IR (Nujol): ν(CO) 1710, ν(C=C) 1643 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 0.98−1.31 (m, 24 H, dippe-C*H*$_3$), 1.76 (s, 15 H, $C_5(CH_3)_5$), 2.02, 2.05, 2.13, and 2.32 (m, 8 H, dippe-C*H* and C*H*$_2$), 2.03 (s, 3 H, COC*H*$_3$), 2.74 and 2.77 (both dd, 1 H each, $^3J_{HbHc}$ = $^3J_{HbHc'}$ = 6.7 Hz, $^2J_{HcHc'}$ = 17.2 Hz, CH^{a}CH^b(Ph)-CH^{c}H$^{c'}$CO), 4.05 (dt, 1 H, $^3J_{HbHc}$ = 6.7 Hz, $^3J_{HaHb}$ = 10.6 Hz, C*H*^{b}-Ph), 4.21 (d, 1 H, $^3J_{HaHb}$ = 10.6 Hz, Ru=C=C*H*^{a}), 7.15, 7.18, and 7.28 (m, 5 H, C_6H_5). $^{31}P\{^1H\}$ NMR (161.89 MHz, $CDCl_3$, 298 K): δ 87.9 and 86.2 (d, $^2J_{PP'}$ = 19.0 Hz). $^{13}C\{^1H\}$ NMR (75.4 MHz,

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$CDCl_3$, 298 K): δ 10.90 (s, $C_5(CH_3)_5$), 18.52−20.34 (m, dippe-CH_3), 21.35 and 25.64 (m, dippe-CH_2), 32.18, 32.57, 33.70, and 34.00 (s, dippe-*C*H), 31.00 (s, $COCH_3$), 33.85 (s, CH_2CO), 52.37 (s, *C*HPh), 102.6 (s, $C_5(CH_3)_5$), 114.4 (s, Ru=C=*C*H), 126.6, 126.8, 128.7, and 144.8 (s, C_6H_5), 206.8 (s, *C*O), 337.9 (t, $^2J_{CP}$ = 14.7 Hz, Ru=*C*).

Compound 5. Yield: 158 mg (79%). Anal. Calcd for $C_{38}H_{59}BF_4P_2RuS$: C, 57.2; H, 7.45. Found: C, 57.4; H, 7.55. IR (Nujol): ν(C=C) 1636 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 0.98−1.40 (m, 24 H, dippe-CH_3), 1.84 (s, 15 H, $C_5(CH_3)_5$), 2.11 and 2.19 (m, 8 H, dippe-C*H* and CH_2), 2.39 (s, 3 H, $CH_3-C_4H_2S$), 4.49 (d, 1 H, $^3J_{HaHb}$ = 10.7 Hz, =C=CH_aCH_b), 4.89 (d, 1 H, $^3J_{HaHb}$ = 10.7 Hz, =C=CH_aCH_b), 6.34 and 6.40 (both d, 1 H each, $^3J_{HH}$ = 3.0 Hz, $CH_3-C_4H_2S$), 7.16, 7.24, and 7.32 (m, 5 H, C_6H_5). $^{31}P\{^1H\}$ NMR (161.89 MHz, $CDCl_3$, 298 K): δ 88.2 and 87.4 (d, $^2J_{PP'}$ = 18.0 Hz). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$, 298 K): δ 10.92 (s, $C_5(CH_3)_5$), 15.20 (s, $CH_3-C_4H_2S$), 18.42, 19.23, and 19.91 (m, dippe-CH_3), 21.39 (m, dippe-CH_2), 25.55 and 32.76 (m, dippe-*C*H), 38.89 (s, *C*HPh), 102.8 (s, $C_5(CH_3)_5$), 115.7 (s, Ru=C=*C*H), 124.1, 124.6, 138.7, and 146.4 (s, CH_3-C_4H_2S), 126.6, 127.1, 128.7, and 143.6 (s, C_6H_5), 336.4 (t, $^2J_{CP}$ = 14.3 Hz, Ru=*C*).

Compound 6. Yield: 170 mg (83%). Anal. Calcd for $C_{41}H_{61}BF_4OP_2Ru$: C, 60.1; H, 7.50. Found: C, 60.0; H, 7.47. IR (Nujol): ν(CO) 1716, ν(C=C) 1675, ν(Ph) 1635 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$, 298 K): δ 0.90−1.44 (m, 24 H, dippe-CH_3), 1.71 (s, 15 H, $C_5(CH_3)_5$), 1.94, 2.01, 2.10, and 2.20 (m, 8 H, dippe-CH_2 and C*H*), 3.16 (dd, 1 H, $^2J_{HcHc'}$ = 16.1 Hz, $^3J_{HbHc}$ = 7.0 Hz, CH^{a}CH^b(Ph)C*H*^{c}H$^{c'}$), 3.20 (dd, 1 H, $^2J_{HcHc'}$ = 16.1 Hz, $^3J_{HbHc'}$ = 5.9 Hz, CH^{a}CH^b(Ph)CH^c*H*$^{c'}$), 4.22 and 4.25 (overlapping m, 2 H, $^3J_{HaHb}$ = 10.4 Hz, Ru=C=C*H*^{a}C*H*^{b}), 7.16−7.92 (m, 10 H, C_6H_5). $^{31}P\{^1H\}$ NMR (161.89 MHz, $CDCl_3$, 298 K): δ 86.1 and 87.8 (d, $^3J_{PP'}$ = 19.7 Hz). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$, 298 K): 10.81 (s, $C_5(CH_3)_5$), 18.31−21.70 (m, dippe-CH_3), 25.38 and 25.76 (m, dippe-CH_2), 31.94, 32.33, 33.76, and 34.15 (s, dippe-*C*H), 34.68 (s, *C*HPh), 47.54 (s, CH_2COPh), 102.5 (s, $C_5(CH_3)_5$), 114.2 (s, Ru=C=*C*H), 126.5, 126.9, 128.0, 128.4, 128.7, 128.8, 133.0, and 133.4 (s, C_6H_5), 197.9 (s, *C*O), 337.4 (t, $^2J_{CP}$ = 14.9 Hz, Ru=*C*).

Compounds 7a + 7b. Yield: 155 mg (79%). Anal. Calcd for $C_{38}H_{61}BF_4OP_2Ru$: C, 58.2; H, 7.85. Found: C, 58.0; H, 7.80. IR (Nujol): ν(CO) 1732, ν(C=C) 1645 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 0.87−1.34 (m, 24 H, dippe-CH_3), 1.73 and 1.75 (s, 15 H, $C_5(CH_3)_5$), 1.97, 2.04, 2.19, and 2.27 (m, 9 H, dippe-CH_2 and C*H* + C*H*CO), 1.92 and 2.12 (m, 6 H, $COCH_2(CH_2)_2$), 4.04 (m, 1 H, Ru=C=C*H*), 4.39 (t, 1 H, $^3J_{HH}$ = 10.4 Hz, C*H*Ph). $^{31}P\{^1H\}$ NMR (161.89 MHz, $CDCl_3$, 298 K): δ 86.4, 86.7, 87.3, and 88.5 (d, $^3J_{PP'}$ = 19.0 Hz). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$, 298 K): 10.81 and 10.88 (s, $C_5(CH_3)_5$), 18.32−22.03 (m, dippe-CH_3), 24.89−26.15 (m, dippe-CH_2), 32.07−34.24 (m, dippe-*C*H), 32.81 ($COCH_2$), 37.21 (s, *C*HCO$CH_2(CH_2)_2$), 36.93, 38.27, 38.76, and 39.31 (s, *C*HCOCH_2(CH_2)$_2$), 55.66 and 56.24 (s, *C*HPh), 102.5 (s, $C_5(CH_3)_5$), 108.9 and 113.7 (s, Ru=C=*C*H), 126.9, 127.0, 127.4, 128.5, 128.6, 141.9, and 143.5 (s, C_6H_5), 219.0 and 219.7 (s, *C*O), 336.4 and 337.4 (both t, $^2J_{CP}$ = 14.4 and 14.6 Hz, Ru=*C*).

Preparation of the [Cp*Ru{=C=CH−CH(L)Ph}(dippe)][BF_4] (L = $CH(COCH_3)_2$ (8), $CH(COOCH_3)_2$ (9), $CH(CN)_2$ (10), $CH(COCH_3)(COOEt)$ (11)). Allenylidene **2** (175 mg, 0.25 mmol) was dissolved in 5 mL of CH_2Cl_2. An excess (0.50 mmol) of the corresponding acetylacetone, dimethylmalonate, malononitrile, or ethyl acetoacetate was added. The mixture was stirred for 2 h at room temperature. Then, the solution was concentrated to less than 1 mL at reduced pressure. Addition of 10 mL of a 1:1 mixture of Et_2O and petroleum ether caused the precipitation of a brown solid, which was washed with petroleum ether and dried under vacuum. Yields, microanalyses, and selected spectral data are as follows.

Compound 8. Yield: 170 mg (85%). Anal. Calcd for $C_{38}H_{61}BF_4O_2P_2Ru$: C, 57.1; H, 7.69. Found: C, 56.7; H, 7.63. IR (Nujol): ν(CO) 1695, ν(C=C) 1644 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 0.99−1.44 (m, 24 H, dippe-CH_3), 1.67 (s, 15 H, $C_5(CH_3)_5$), 2.03, 2.17, and 2.44 (m, 8 H, dippe-CH_2 and C*H*), 1.82 and 2.28 (both s, 3 H each, $CH(COCH_3)_2$), 4.20 (t, 1 H, $^3J_{HaHb}$ = $^3J_{HbHc}$ = 10.5 Hz, CH^{a}C*H*^{b}(Ph)CH^c), 4.38 (d, 1 H, $^3J_{HbHc}$ = 10.5 Hz, C*H*^{c}), 4.50 (d, 1 H, $^3J_{HaHb}$ = 10.5 Hz, Ru=C=C*H*^{a}), 7.16, 7.24, and 7.27 (m, 5 H, C_6H_5). $^{31}P\{^1H\}$ NMR (161.89 MHz, $CDCl_3$, 298 K): δ 87.6 and 85.0 (d, $J_{PP'}$ = 19.7 Hz). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$, 298 K): δ 10.70 (s, $C_5(CH_3)_5$), 18.21−21.43 (m, dippe-CH_3), 25.32 and 25.35 (m, dippe-CH_2), 30.80, 31.20, 36.02, and 36.40 (s, dippe-*C*H), 31.99 and 32.23 (s, $CH(COCH_3)_2$), 38.56 (s, *C*H$(COCH_3)_2$), 72.60 (s, *C*HPh), 102.4 (s, $C_5(CH_3)_5$), 111.9 (s, Ru=C=*C*H), 127.6, 128.7, 130.8, and 142.7 (s, C_6H_5), 202.4 and 202.6 (s, *C*O), 338.6 (t, $^2J_{CP}$ = 14.5 Hz, Ru=*C*).

Compound 9. Yield: 191 mg (92%). Anal. Calcd for $C_{38}H_{61}BF_4O_4P_2Ru$: C, 54.9; H, 7.39. Found: C, 55.0; H, 7.39. IR (Nujol): ν(COOMe) 1746, ν(C=C) 1634 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 1.01−1.35 (m, 24 H, dippe-CH_3), 1.66 (s, 15 H, $C_5(CH_3)_5$), 2.08 and 2.30 (m, 8 H, dippe-CH_2 and C*H*), 3.42 (d, 1 H, $^3J_{HbHc}$ = 9.4 Hz, CH^{a}CH^b(Ph)C*H*^{c}), 3.46 and 3.66 (both s, 3 H each, $CH(COOCH_3)_2$), 4.17 (d, 1 H, $^3J_{HaHb}$ = 10.5 Hz, C*H*^{a}), 4.27 (t, 1 H, $^3J_{HaHb}$ = $^3J_{HbHc}$ = 9.6 Hz, Ru=C=C*H*^{b}), 7.11, 7.20, and 7.27 (m, 5 H, C_6H_5). $^{31}P\{^1H\}$ NMR (161.89 MHz, $CDCl_3$, 298 K): δ 85.7 and 87.9 (d, $^3J_{PP'}$ = 19.0 Hz). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$, 298 K): δ 10.80 (s, $C_5(CH_3)_5$), 18.01−21.90 (m, dippe-CH_3), 25.45 and 25.83 (m, dippe-CH_2), 31.12, 31.58, 35.24, and 35.51 (s, dippe-*C*H), 38.00 (s, *C*H$(COCH_3)_2$), 52.53 and 52.79 (s, $CH(COOCH_3)_2$), 58.66 (s, *C*HPh), 102.8 (s, $C_5(CH_3)_5$), 111.3 (s, Ru=C=*C*H), 127.1, 127.7, 128.7, and 142.1 (s, C_6H_5), 167.2 and 167.9 (s, $CH(COOCH_3)_2$), 336.3 (t, $^2J_{CP}$ = 14.6 Hz, Ru=*C*).

Compound 10. Yield: 171 mg (89%) Anal. Calcd for $C_{36}H_{55}BF_4N_2P_2Ru$: C, 56.5; H, 7.24; N, 3.66. Found: C, 57.1; H, 7.23; N, 3.70. IR (Nujol): ν(C≡N) 2258, ν(C=C) 1644 cm^{-1}. ^1H NMR (400 MHz, CD_2Cl_2, 298 K): δ 0.99−1.38 (m, 24 H, dippe-CH_3), 1.73 (s, 15 H, $C_5(CH_3)_5$), 1.84−2.42 (m, 8 H, dippe-CH_2 and C*H*), 4.17 (dd, 1 H, $^3J_{HaHb}$ = 8.2 Hz, $^3J_{HbHc}$ = 10.4 Hz, CH^{a}C*H*^{b}(Ph)-CH^c), 5.29 (d, 1 H, $^3J_{HbHc}$ = 10.4 Hz, C*H*^{c}), 5.70 (d, 1 H, $^3J_{HaHb}$ = 8.2 Hz, Ru=C=C*H*^{a}), 7.29, 7.37, and 7.57 (m, 5 H, C_6H_5). $^{31}P\{^1H\}$ NMR (161.89 MHz, CD_2Cl_2, 298 K): δ 86.0 and 89.1 (d, $^3J_{PP'}$ = 19.0 Hz). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$, 298 K): δ 10.96 (s, $C_5(CH_3)_5$), 18.68−21.76 (m, dippe-CH_3), 25.46 and 25.70 (m, dippe-CH_2), 31.44, 31.84, 35.35, and 35.74 (s, dippe-*C*H), 31.25 (s, *C*H(C≡N)$_2$), 40.63 (s, *C*HPh), 103.0 (s, $C_5(CH_3)_5$), 109.4 (s, Ru=C=*C*H), 112.9 and 113.4 (s, CH(*C*≡N)$_2$), 127.7, 128.7, 129.2, and 138.8 (s, C_6H_5), 334.5 (t, $^2J_{CP}$ = 15.1 Hz, Ru=*C*).

Compounds 11a + 11b. Yield: 191 mg (92%). Anal. Calcd for $C_{39}H_{63}BF_4O_3P_2Ru$: C, 56.5; H, 7.65. Found: C, 56.5; H, 7.66. IR (Nujol): ν(COOEt) 1740, ν(CO) 1714, ν(C=C) 1634 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 0.85 (t, 3 H, $^3J_{HH}$ = 7.4 Hz, $COOCH_2CH_3$), 0.92−1.32 (m, 48H+3H, dippe-CH_3 + $COOCH_2$-CH_3), 1.58 (s, 30 H, $C_5(CH_3)_5$), 1.78 and 2.18 (s, 3 H each, $COCH_3$), 1.97, 2.05, and 2.32 (m, 16 H, dippe-CH_2 and C*H*), 3.61 and 3.80 (d, 1 H each, $^3J_{HbHc}$ = 10.1 Hz, Ru=C=CH^{a}CH^b(Ph)C*H*^{c}), 3.76 (q, 2 H, $^3J_{HH}$ = 7.4 Hz, $COOCH_2CH_3$), 4.00−4.05 (overlapping m, 2H+2H, C*H*^{a} + $COOCH_2CH_3$), 4.19 (t, 2 H, $^3J_{HaHb}$ = $^3J_{HbHc}$ = 10.4 Hz, C*H*^{b}), 7.03−7.22 (m, 10 H, C_6H_5). $^{31}P\{^1H\}$ NMR (161.89 MHz, $CDCl_3$, 298 K): δ 85.1, 85.5, 87.6, and 87.8 (d, $^3J_{PP'}$ = 19.3 Hz). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$, 298 K): δ 10.58 and 10.62 (s, $C_5(CH_3)_5$), 13.56 and 13.91 (s, $COOCH_2CH_3$), 18.23−21.42 (m, dippe-CH_3), 25.17−25.83 (m, dippe-CH_2), 30.80 and 31.45 (s, $COCH_3$), 30.62, 30.70, 31.02, 31.16, 35.59, 31.77, 31.98, and 36.15 (s, dippe-*C*H), 37.54 (s, *C*H$(COCH_3)$(COOEt)), 61.12 and 61.52 (s, *C*HPh), 65.38 and 65.59 (s, $COOCH_2CH_3$)$_2$), 102.4 and 102.6 (s, $C_5(CH_3)_5$), 111.6 and 111.8 (s, Ru=C=*C*H), 127.0, 127.1, 127.3, 127.4, 128.4, 128.7, 142.3, and 142.5 (s, C_6H_5), 166.9 and 167.4 (s, *C*O$COCH_3$)$_2$), 200.9 and 202.3 (s, $COCH_3$), 336.9 and 337.8 (t, $^2J_{CP}$ = 14.8 Hz, Ru=*C*).

Table 1. Crystal Data and Details of the Structure Determination of Compound 4

Crystal Data	
formula	$C_{36}H_{59}OBF_4P_2Ru$
fw	757.65
cryst syst	monoclinic
space group	*P*21/*c* (No. 14)
a, *b*, *c* [Å]	14.780(3), 11.933(2), 20.543(4)
α, *β*, *γ* [deg]	90, 93.15(3), 90
volume [Å^3]	3617.7(12)
Z	4
D_{calc} [g/cm^3]	1.391
μ(Mo Kα) [mm^{-1}]	0.570
F(000)	1592
cryst size [mm]	0.24 × 0.30 × 0.43
Data Collection	
temperature [K]	100
radiation [Å]	Mo Kα 0.71073
θ min., max. [deg]	2.0, 25.1
dataset	−17:14; −12:14; −4: 24
no. of total, unique data, *R*(int)	16 201, 6341, 0.028
no. of obsd data [$I > 2.0\sigma I$]	5893
Refinement	
N_{ref}, N_{par}	6341, 560
R, R_w^2, S^a	0.0616, 0.1314, 1.07
max. and av shift/error	0.09, 0.00
min. and max. resd dens [e Å^{-3}]	−0.71, 0.76

[a] $w = 1/[S^2(F_o^2) + (0.0385P)^2 + 14.0484P]$ where $P = (F_o^2 + 2F_c^2)$].

X-ray Structure Determination. A single crystal of compound **4** was mounted on a glass fiber to carry out the crystallographic study. Crystal data and experimental details are given in Table 1. X-ray diffraction data collection was measured at 100 K on a Bruker Smart APEX CCD three-circle diffractometer using a sealed tube source and graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at the Servicio Central de Ciencia y Tecnología de la Universidad de Cádiz. Data were recorded in four sets of frames over a hemisphere of the reciprocal space by omega scans with $\delta(\omega)$ 0.30° and exposure of 10 s per frame. Correction for absorption and crystal decay (insignificant) were applied by semiempirical methods from equivalents using the program SADABS.[19] The structure was solved by direct methods, completed by subsequent difference Fourier syntheses, and refined on F^2 by full-matrix least-squares procedures using the programs contained in the SHELXTL package.[20] Most non-hydrogen atoms were refined with anisotropic displacement parameters. The $[BF_4]^{-1}$ anion, isopropyl groups, and $-CH_2-CH_2-$ chain in the dippe ligand showed orientation disorder. All these fragments were refined in two orientations with complementary site occupation factors. The hydrogen atoms were refined using the SHELX riding model. The program ORTEP-3[21] was used for plotting.

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Supporting Information Available: ^{1}H spectra for compounds **2**, **3**, and **4**-d_6 (by reaction with deuterated acetone), ^{1}H and ^{13}C-{^{1}H} NMR spectra for compounds **4**−**11**, and CIF file giving crystallographic data for **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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