The Contribution Made by Triphenylphosphane in the Putative Catalysis by Ruthenium Species in Conjugate Additions of β-Dicarbonyl Compounds

Maria Lumbierres,[a] Caroline Marchi,[a] Marcial Moreno-Mañas,*[a] Rosa M. Sebastián,[a] Adelina Vallribera,[a] Elena Lago,[b] and Elies Molins[b]

Keywords: Catalysis / Michael additions / Ruthenium / Hydrides / Chlorides / Triphenylphosphane

Triphenylphosphane catalyzes conjugate additions of β-dicarbonyl compounds to π-acceptor olefins and dialkyl azodicarboxylates. Formation of quaternary centers at the nucleophiles has been achieved. The catalytic action of tris(triphenylphosphane)ruthenium(II) chloride and tetrakis(triphenylphosphane)ruthenium(II) hydride is at least partially due to the phosphane ligand.

Introduction

Conjugate addition of active methylene compounds (β-dicarbonyl moieties and the like) to electron-deficient alkenes and related species constitutes a useful reaction for forming C−C bonds.[1,2] In general, it is carried out in the presence of strong bases. Transition metal-catalyzed and lanthanide-catalyzed conjugate additions are valuable alternatives, since they are performed in essentially neutral media, thus avoiding side reactions caused by the basic catalyst. This variant has been reviewed and its advantages discussed in depth.[3] For instance, monosubstitution at the intercarbonyl position affords compounds still possessing an active proton, which under basic conditions compromises the stereochemical identity of the new stereogenic center. This renders the metal-catalyzed version of the conjugate addition, operating in neutral media, very attractive.

These metal-catalyzed reactions are quite general in terms of the nucleophile, but far less general as far as the electrophile is concerned, many of the catalysts reported only being useful for additions to butenone or other α,β-unsaturated ketones. Ruthenium species are useful and versatile catalysts in many organic reactions.[4−6] In particular, tetrakis(triphenylphosphane)ruthenium(II) hydride catalyzes conjugate additions of β-dicarbonyl compounds and β-cyanocarbonyls to α,β-unsaturated ketones, aldehydes, esters, nitriles, and acetylenic esters, and also permits the formation of quaternary centers.[7−9] If ruthenium(II) hydride is anchored to a phosphane-containing dendrimer, recovery and reutilization of the catalytic material is possible.[10] Other phosphane-containing complexes of ruthenium(II) have been reported to be active in conjugate additions.[11−14]

Our interest in this field prompted us to explore nickel(II) complexes with success, both for the generation of quaternary centers and, when working with acetoacetyl derivatives of chiral inductors, for induction of diastereoselectivity.[15,16] With the goal of improving our results obtained with nickel, our attention was drawn towards other metals, and in particular towards ruthenium.

Results and Discussion

In principle, we wanted to use catalysis by $RuH_2(PPh_3)_4$,[17] as described by Murahashi[7,8] and by Echavarren[9] in the additions of acetoacetyl derivatives of chiral inductors to electronically deficient olefins and azodicarboxylates. Soon we realized that the more accessible $RuCl_2(PPh_3)_3$ was not inferior to $RuH_2(PPh_3)_4$ in catalytic activity. It had been mentioned previously[9] that the chloride showed some catalytic activity in the reaction between dimethyl malonate and butenone, but no more attention had been paid to this. Since $RuCl_2(PPh_3)_3$ is the synthetic precursor of $RuH_2(PPh_3)_4$[17] we decided to follow up our initial results. We then found that triphenylphosphane also catalyzed our reactions. The catalytic role of triphenylphosphane had already been suggested by Echavarren,[9] although the conclusion in this case was that the catalysis of Michael additions by $RuH_2(PPh_3)_4$ was more general than triphenylphosphane-based catalysis. We present our results in this field in this report.

$RuCl_2(PPh_3)_3$ and triphenylphosphane are efficient and general catalysts for reactions between β-dicarbonyl compounds and activated π-systems (Table 1), including those involving generation of quaternary centers (Scheme 1 and Table 2). In the course of this investigation, several control experiments, with both ruthenium species and triphenylphosphane absent, failed to afford any reaction product.

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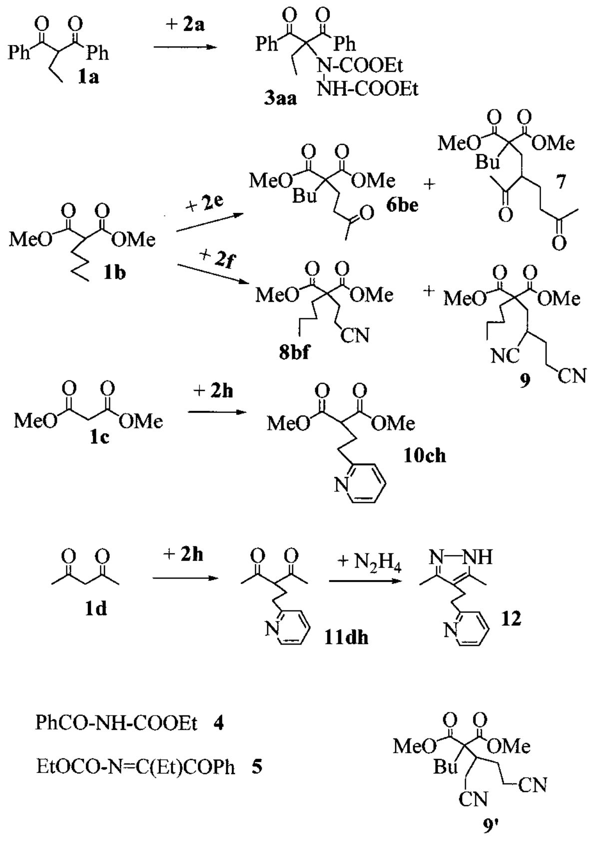
[a] Department of Chemistry, Universitat Autònoma de Barcelona,
08193 Cerdanyola, Barcelona, Spain
Fax: (internat.) + 34 935811265
E-mail: marcial.moreno@uab.es
[b] Institut de Ciència de Materials de Barcelona (CSIC), Campus de la UAB,
08193 Cerdanyola, Spain

1434−193X/01/0612−2121 $ 17.50+.50/0

Table 1. List of electrophiles E

E	
EtOCON=NCOOEt	**2a**
BzlOCON=NCOOBzl	**2b**
*i*PrOCON=NCOO*i*Pr	**2c**
*t*BuOCON=NCOO*t*Bu	**2d**
$CH_2=CHCOCH_3$	**2e**
$CH_2=CHCN$	**2f**
$CH_2=CHCOOEt$	**2g**
2-vinylpyridine	**2h**



Scheme 1

Typical reaction conditions are given in Table 2. β-Diketone **1a** reacted with diethyl azodicarboxylate (**2a**) in refluxing acetonitrile in the presence of 6% molar ruthenium chloride at 0.2 M catalyst concentration to afford **3aa** (83%, run 1). Reactions between **1a** and **2a** proved to be capricious, in some cases affording the cleavage products **4** and **5**, as in run 2 (ruthenium hydride). Vigorous refluxing acts to favor cleavage. However, when performed at room temperature in the presence of 10% molar triphenylphosphane, the reaction afforded **3aa** in quantitative yield (run 3). It is noteworthy that the cationic complex [CpRu(acetonitrile)$_3$]PF_6[20] – featuring no phosphane moieties – is inactive (run 4).

Table 2. Conjugate additions promoted by ruthenium complexes or by triphenylphosphane (Scheme 1)

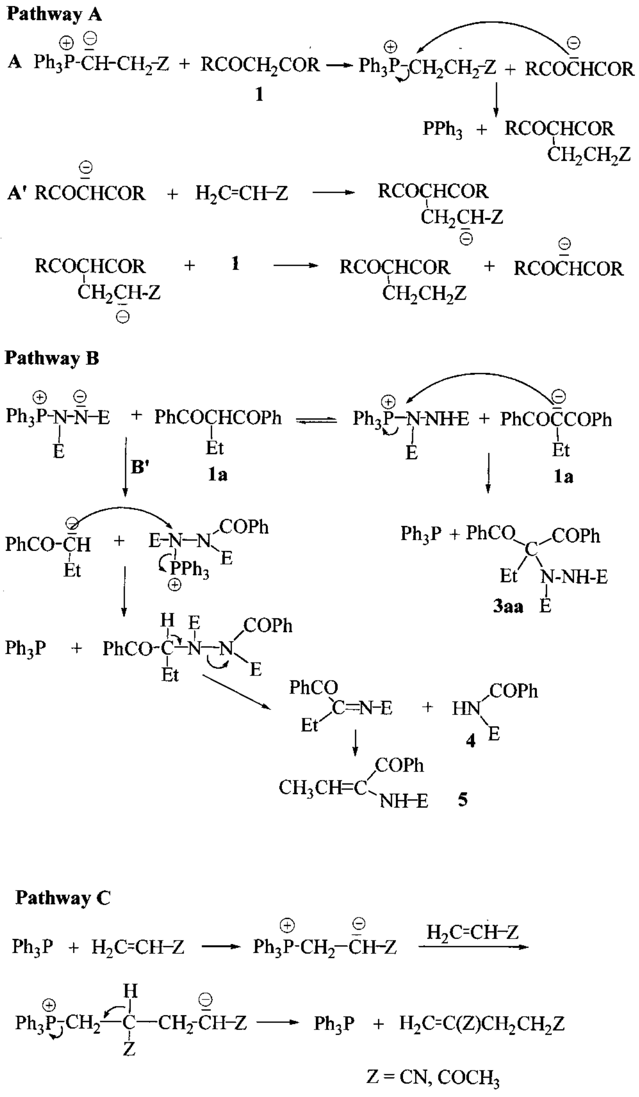
Run	Nu[a]	E[b]	Nu/E[c]	Catalyst[d]	Yield (%)
1	**1a**	**2a**	1:1.5	$RuCl_2(PPh_3)_3$	**3aa** (83)
2	**1a**	**2a**	1:1.5	$RuH_2(PPh_3)_4$	**4** (51)+ **5** (71)
3	**1a**	**2a**	1:1.5	PPh_3[e]	**3aa** (100)
4	**1a**	**2a**	1:1.5	[CpRu(NCMe)$_3$]PF_6[g]	–
5	**1b**	**2e**	1:4	$RuCl_2(PPh_3)_3$	**6be** (67,94)[h]
6	**1b**	**2e**	1:4	$RuH_2(PPh_3)_4$	**6be** (46)
7	**1b**	**2e**	1:4	PPh_3	**6be** (66) + **7** (17)
8	**1b**	**2e**	1:4	PPh_3[f]	**6be** (62) + **7** (15)
9	**1b**	**2e**	1:4	[CpRu(NCMe)$_3$]PF_6 [g]	–
10	**1b**	**2f**	1:6.3	$RuCl_2(PPh_3)_3$	**8bf** (45) + **9** (25)
11	**1b**	**2f**	1:6.3	PPh_3 [f][i]	**8bf** (78)
12	**1c**	**2h**	1:5	$RuCl_2(PPh_3)_3$	**10ch**[j]
13	**1d**	**2h**	1:4.7	$RuCl_2(PPh_3)_3$	**11dh** (49)[k]

[a] **1a**, m.p. 85–86 °C (ref.[18] 83–84 °C); **1b** bp 79–82 °C/4 Torr (ref.[19] bp 219–221 °C/760 Torr). [Nu] = 3.3 M. – [b] See Table 1. – [c] Molar ratio. – [d] All reactions were performed in refluxing acetonitrile, under argon, for 24 h in the dark, using 6% molar ruthenium or 18% PPh_3 unless otherwise stated. – [e] 10% molar. – [f] At room temp. – [g] For preparation of this cationic complex see ref.[20] – [h] Yields of two independent reactions. – [i] Reaction time: 72 hours. – [j] Compound **10ch** reverted to starting materials upon attempted purification. – [k] Overall yield of pyrazole **12**.

The proposed mechanism, taking account of all experimental data, is shown in Scheme 2. Triphenylphosphane reacts in a way reminiscent of the Baylis–Hillman reaction,[21] attacking at the electrophilic end of electronically deficient olefins to afford a phosphonium ylide intermediate, which generates the conjugate base of dicarbonyl **1** by proton transfer. Nucleophilic attack of the conjugate base of **1** on the phosphonium cation affords the addition product, with recovery of the phosphane (Pathway A). Another alternative, proposed by Echavarren,[9] is based on a cyclic mechanism incorporating attack of the conjugate base onto the olefin and transprotonation (Pathway A′). When diethyl azodicarboxylate (**2a**) is the electrophilic partner, a phosphonium imidate is generated. Proton transfer (Pathway B) produces the conjugate addition product **3aa** as before, either directly or by the cyclic mechanism. However, the reversibility of the proton transfer opens the way for debenzoylative attack on **1a** (Pathway B′). The intermediate formed upon liberation of the phosphane decomposes into **4** and **5**.

More reactions were now studied (Scheme 1 and Table 2). Thus, β-diester **1b** reacted with butenone (**2e**) to afford the addition product **6be** (67 and 94% in two different reactions, run 5). The same reaction performed under ruthenium hydride catalysis conditions gave a lower yield of **6be** (run 6). Again, triphenylphosphane catalyzed the conjugate addition, affording satisfactory yields of **6be** (runs 7 and 8). In both cases, minor quantities of compound **7** (vide infra) were isolated. The cationic ruthenium complex was again inactive (run 9).

In the case of acrylonitrile (**2f**) as electrophile, compounds **8bf** (45%) and **9** (25%) were obtained under ruthenium(II) chloride catalysis conditions (run 10). Compound



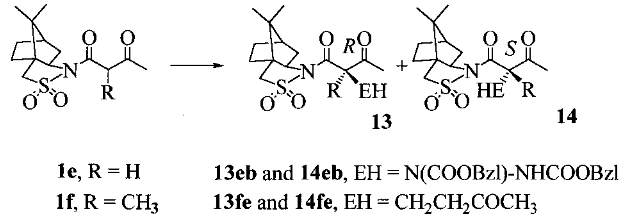
Scheme 2

9 comes from a reaction between **1b** and a dimer of acrylonitrile. The formation of linear dimers of acrylonitrile ($NCCH_2CH_2CH{=}CHCN$) through ruthenium catalysis is known;[5] however, product **9** originates from a branched dimer of acrylonitrile. Structure **9** is proposed on the bases of ^{13}C NMR spectroscopic data, mainly the signal at $\delta = 26.4$ assigned to *C*H−CN by distortionless enhancement by polarization transfer (DEPT) experiments. The formation of the required branched dimer of acetonitrile is indicated in Scheme 2 (Pathway C). Similarly, compound **7** (runs 7 and 8) was produced from the reaction between **1b** and a branched dimer of butenone. Complementary experiments showed that acrylonitrile and butenone gave dimers in the presence of triphenylphosphane in acetonitrile, at reflux or at room temperature, respectively. The formation of such branched dimers of acrylonitrile and butenone in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) has been reported[22] − DABCO is another catalyst for the Baylis−Hillman reaction.[21]

Use of triphenylphosphane alone in treatment of **1b** and **2f** resulted in **8bf** in 78% yield (run 11). No reaction took place between esters **1b** and **2g** in the presence of either ruthenium or triphenylphosphane.

Treatment of dimethyl malonate (**1c**) with 2-vinylpyridine (**2h**) in the presence of ruthenium chloride (run 12) afforded **10ch** (NMR monitoring). However, **10ch** reverted to starting materials upon attempted distillation or chromatography, with vinylpyridine **2h** being recovered. We next studied the reaction between acetylacetone (**1d**) and **2h**. The addition product **11dh** was immediately treated with hydrazine to afford the stable pyrazole **12**, which was isolated and fully characterized (run 13).

We then studied ruthenium catalysis in acetoacetyl derivatives of chirality inductors. Some results obtained with the Oppolzer sultam[23] are given in Scheme 3 and Table 3. *N*-Acetoacetyl-(2*R*)-bornane-10,2-sultam (**1e**) reacted with dibenzyl azodicarboxylate (**2b**) in the presence of either ruthenium catalyst to afford, in both cases, quantitative yields of diastereoisomers **13eb** and **14eb** in the same diastereomeric excess (*de*) (runs 1 and 2). Triphenylphosphane catalyzed the same reaction (run 3), although the *de* was lower.



Scheme 3

Table 3. Conjugate additions of acetoacetyl derivatives of Oppolzer sultam promoted by ruthenium complexes or by triphenylphosphane (Scheme 3)

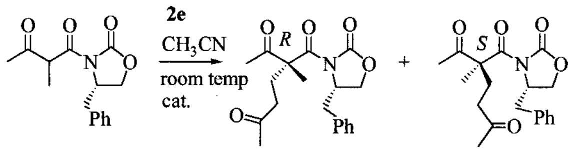
Run	Nu	E	Nu/E[a]	[Nu]	Catalyst[b]	Yield (%)	*de*[c] (%)
1	**1e**	**2b**	1:1.2	0.6 M	$RuH_2(PPh_3)_4$	**13eb** + **14eb** (100)	81
2	**1e**	**2b**	1:1.2	0.6 M	$RuCl_2(PPh_3)_3$	**13eb** + **14eb** (100)	79
3	**1e**	**2b**	1:1.2	0.6 M	PPh_3	**13eb** + **14eb** (86)	22
4	**1f**	**2e**	1:2.4	2 M	$RuH_2(PPh_3)_4$[d]	**13fe** (33)	[e]
5[f]	**1f**	**2e**	1:2.4	2 M	PPh_3	**13fe** + **14fe** (63)	86

[a] Molar ratio. − [b] All reactions were performed in refluxing acetonitrile, under argon, for 24 h in the dark, using 6% molar ruthenium or 18% PPh_3, unless otherwise stated. − [c] Diastereomeric excesses were determined by ^1H NMR integration of well separated signals. − [d] 3% M ruthenium. − [e] Only one diastereoisomer detected. X-ray analysis of **13fe**: CCDC deposition number 147764. − [f] At room temp.

N-(2′-Methyl-3′-oxobutanoyl)-(2*R*)-bornane-10,2-sultam (**1f**) was much less reactive. However, **1f** reacted with butenone under ruthenium hydride catalysis conditions to afford one single diastereoisomer, albeit in low yield (33%). The corresponding reaction under ruthenium chloride catalysis conditions was not attempted. An X-ray diffraction study of this diastereoisomer found the (*R*) configuration at the new stereogenic center at C2′ of the N-chain (**13fe**) (run

4). This stereochemical preference is the same as that previously described for the same chirality inductor in conventional alkylations of **1e**.[24,25] We assume the same stereochemical behavior in assigning configurations to diastereoisomers **13eb** and **14eb**. The reaction between **1f** and **2e**, when catalyzed by triphenylphosphane at room temp, afforded a better yield of addition products **13fe** and **14fe** in excellent *de* (run 5).

(*4S*)-*N*-(2′-Methyl-3′-oxobutanoyl)-4-benzyloxazolidin-2-one (**1g**) reacted with butenone (**2e**) at room temperature under ruthenium hydride catalysis conditions (6% molar) to afford a mixture of diastereoisomers **15ge** and **16ge** in good yield (77%) and 47% *de* (Scheme 4). The same reaction in the presence of triphenylphosphane (18% molar) was somewhat inferior (Scheme 4). Again, assignment of configuration to the major and to the minor diastereoisomers was made by analogy with previous alkylations of (*4S*)-*N*-(3′-oxobutanoyl)-4-benzyloxazolidin-2-one.[25] Ketoamide **1g** was inert towards acrylonitrile (**2f**) and ethyl acrylate (**2g**) in the presence of ruthenium hydride.



1g **15ge** **16ge**

Cat: $RuH_2(PPh_3)_4$,77% yield, 47% de
Cat: Triphenylphosphine, 57% yield, 36% de

Scheme 4

The 2-methylacetoacetate of D-ribonolactone acetonide (**1h**) is a more versatile substrate than **1f** or **1g**. Alkylations on **1h** and on its 2-butyl congener occurred with good diastereoselectivities, in spite of the differentiating center being one carbon atom more distant than in **1g**. Further transformations on the acetyl group and on the primary ester permitted the preparation of optically pure α,α-disubstituted glycines.[25,26] We therefore undertook an exploration of the conjugate additions of **1h** under ruthenium catalysis and triphenylphosphane catalysis conditions (Table 4 and Scheme 5). Even though the *de*s were moderate or low, the reactivity of **1h** is remarkable in terms of chemical yields and broad range of electrophiles.

Ruthenium(II) chloride gave better yields than ruthenium(II) hydride in the reaction with butenone **2e** (runs 1 and 2), affording **17he** and **18he**. Triphenylphosphane also gave excellent chemical yields (runs 3 and 4). In all cases, the *de*s were only moderate and in a similar range.

The less active ethyl acrylate (**2g**) reacted in the presence of ruthenium hydride (run 5) to afford reasonable yields of **17hg** and **18hg**. No other catalysts were tested.

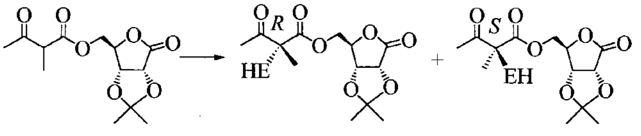
Acrylonitrile (**2f**) reacted without dimerization to afford an equimolar mixture of **17hf** and **18hf** (run 6). Only ruthenium hydride was tested.

A comparison of the performance of the three catalysts was made for two dialkyl azodicarboxylates: **2a** and **2b** (runs 8−10 and 11−13). Again, chemical yields were synthetically useful but *de*s were moderate or very low, even when working at lower temp and with longer reaction times (run 12).

Table 4. Conjugate additions of **1h** promoted by ruthenium complexes or by triphenylphosphane (Scheme 5)

Run[a]	E	Nu/E[b]	Catalyst	Yield (%)	*de*[c] (%)
1	**2e**	1:2.4	$RuCl_2(PPh_3)_3$	**17he** + **18he** (92)	30
2	**2e**	1:2.4	$RuH_2(PPh_3)_4$	**17he** + **18he** (69)	27
3	**2e**	1:2.4	PPh_3[d]	**17he** + **18he** (100)	30
4	**2e**	1:2.4	PPh_3	**17he** + **18he** (90)	42
5	**2g**	1:2.4	$RuH_2(PPh_3)_4$	**17hg** + **18hg** (51)	42
6	**2f**	1:2.4	$RuH_2(PPh_3)_4$	**17hf** + **18hf** (52)	2
7	**2h**	1:2.4	$RuH_2(PPh_3)_4$	···	–
8	**2a**	1:1.2	$RuCl_2(PPh_3)_3$	**17ha** + **18ha** (92)	13
9	**2a**	1:1.2	$RuH_2(PPh_3)_4$	**17ha** + **18ha** (72)	33
10	**2a**	1:1.2	PPh_3	**17ha** + **18ha** (83)	48
11	**2b**	1:1.2	$RuCl_2(PPh_3)_3$	**17hb** + **18hb** (98)	5
12[e]	**2b**	1:1.2	$RuH_2(PPh_3)_4$	**17hb** + **18hb** (64)	34
13	**2b**	1:1.2	PPh_3	**17hb** + **18hb** (65)	0
13	**2c**	1:2.6	$RuH_2(PPh_3)_4$	**17hc** + **18hc** (69)	40
14	**2d**	1:1.2	$RuCl_2(PPh_3)_3$	**17hd** + **18hd** (75)	0
15	**2d**	1:1.2	$RuH_2(PPh_3)_4$	**17hd** + **18hd** (55)	19

[a] General reaction conditions: reaction time of 24 h at room temp, [Nu] = 2 M, 3% molar of metal catalyst or 9% molar triphenylphosphane unless otherwise stated. − [b] Molar ratio. − [c] Diastereomeric excesses were determined by ^1H NMR integration of well separated signals. − [d] 18% Molar triphenylphosphane. − [e] 72 h at −12 °C.



1h **17h(a-h)** **18h(a-h)**

17ha and **18ha**, EH = N(COOEt)-NHCOOEt
17hb and **18hb**, EH = N(COOBzl)-NHCOOBzl
17hc and **18hc**, EH = N(COO*i*Pr)-NHCOO*i*Pr
17hd and **18hd**, EH = N(COO*t*Bu)-NHCOO*t*Bu)
17he and **18he**, EH = $CH_2CH_2COCH_3$
17hf and **18hf**, EH = CH_2CH_2CN
17hg and **18hg**, EH = CH_2CH_2COOEt
17hh and **18hh**, EH = CH_2CH_2-(2-pyridyl)

Scheme 5

Conclusion

Not all possible comparative studies between the three catalysts were carried out. Only a number of selected examples are gathered in Table 2−Table 4 and in Scheme 4. The conclusion is that ruthenium(II) chloride is slightly better than ruthenium hydride, and in any case no worse in terms of chemical yields. Moreover, the stable tris(triphenylphosphane)ruthenium(II) chloride has the added bonus of being the synthetic precursor of tetrakis(triphenylphosphane)ruthenium(II) hydride.[17]

In all cases studied, however, triphenylphosphane had the same effect as the two ruthenium catalysts. Curiously enough, all other reports on catalysis by ruthenium species in conjugate additions refer to phosphane-containing ruthenium complexes.[7−14] It is particularly worth mentioning the inertness of the cationic complex [CpRu(NCCH$_3$)$_3$]PF$_6$ (see runs 4 and 9 in Table 2), whereas salts based on the related cation [CpRu(PPh$_3$)$_2$] are active in conjugate additions of methylene and methyne groups activated by nitriles.[13] However, nitriles permit a different mechanism of activation, involving coordination of nitrogen atom to the cationic ruthenium atom.

For β-diketones, keto esters, and ketoamides, a reasonable hypothesis is that triphenylphosphane (or other phosphanes) released from the metal contributes totally or partially to the catalysis, through mechanisms reminiscent of the Baylis−Hillman reaction (Scheme 2). The question of the involvement of phosphanes as real catalysts in supposedly palladium-catalyzed[27,28] or ruthenium-, rhenium-, and iridium-catalyzed reactions[29,30] has been raised before.

In summary, the above hypothesis suggests a reasonable conclusion: it would be advisable to test triphenylphosphane before examining ruthenium chloride or hydride in any reaction of this type.

Experimental Section

General Remarks: Melting points were determined with a Kofler apparatus and are uncorrected. − IR spectra were recorded with a Nicolet FT-IR 510 ZDX. − NMR spectra were recorded with a Bruker AC 250 or a Bruker AM 400. − ^{1}H NMR chemical shifts are reported relative to tetramethylsilane at δ = 0.00. Coupling constants are reported in Hz. − ^{13}C NMR chemical shifts are expressed relative to tetramethylsilane at δ = 0.0. − Mass spectra (EIMS) were obtained with a Hewlett−Packard 5989A spectrometer and determined at an ionizing voltage of 70 eV; relevant data are listed as *m/z* (%). − Elemental analyses were performed at the "Servei d'Anàlisi Química de la Universitat Autònoma de Barcelona".

Diethyl *N*-(1,1-Dibenzoylpropyl)hydrazine-*N,N'*-dicarboxylate (3aa) under Tris(triphenylphosphane)ruthenium Chloride Catalysis Conditions. − General Method: A mixture of 2-ethyl-1,3-diphenyl-1,3-propanedione (**1a**) (1.26 g, 5.0 mmol), diethyl azodicarboxylate (**2a**) (1.2 mL, 7.5 mmol), tris(triphenylphosphane)ruthenium(II) chloride[31] (0.2 g, 0.3 mmol), and anhydrous acetonitrile was refluxed with stirring, under an argon atmosphere and in the dark, for 24 hours. The solvent was evaporated off and the residue was chromatographed through silica gel. Compound **3aa** was eluted with hexanes/diethyl ether (40:60) as a white solid (1.77 g, 83%), m.p. 122−125 °C (cyclohexane). − IR (KBr): $\tilde{\nu}$ = 3330, 1759, 1728, 1719 cm^{-1}. − ^{1}H NMR (400 MHz, 366 K, [D$_6$]benzene): δ = 0.94 (t, *J* = 7 Hz, 6 H), 1.30−1.33 (br. s, 3 H), 2.42 (q, *J* = 7 Hz, 2 H), 3.98 (q, *J* = 7 Hz, 4 H), 6.86 (s, 1 H), 6.99−7.15 (m, 6 H), 7.53 (d, *J* = 8 Hz, 2 H), 8.09 (d, *J* = 8 Hz, 2 H). − ^{13}C NMR (100 MHz, 336 K, [D$_6$]benzene): δ = 12.8, 14.7, 22.9, 62.2, 62.9, 128.8, 128.9, 129.3, 129.4, 130.5, 130.7, 132.4, 133.7, 135.4, 143.6, 155.6, 156.6, 165.2. − MS: *m/z* (%) = 105 [100], 77 [46]. − $C_{23}H_{26}N_2O_6$ (426.5): calcd. C 64.78, H 6.14, N 6.57; found C 64.80 and 64.94, H 6.14 and 6.13, N 6.47 and 6.44.

Diethyl *N*-(1,1-Dibenzoylpropyl)hydrazine-*N,N'*-dicarboxylate (3aa) under Triphenylphosphane Catalysis Conditions. − General Method: Diketone **1a** (0.32 g, 1.25 mmol) and triphenylphosphane (0.033 g, 0.125 mmol) were dissolved in anhydrous acetonitrile (0.5 mL), with stirring under argon atmosphere. Azodicarboxylate **2a** (0.35 mL, 1.87 mmol) was then added to the mixture, with an exothermic reaction being observed. The mixture was stirred for 24 h at room temp and finally evaporated. The residue was chromatographed through a column of silica gel, using hexanes/diethyl ether (50:50), to afford **3aa** (0.53 g, 100%). See above for physical constants.

All other compounds were prepared by this general method under the particular experimental conditions and with the nature of catalyst, ratios of reagents and catalyst, concentrations, and yields stated in the Tables.

***N*-(Ethoxycarbonyl)benzamide (4):** M.p. 108−110 °C (ref.[32] m.p. 112 °C). − IR (KBr): $\tilde{\nu}$ = 3247, 1799, 1751, 1702 cm^{-1}. − ^{1}H NMR (250 MHz, CDCl$_3$): δ = 1.32 (t, *J* = 7 Hz, 3 H), 4.28 (q, *J* = 7 Hz, 2 H), 7.47 (tt, *J* = 7 and 1 Hz, 2 H), 7.58 (tt, *J* = 7 and 1 Hz, 1 H), 7.85−7.88 (m, 2 H), 8.45 (br. s, 1 H). − ^{13}C NMR (62.5 MHz, CDCl$_3$): δ = 14.2, 62.3, 127.6, 128.7, 132.8, 151.2, 165.0. − MS: *m/z* (%) = 193 [M] (11), 105 [100], 77[47].

2-(Ethoxycarbonylimino)-1-phenyl-1-butanone (5): Oil. − IR (film): $\tilde{\nu}$ = 3211, 1723, 1658 cm^{-1}. − ^{1}H NMR (250 MHz, CDCl$_3$): δ = 1.08 (t, *J* = 7 Hz, 3 H), 1.74 (d, *J* = 7 Hz, 3 H), 4.08 (q, *J* = 7 Hz, 2 H), 6.02 (q, *J* = 7 Hz, 1 H), 6.92 (br. s, 1 H), 7.19−7.29 (m, 3 H), 7.78 (dd, *J* = 8 and 1.5 Hz, 2 H). − ^{13}C NMR (62.5 MHz, CDCl$_3$): δ = 14.3, 61.6, 128.1, 129.2, 132.0, 133.7, 134.9, 137.0, 154.0, 193.2. − MS: *m/z* (%) = 233 [M] (24), 160 [34], 144 [57], 105 [100], 77 [64], 56 [40].

Dimethyl 2-Butyl-2-(3-oxobutyl)malonate (6be): M.p. 43−45 °C (hexanes/diethyl ether). − IR (KBr): $\tilde{\nu}$ = 1732 (br.) cm^{-1}. − ^{1}H NMR (250 MHz, CDCl$_3$): δ = 0.89 (t, *J* = 7 Hz, 3 H), 1.05−1.20 (m, 2 H), 1.20−1.35 (m, 2 H), 1.83−1.89 (m, 2 H), 2.14 (t, J = 7 Hz, 2 H), 2.15 (s, 3 H), 2.43 (t, J = 7 Hz, 2 H), 3.72 (s, 6 H). − ^{13}C NMR (62.9 MHz, CDCl$_3$): δ = 13.8, 22.9, 26.3, 26.7, 29.9, 33.4, 38.8, 52.3, 56.9, 172.0, 207.3. − MS: *m/z* (%) = 259 [M + 1] (5), 202 [22], 145 [98], 113 [36], 81[25], 43 [100]. − $C_{13}H_{22}O_5$ (258.3): calcd. C 60.45, H 8.58; found C 60.54 and 60.47, H 8.82 and 8.73.

Methyl 4-Acetyl-2-butyl-2-methoxycarbonyl-7-oxooctanoate (7): IR (film): $\tilde{\nu}$ = 2957, 1731, 1715 cm^{-1}. − ^{1}H NMR (250 MHz, CDCl$_3$): δ = 0.80 (t, *J* = 7.2 Hz, 3 H), 1.05 (m, 2 H), 1.19 (m, 2 H), 1.42−1.60 (m, 2 H), 1.79 (m, 2 H), 2.07 (s, 3 H), 2.08 (s, 3 H), 2.25 (m, 2 H), 2.40 (m, 2 H), 2.54 (m, 1 H), 3.56 (s, 3 H), 3.59 (s, 3 H). − ^{13}C NMR (62.5 MHz, CDCl$_3$): δ = 12.9, 22.0, 25.5, 28.1, 29.1, 32.2, 33.2, 39.0, 46.3, 51.4, 51.5, 56.2, 171.2, 206.7, 209.4. − MS: *m/z* (%) = 229 [31], 188 [60], 145 [100], 43 [79].

Dimethyl 2-Butyl-2-(2-cyanoethyl)malonate (8bf): This compound was eluted with hexanes/diethyl ether (40:60), as an oil. − IR (film): $\tilde{\nu}$ = 2250, 1732 cm^{-1}. − ^{1}H NMR (250 MHz, CDCl$_3$): δ = 0.93 (t, *J* = 7 Hz, 3 H), 1.11−1.23 (m, 2 H), 1.29−1.41 (m, 2 H), 1.89−1.96 (m, 2 H), 2.24−2.30 (m, 2 H), 2.39−2.46 (m, 2 H), 3.78 (s, 6 H). − ^{13}C NMR (62.9 MHz, CDCl$_3$): δ = 12.9, 13.6, 22.6, 26.0, 28.7, 32.9, 52.5, 56.5, 118.9, 170.8. − MS: *m/z* (%) = 145 [100], 113 [48], 55 [35]. − $C_{12}H_{19}NO_4$ (241.3): calcd. C 59.73, H 7.94, N 5.80; found C 59.80 and 59.82, H 8.02 and 8.04, N 5.63 and 5.62.

Dimethyl 2-Butyl-2-(2,4-dicyanobutyl)malonate (9): This compound was eluted with hexanes/diethyl ether (4:6), as an oil. − IR (film):

ṽ = 2248 (with shoulder), 1732 cm^{-1}. − ^{1}H NMR (250 MHz, CDCl$_3$): δ = 0.93 (t, J = 7 Hz, 3 H), 1.00−1.42 (m, 4 H), 1.95−2.15 (m, 4 H), 2.19−2.24 (m, 2 H), 2.51−2.73 (m, 2 H), 2.78−2.89 (m, 1 H), 3.80 (s, 3 H), 3.81 (s, 3 H). − ^{13}C NMR (62.9 MHz, CDCl$_3$): δ = 13.7, 15.1, 22.7, 26.3, 26.7, 29.7, 33.6, 35.5, 52.8, 52.9, 56.5, 117.8, 119.9, 170.8, 171.0. − MS: *m/z* (%) = 295 [M + 1] (11), 145 [100], 113 [54], 68 [34], 55[32]. − C$_{15}$H$_{22}$N$_2$O$_4$ (294.4): calcd. C 61.21, H 7.53, N 9.52; found C 61.35 and 61.39, H 7.56 and 7.41, N 9.34 and 9.16.

3-[2-(2-Pyridyl)ethyl]-2,4-pentanedione (11dh): This compound was filtered through silica gel to remove metallic species. It was an oil. − IR (film): ṽ = 1696 cm^{-1}. − ^{1}H NMR (250 MHz, CDCl$_3$): δ = 2.08 (s, 6 H, enol), 2.20 (s, 3 H, keto), 2.0−3.0 (m, 4 H, keto + enol), 3.70 (t, J = 7 Hz, 1 H, keto), 7.0−7.8 (m, 3 H, keto + enol), 8.53 (d, J = 4 Hz, 1 H, keto), 8.61 (d, J = 4 Hz, 1 H, enol), 16.27 (s, 1 H, enol).

3,5-Dimethyl-4-[2-(2-pyridyl)ethyl]pyrazole (12): The oil from the previous operation (1.92 g) was treated with aqueous hydrazine (7.3 mL, 150 mmol) in ethanol (20 mL). The solution was refluxed for 48 hours. The solvent was evaporated off and the residue was partitioned between water and chloroform. The organic layer was dried and evaporated. The resulting oil was passed through silica gel, eluting with hexanes/ethyl acetate/methanol (25:70:5), to afford **12** as an oil (94%). − IR (film): ṽ = 3500−2700 (broad), 3203, 3153, 3087, 3010, 2924, 2880 cm^{-1}. − ^{1}H NMR (250 MHz, CDCl$_3$): δ = 2.06 (s, 6 H), 2.79 (t, J = 5 Hz, 2 H), 2.91 (t, J = 5 Hz, 2 H), 6.95 (d, J = 5 Hz, 1 H), 7.10 (t, J = 8 Hz, 1 H), 7.52 (t, J = 8 Hz, 1 H), 8.56 (d, J = 5 Hz, 1 H). − ^{13}C NMR (62.9 MHz, CDCl$_3$): δ = 11.0, 23.8, 39.5, 114.8, 121.5, 123.7, 136.6, 142.6, 149.7, 161.8. − HRMS: *m/z* (%) calcd. 201.1266 amu; found 201.1274 amu. Dipicrate of **12**: m.p. 226−227 °C (ethanol).

(2*R*,2*R*′)-*N*-{2-[*N,N*′-Bis(benzyloxycarbonyl)hydrazino]-3-oxobutanoyl}bornane-10,2-sultam (13eb): This major diastereoisomer was separated by chromatography on silica gel, eluting with hexanes/diethyl ether (1:1). It was a solid, m.p. 61−63 °C. − IR (KBr): ṽ = 3340, 3324, 1735, 1699, 1332, 1218 cm^{-1}. − ^{1}H NMR (250 MHz, 336 K, [D$_6$]benzene): δ = 0.43 (s, 3 H), 0.67−1.39 (m, 5 H), 1.04 (s, 3 H), 1.79 (dd, J = 14 and 8 Hz, 1 H), 2.25 (dq, J = 14 and 4 Hz, 1 H), 2.44 (s, 3 H), 2.72 (center of AB system, 2 H), 3.50 (dd, J = 8 and 5 Hz, 1 H), 4.90 (center of AB system, 2 H), 5.05 (center of AB system, 2 H), 6.57 (s, 1 H), 6.97−7.31 (m, 10 H). − ^{13}C NMR (62.9 MHz, 336 K, [D$_6$]benzene): δ = 20.2, 20.4, 20.9, 27.1, 30.7, 33.0, 38.3, 38.5, 38.6, 45.4, 48.4, 49.6, 52.7, 52.9, 53.0, 65.5, 65.6, 68.2, 68.3, 68.5, 69.7, 69.8, 69.9, 70.7, 70.9, 127.9, 128.2, 128.6, 129.0, 129.2, 136.8, 137.2, 156.5, 156.9, 167.9, 198.2. − $[\alpha]_D^{25}$ = +28.3 (c = 1.06, chloroform). − C$_{30}$H$_{35}$N$_3$O$_8$S (597.7): calcd. C 60.29, H 5.90, N 7.03; found C 60.56 and 60.38, H 6.25 and 6.18, N 6.79 and 6.79.

(2*R*,2*R*′)-*N*-(2′-Acetyl-2′-methyl-1′,5′-dioxohexyl)bornane-10,2-sultam (13fe): This compound was isolated by chromatography on silica gel, eluting with hexanes/diethyl ether. It was a solid, m.p. 112−114 °C. − IR (KBr): ṽ = 1716, 1668, 1336, 1190, 1171 cm^{-1}. − ^{1}H NMR (250 MHz, CDCl$_3$): δ = 0.92 (s, 3 H), 1.10 (s, 3 H), 1.42 (s, 3 H), 1.30−1.50 (m, 2 H), 1.80−1.95 (m, 3 H), 2.13 (s, 3 H), 2.21 (s, 3 H), 2.05−2.22 (m, 3 H), 2.35−2.65 (m, 3 H), 3.35 (s, 2 H), 3.90 (t, J = 7 Hz, 1 H). − ^{13}C NMR (62.9 MHz, CDCl$_3$): δ = 19.9, 20.0, 22.2, 26.1, 26.6, 28.7, 30.0, 32.6, 38.2, 38.5, 44.0, 52.7, 61.6, 66.2, 171.8, 206.7, 207.5. − $[\alpha]_D^{25}$ = −36 (c = 1.05, chloroform). − C$_{19}$H$_{29}$NO$_5$S (383.5): calcd. C 59.51, H 7.63, N 3.65, S 8.34; found C 59.64 and 59.59, H 7.51 and 7.49, N 3.57 and 3.48, S 8.20 and 8.14.

(4*S*,2′*R*)-*N*-(2′-Acetyl-2′-methyl-1′,5′-dioxohexyl)-4-benzyloxazolidin-2-one (15ge): This major diastereoisomer was separated by chromatography on silica gel with hexanes/diethyl ether (3:7). It was eluted second, as an oil. − IR (film) 1779, 1697 (br.) cm^{-1}. − ^{1}H NMR (250 MHz, CDCl$_3$): δ = 1.59 (s, 3 H), 2.12 (s, 3 H), 2.25 (s, 3 H), 2.11−2.33 (m, 2 H), 2.33−2.46 (m, 1 H), 2.55−2.68 (m, 1 H), 2.78 (dd, J = 13 and 9 Hz, 1 H), 3.24 (dd, J = 13 and 4 Hz, 1 H), 4.17 (dd, J = 9 and 2 Hz, 1 H), 4.27 (t, J = 9 Hz, 1 H), 4.62−4.74 (m, 1 H), 7.19−7.34 (m, 5 H). − ^{13}C NMR (62.9 Hz, CDCl$_3$): δ = 21.8, 25.7, 29.1, 30.3, 37.8, 38.9, 56.0, 66.6, 127.4, 128.9, 129.5, 135.2, 153.9, 172.1, 207.3, 207.4. − $[\alpha]_D^{25}$ = +132 (c = 1.03, chloroform).

(2*R*)-2-[*N,N*′-Bis(ethoxycarbonyl)hydrazino]-2-methyl-3-oxobutanoate of D-Ribonolactone (17ha): This major diastereoisomer was separated by chromatography on silica gel, eluting with hexanes/diethyl ether (2:8). It was eluted first, as a solid, m.p. 48−50 °C. − IR (KBr): ṽ = 3325, 1799, 1752, 1724 cm^{-1}. − ^{1}H NMR (250 MHz, 336 K, [D$_6$]benzene): δ = 0.96 (t, J = 7 Hz, 6 H), 1.22 (s, 3 H), 1.25−1.5 (m, 8 H), 2.11 (br. s, 3 H), 3.84−4.11 (m, 7 H), 4.22 (s, 1 H), 4.56 (d, J = 6 Hz, 1 H), 6.00 (br. s, 1 H). − ^{13}C NMR (62.9 MHz, 366 K, [D$_6$]benzene): δ = 14.1−14.4, 19.4, 25.7, 26.8, 27.3, 62.1−62.6, 63.5−64.0, 64.8−65.4, 75.8−76.2, 78.1−78.4, 79.8−80.2, 113.5, 156.7, 156.9, 169.0, 173.3. − $[\alpha]_D^{25}$ = −43 (c = 1.07, chloroform).

(2*R*)-2-[*N,N*′-Bis(benzyloxycarbonyl)hydrazino]-2-methyl-3-oxobutanoate of D-Ribonolactone (17hb): This major diastereoisomer was separated by chromatography on silica gel, eluting with hexanes/diethyl ether (2:8). It was eluted first, as a solid, m.p. 53−56 °C (hexanes/diethyl ether). − IR (KBr): ṽ = 3323, 1797, 1750, 1727 cm^{-1}. − ^{1}H NMR (250 MHz, 336 K, [D$_6$]benzene): δ = 1.29 (s, 3 H), 1.43 (s, 6 H), 2.17 (br. s, 3 H), 3.85−4.11 (m, 2 H), 4.25 (m, 1 H), 4.53 (d, J = 6 Hz, 1 H), 4.63−4.65 (m, 5 H), 6.54 (br. s, 1 H), 7.09−7.23 (m, 10 H). − ^{13}C NMR (62.9 MHz, 336 K, [D$_6$]benzene): δ = 19.4, 25.8, 26.8, 64.8−65.3, 68.2−68.4, 69.4, 75.9−76.3, 78.1−78.4, 79.9−80.2, 113.5, 136.0, 136.3, 156.6, 168.8, 173.4. − $[\alpha]_D^{25}$ = −37 (c = 1.21, chloroform). − C$_{29}$H$_{32}$N$_2$O$_{11}$ (584.6): calcd. C 59.58, H 5.52, N 4.79; found C 59.43 and 59.49, H 5.69 and 5.70, N 4.38 and 4.35.

(2*R*)-2-[*N,N*′-Bis(isopropyloxycarbonyl)hydrazino]-2-methyl-3-oxobutanoate of D-Ribonolactone (17hc): This major diastereoisomer was separated by chromatography on silica gel, eluting with hexanes/diethyl ether (3:7). It was eluted first, as a solid, m.p. 56−58 °C (hexanes/diethyl ether). − IR (KBr): ṽ = 1799, 1750, 1725 cm^{-1}. − ^{1}H NMR (250 MHz, 336 K, [D$_6$]benzene): δ = 1.03 (d, J = 7 Hz, 6 H; two minor doublets appear at δ = 0.97 and 1.06), 1.22 (s, 3 H), 1.35 (s, 3 H), 1.37 (s, 3 H), 2.16 (br. s, 3 H), 4.11 (br. signal, 2 H), 4.35 (t, J = 2 Hz, 1 H), 4.62 (d, J = 5 Hz, 1 H), 4.88 (septet, J = 7 Hz, 2 H), 6.31 (br. s, 1 H). − ^{13}C NMR (62.9 MHz, 336 K, [D$_6$]benzene): δ = 19.4, 21.8, 25.7, 26.8, 27.3, 65.1−65.3, 70.1−70.2, 71.9, 75.8, 78.1−78.3, 79.9, 80.2, 113.4, 156.4, 169.1, 173.4. − $[\alpha]_D^{25}$ = −29 (c = 0.83, chloroform).

(2*R*)-2-[*N,N*′-Bis(*tert*-butyloxycarbonyl)hydrazino]-2-methyl-3-oxobutanoate of D-Ribonolactone (17hd): This major diastereoisomer was separated by chromatography on silica gel, eluting with hexanes/diethyl ether (4:6). It was eluted first, as a solid, m.p. 64−67 °C (hexanes/diethyl ether). − IR (KBr): ṽ = 3337, 1801, 1749, 1725 cm^{-1}. − ^{1}H NMR (250 MHz, 336 K, [D$_6$]benzene): δ = 1.24−1.44 (several s, 27 H), 2.15 (br. s, 3 H), 3.32 (m, 1 H), 3.91 (d, J = 12 Hz, 1 H), 4.08 (br. d, J = 3 Hz, 1 H), 4.26 (t, J = 3 Hz, 1 H), 4.58 (d, J = 12 Hz, 1 H), 5.96 (br. s, 1 H). − ^{13}C NMR (62.9 MHz, 336 K, [D$_6$]benzene): δ = 20.2, 26.4, 27.4, 28.7, 28.8, 65.2−65.8, 76.4, 78.6−78.9, 80.4−80.7, 82.0, 83.9, 114.0, 156.2, 156.5, 169.8, 173.7. − $[\alpha]_D^{25}$ = −23 (c = 1.06, chloroform). − $C_{23}H_{36}N_2O_{11}$ (516.5): calcd. C 53.48, H 7.02, N 5.42; found C 53.58 and 53.63, H 6.75 and 6.83, N 5.36 and 5.39.

2-Acetyl-2-methyl-5-oxohexanoates of D-Ribonolactone (17he and 18he): This compound was eluted with hexanes/ethyl acetate (4:6), as an oily mixture of diastereoisomers. − IR (film): $\tilde{\nu}$ = 1790, 1746, 1712 cm^{-1}. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.35, 1.41 and 1.48 (s, 9 H), 1.9−2.3 (m, 2 H), 2.14 and 2.15 (s, 6 H), 2.35−2.50 (m, 2 H), 4.26 (dd, J = 12 and 3 Hz, 1 H), 4.42 (dt, J = 12 and 3 Hz, 1 H), 4.65−4.80 (m, 3 H). − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 19.2 and 19.6, 25.5, 25.9 and 26.0, 26.6, 28.2 and 28.3, 29.9 and 30.0, 38.2 and 38.4, 58.8, 64.3 and 64.4, 75.0, 77.5, 79.5, 113.8 and 113.9, 171.6 and 171.7, 173.1 and 173.3, 205.1 and 205.3, 207.1. − $C_{17}H_{24}O_8$ (356.2): calcd. C 57.30, H 6.79; found C 57.03 and 57.24, H 6.88 and 6.91.

2-Acetyl-4-cyano-2-methylbutanoates of D-Ribonolactone (17hf and 18hf): The two diastereoisomers were separated by chromatography on silica gel, eluting with hexanes/diethyl ether. The first diastereoisomer eluted was an oil. − IR (film): $\tilde{\nu}$ = 2250, 1770, 1747, 1714 cm^{-1}. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.38 (s, 3 H), 1.41 (s, 3 H), 1.46 (s, 3 H), 2.0−2.5 (m, 4 H), 2.16 (s, 3 H), 4.31 (dd, J = 12 and 3 Hz, 1 H), 4.48 (dd, J = 12 and 3 Hz, 1 H), 4.63 (d, J = 6 Hz 1 H), 4.70 (d, J = 6 Hz, 1 H), 4.77 (t, J = 3 Hz, 1 H). − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 12.7, 18.9, 25.4, 25.9, 26.5, 30.5, 58.4, 64.6, 74.8, 77.3, 79.4, 113.9, 118.9, 170.5, 173.1, 204.0. − $[\alpha]_D^{25}$ = −30 (c = 2.05, chloroform). − $C_{16}H_{21}NO_7$ (339.3): calcd. C 55.94, H 6.79; found C 56.18 and 56.06, H 6.65 and 6.63. − The second diastereoisomer eluted was also an oil. − IR (film): $\tilde{\nu}$ = 2249, 1794, 1746, 1714 cm^{-1}. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.39 (s, 3 H), 1.43 (s, 3 H), 1.48 (s, 3 H), 2.0−2.5 (m, 4 H), 2.18 (s, 3 H), 4.32 (dd, J = 12 and 3 Hz, 1 H), 4.48 (dd, J = 12 and 3 Hz, 1 H), 4.71 (s, 2 H), 4.79 (t, J = 3 Hz, 1 H). − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 12.9, 19.0, 26.0, 26.1, 26.6, 30.4, 58.6, 64.7, 74.9, 77.4, 79.4, 114.1, 118.8, 170.7, 172.9, 203.4. − $[\alpha]_D^{25}$ = −9 (c = 1.57, chloroform).

2-Acetyl-4-ethoxycarbonyl-2-methylbutanoates of D-Ribonolactone (17hg and 18hg): The two diastereoisomers were separated by chromatography on silica gel, eluting with hexanes/diethyl ether (2:8).

(2*R*)-2-Acetyl-4-ethoxycarbonyl-2-methylbutanoate of D-Ribonolactone (17hg): This diastereoisomer was eluted second, as an oil. − IR (film): $\tilde{\nu}$ = 1794, 1734, 1716 cm^{-1}. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.24 (t, J = 7 Hz, 3 H), 1.34 (s, 3 H), 1.38 (s, 3 H), 1.46 (s, 3 H), 2.0−2.3 (m, 4 H), 2.15 (s, 3 H), 4.13 (q, J = 7 Hz, 2 H), 4.27 (dd, J = 12 and 3 Hz, 1 H), 4.41 (dd, J = 12 and 3 Hz, 1 H), 4.68−4.77 (m, 3 H). − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.0, 18.9, 25.4, 25.9, 26.6, 29.3, 29.5, 59.0, 60.7, 64.3, 76.5, 77.4, 77.5, 113.8, 171.5, 172.3, 173.0, 204.6. − $[\alpha]_D^{25}$ = −23 (c = 1.45, chloroform).

(2*S*)-2-Acetyl-4-ethoxycarbonyl-2-methylbutanoate of D-Ribonolactone (18hg): This diastereoisomer was eluted first, as an oil. − IR (film): $\tilde{\nu}$ = 1794, 1735, 1726 cm^{-1}. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.26 (t, J = 7 Hz, 3 H), 1.37 (s, 3 H), 1.40 (s, 3 H), 1.48 (s, 3 H), 2.1−2.4 (m, 4 H), 2.16 (s, 3 H), 4.13 (q, J = 7 Hz, 2 H), 4.28 (dd, J = 12 and 2 Hz, 1 H), 4.43 (dd, J = 12 and 2 Hz, 1 H), 4.68−4.79 (m, 3 H). − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.0, 18.8, 25.3, 25.8, 26.5, 29.2, 29.6, 58.9, 60.6, 64.4, 74.9, 77.5, 79.4, 113.7, 171.4, 172.4, 173.1, 204.8. − $[\alpha]_D^{25}$ = −28 (c = 0.96, chloroform). − $C_{18}H_{26}O_9$ (386.4): calcd. C 55.94, H 6.79; found C 56.18 and 56.06, H 6.65 and 6.63.

X-ray Crystallographic Study of 13fe: A crystal of approximate dimensions 0.78 × 0.20 × 0.06 mm was used for the cell determination and data collection. The resulting crystal data were a = 7.826(2), b = 9.191(1), c = 14.108(4) Å, β = 106.03(2)°, V = 975.3(4) Å^3, Z = 2, ρc = 1.306 g/cm^3, monoclinic P21 space group, μ(Mo-K) = 0.195, T = 293(2) K. Data were recorded using the −2θ scan mode, up to a 2θ of 68.36. The 3040 collected intensities gave 2944 unique data (R_{int} = 0.0278), which were corrected from the Lorentz, polarization, and absorption effects (empirical Psi scan, max. and min. transmission were 0.9317 and 0.8249, respectively). The structure was solved by direct methods using SHELXS-97 and refined by full-matrix, least-squares methods on F^2 over the complete set of data, using SHELXL-97. Anisotropic thermal parameters were refined for the non-hydrogen atoms and the hydrogen atoms were introduced in calculated positions. The final R indices for reflections with [I > 2sigma(I)] were R1 = 0.0427, wR2 = 0.0891, and those for all data, R1 = 0.1046, wR2 = 0.0984. The Flack absolute structure parameter was −0.09(9). The largest difference peak and hole were 0.238 and −0.257 e/Å^3.

Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-147764. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

We acknowledge financial support from DGICYT and DGESIC (MEC of Spain, projects PB93-0896 and PB98-0902) and CIRIT (Generalitat de Catalunya, projects SGR98-0056 and SGR2000-0062). We are very grateful to one referee for his or her important observations

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[1] M. E. Jung, *Stabilized Nucleophiles with Electron Deficient Alkenes and Alkynes*, Vol. 4, Chapter 1.1. In: *Comprehensive Organic Synthesis* (Eds.: B. M. Trost, I. Fleming); Pergamon Press, **1991**.

[2] P. Perlmutter, *Conjugate Addition Reactions in Organic Synthesis*; Pergamon Press, **1992**.

[3] J. Christoffers, *Eur. J. Org. Chem.* **1998**, 1259−1266.

[4] F. H. Jardine, *Prog. Inorg. Chem.* **1984**, *31*, 265−370.

[5] T. Naota, H. Takaya, S. Murahashi, *Chem. Rev.* **1998**, *98*, 2599−2660.

[6] Y. Guari, S. Sabo-Etienne, B. Chaudret, *Eur. J. Inorg. Chem.* **1999**, 1047−1055.

[7] T. Naota, H. Taki, M. Mizuno, S. Murahashi, *J. Am. Chem. Soc.* **1989**, *111*, 5954−5955.

[8] S. Murahashi, T. Naota, H. Taki, M. Mizuno, H. Takaya, S. Komiya, Y. Mizuho, N. Oyasato, M. Hiraoka, M. Hirano, A. Fukuoka, *J. Am. Chem. Soc.* **1995**, *117*, 12436−12451.

[9] E. Gómez-Bengoa, J. M. Cuerva, C. Mateo, A. M. Echavarren, *J. Am. Chem. Soc.* **1996**, *118*, 8553−8565.

[10] V. Maraval, R. Laurent, A.-M. Caminade, J.-P. Majoral, *Organometallics* **2000**, *19*, 4025−4029.

[11] S. G. Alvarez, S. Hasegawa, M. Hirano, S. Komiya, *Tetrahedron Lett.* **1998**, *39*, 5209−5212.

[12] M. Picquet, C. Bruneau, P. H. Dixneuf, *Tetrahedron* **1999**, *55*, 3937−3948.

[13] S. Murahashi, K. Take, T. Naota, H. Takaya, *Synlett* **2000**, 1016−1018.

[14] S. Murahashi, H. Takaya, *Acc. Chem. Res.* **2000**, *33*, 225−233.

[15] J. Clariana, N. Gálvez, C. Marchi, M. Moreno-Mañas, A. Vallribera, E. Molins, *Tetrahedron* **1999**, *55*, 7331−7344.

[16] M. Meseguer, M. Moreno-Mañas, A. Vallribera, *Tetrahedron Lett.* **2000**, *41*, 4093−4095.
[17] For preparation of $RuH_2(PPh_3)_4$ from $RuCl_2(PPh_3)_3$ see: R. Young, G. Wilkinson, *Inorg. Synth.* **1990**, *28*, 337−338.
[18] J. Straukas, J. Degutis, *Lietuvos TSR Mokslu Akad. Darbai, Ser. B* **1965**, *4*, 47−53; *Chem. Abst.* **1966**, *64*, 14124c.
[19] C. Barrington, B. L. Walworth, *U. S. Patent* 3958001; *Chem. Abst.* **1976**, *85*, 63065a.
[20] T. P. Gill, K. R. Mann, *Organometallics* **1982**, *1*, 485−488.
[21] E. Ciganek, *Org. React.* **1997**, *51*, 201−350.
[22] D. Basavaiah, V. V. L. Gowriswari, T. K. Bharathi, *Tetrahedron Lett.* **1987**, *28*, 4591−4592.
[23] For a review on the use of Oppolzer's sultam see: W. Oppolzer, *Tetrahedron* **1987**, *43*, 1969−2004.
[24] M. Moreno-Mañas, R. M. Sebastián, A. Vallribera, E. Molins, *Tetrahedron* **1995**, *51*, 10795−10800.
[25] N. Gàlvez, E. Molins, M. Moreno-Mañas, R. M. Sebastián, N. Serra, E. Trepat, A. Vallribera, *J. Heterocycl. Chem.* **2000**, *37*, 895−905.
[26] M. Moreno-Mañas, E. Trepat, R. M. Sebastián, A. Vallribera, *Tetrahedron: Asymmetry* **1999**, *10*, 4211−4224.
[27] B. M. Trost, T. Schmidt, *J. Am. Chem. Soc.* **1988**, *110*, 2301−2303.
[28] B. M. Trost, U. Kazmaier, *J. Am. Chem. Soc.* **1992**, *114*, 7933−7935.
[29] D. Ma, Y. Yu, X. Lu, *J. Org. Chem.* **1989**, *54*, 1105−1109.
[30] C. Guo, X. Lu, *J. Chem. Soc., Perkin Trans. 1* **1993**, 1921−1923.
[31] For preparation of $RuCl_2(PPh_3)_3$ see: P. S. Hallman, T. A. Stephenson, G. Wilkinson, *Inorg. Synth.* **1970**, *12*, 237−240.
[32] P. Caramella, T. Bandiera, F. Marinone Albini, A. Gamba, A. Corsaro, G. Perrini, *Tetrahedron* **1988**, *44*, 4917−4925.

Received July 31, 2000
[O00401]