

Ruthenium-Catalyzed Aldol and Michael Reactions of Nitriles. Carbon–Carbon Bond Formation by α -C–H Activation of Nitriles

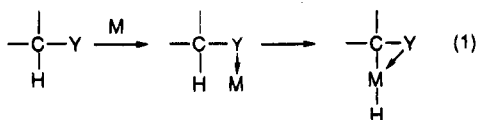
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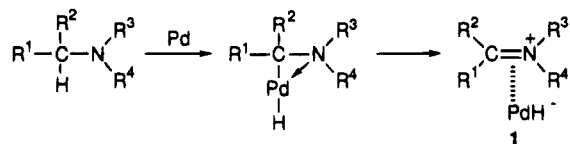
Abstract: The ruthenium(II)-catalyzed reaction of nitriles with carbonyl compounds proceeds highly efficiently under neutral and mild conditions to give α,β -unsaturated nitriles. Under similar reaction conditions, nitriles react with olefins bearing electron-withdrawing groups to give the corresponding Michael adducts. The efficiency of the reaction is illustrated by the selective additions to α,β -unsaturated aldehydes and acetylenes bearing electron-withdrawing groups, which are difficult to perform using conventional bases. Chemoselective aldol and Michael reactions of nitriles can be performed in the presence of other active methylene compounds. Tandem Michael and Michael–aldol condensations of nitriles **30** can be performed with high diastereoselectivity. These reactions can be rationalized by assuming oxidative addition of ruthenium(0) to the α -C–H bond of nitriles and subsequent insertions to carbonyl compounds or olefins. As the key intermediates and active catalysts hydrido(*N*-bonded enolato)ruthenium(II) complexes, *mer*-RuH(NCCHCO₂R)(NCCH₂CO₂R)(PPh₃)₃ (R = Me (**41a**), Et (**41b**), *n*-Bu (**41c**)) have been isolated upon treatment of RuH₂(PPh₃)₄ (**3**) or RuH(C₂H₄)(PPh₃)₂(PPh₂C₆H₄) (**4**) with alkyl cyanoacetates. Kinetic study of the catalytic aldol reaction of ethyl cyanoacetate with benzaldehyde indicates that the rate-determining step is the reaction of enolato complex **41** with aldehydes.

The C–H activation with transition metal complexes will open a new chemistry of catalytic carbon–carbon bond formation because of its potent ability to generate carbon nucleophiles and to make reactions under neutral and mild conditions. The activation of the sp³ C–H bonds has been investigated extensively with many aspects. One is the oxidative addition of low-valent metals to the C–H bonds.^{1,2} A second approach is the hydrogen abstraction by metal oxo species likewise cytochrome P-450.³ A third method is the activation of α -C–H bonds adjacent to heteroatoms by using the α -heteroatom effect.⁴ This concept is depicted in eq 1. Coordination of low-valent

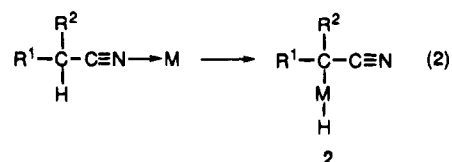


metal (M) to heteroatom (Y) increases both the basicity of metal

complexes and acidity of the C–H bonds adjacent to Y, resulting in oxidative addition of metal into the α -C–H bonds. Our first approach was the investigation of the activation of α -C–H bond adjacent to nitrogen. The activation of α -C–H bond of tertiary amines proceeds upon treatment with palladium(0) catalyst. As we expected, coordination of palladium to the nitrogen of amines, followed by oxidative addition at the α -C–H bond gives iminium ion palladium complex **1**.⁴ This concept leads to a



new methodology for the activation of nitriles under neutral conditions. The basic strategy for constructing a new catalytic reaction is shown in eq 2. Coordination of nitriles to low-valent metal complexes (M) would increase both the basicity of the metal and the acidity of the α -C–H bond, and hence oxidative addition of the metal into the α -C–H bond of nitriles would occur readily to afford hydrido- α -cyanoalkyl complex **2**, which



can be trapped with electrophiles to give a carbon–carbon bond at the α -position of nitriles under neutral conditions. Actually, we have found that the low-valent hydridoruthenium phosphine

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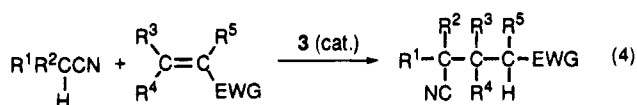
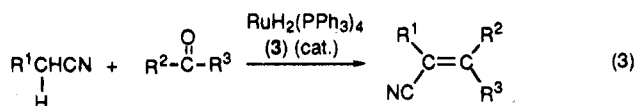
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complexes are effective catalysts for the activation of the α -C—H bond of nitriles. Upon treatment with carbon electrophiles, catalytic aldol and Michael reactions of nitriles can be performed under neutral and mild reaction conditions as depicted in eqs 3 and 4, respectively.⁵



Transition metal-catalyzed aldol and Michael reactions are attractive methods for carbon—carbon bond formations, since these provide a novel strategy which can be used catalytically under neutral reaction conditions and also for controlling stereoselectivity by chelation effects. Catalytic aldol and Michael reactions promoted by transition metal complexes have been reported; however, these are limited to the Lewis acid-catalyzed reactions of silyl enolates^{6,7} and the reactions of active methylene compounds with base metal salt catalysts.^{8,9} Development of catalytic methods that proceed under neutral conditions still awaits exploration. In this regard, the present ruthenium-catalyzed reaction, which proceeds under neutral and mild reaction conditions, is highly efficient. Further, the present reactions show specific chemo- and stereoselectivity for carbon—

carbon bond formation of nitriles, which have never been observed with the conventional base-catalyzed reactions. The key step of the catalytic reaction is the oxidative addition of low-valent ruthenium into the α -C—H bond of nitriles. Actually, the oxidative addition products, *mer*-RuH(NCCHCO₂R)(NCCH₂CO₂R)(PPh₃)₃ (**41**), which are active catalysts for the ruthenium-catalyzed aldol and Michael reactions, have been isolated from the reaction of alkyl cyanoacetates with either RuH₂(PPh₃)₄ (**3**) or RuH(C₂H₄)(PPh₃)₂(PPh₂C₆H₄) (**4**).¹⁰

In this paper, full details of the catalytic aldol and Michael reactions of nitriles with respect to scope, synthetic application, and mechanism are described.

Results and Discussion

Catalytic Aldol Condensation of Nitriles with Carbonyl Compounds. The reaction of nitriles with aldehydes in the presence of hydridoruthenium complex catalysts proceeds under neutral conditions to give the corresponding α,β -unsaturated nitriles. The catalytic activity of low-valent metal complexes has been examined with respect to the reaction of less reactive benzyl cyanide with butanal. In the presence of 3 mol % of catalysts in dry THF at room temperature under an argon atmosphere, the conversions of benzyl cyanide and the yields of (*E*)-2-phenyl-2-hexenenitrile (**5**) were determined. RuH₂(PPh₃)₄ (**3**) is the best catalyst among the catalysts examined. Ruthenium ethylene complex, RuH(C₂H₄)(PPh₃)₂(PPh₂C₆H₄) (**4**) also gave satisfactory results. Transition metal hydridocarbonyl complexes such as RuH₂(CO)(PPh₃)₃ and IrH(CO)(PPh₃)₃ showed almost no catalytic activity. Recently, IrH₃(P-*i*-Pr)₂,¹¹ ReH₇(P-*i*-Pr)₂,¹¹ and ReH(N₂)(PMe₂Ph)₄,¹² and a combination of Pd₂(dba)₃·CHCl₃¹³ have been reported as effective catalysts for aldol reactions of nitriles; however, these complexes require higher reaction temperature or activated substrates. RhH(CO)(PPh₃)₃ has proven to be a good catalyst for Michael addition of nitriles,^{14,15} although no catalytic activity was observed for the present condensation reaction. Nonpolar solvents such as benzene and toluene and ethereal solvents such as THF and 1,4-dioxane can be used, although other polar solvents such as ethanol, acetonitrile, and chloroform retarded the reaction.

Representative results of the RuH₂(PPh₃)₄-catalyzed reaction of nitriles with carbonyl compounds are shown in Table 1. Various activated nitriles such as alkyl cyanoacetates, malononitrile, and benzyl cyanides undergo condensation with aldehydes and ketones under mild conditions to afford the corresponding (*E*)- α,β -unsaturated nitriles selectively. The stereochemistry of the products was determined to be *E* (entries 1–5 and 8) by means of NMR spectral analyses;¹⁶ selective formation of *E*-olefins is ascribed to the thermodynamic control of dehydration reaction. Protic substituents such as hydroxy groups tolerate the reaction (entry 3). Addition of an electron-donating phosphine ligand enhances the condensation remarkably. The conversion of the reaction of less reactive benzyl cyanide with butanal for 1 h was 51% at 60 °C; however, under the same reaction conditions, addition of a catalytic amount of a diphosphine such as 1,1-bis(diphenylphosphino)methane

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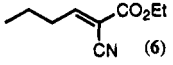
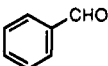
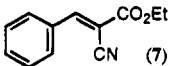
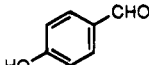
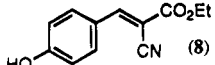
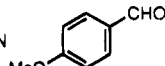
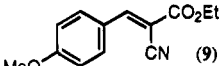
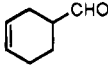
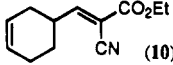
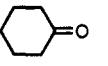
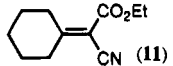
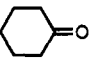
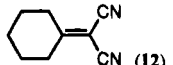
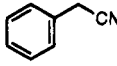
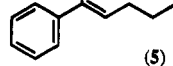
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Table 1. Ruthenium-Catalyzed Aldol Condensation of Nitriles with Carbonyl Compounds^a

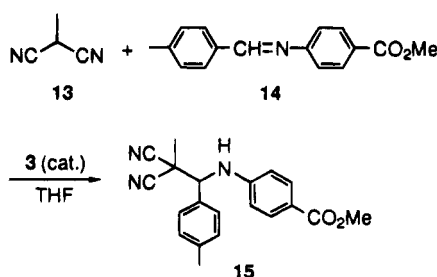
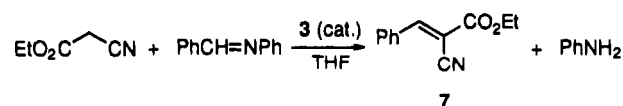
| entry | nitrile | carbonyl compound | product | yield, ^b (%) |
|-------|--|---|--|-------------------------|
| 1 | EtO ₂ CCH ₂ CN | CH ₃ CH ₂ CHO |  (6) | 83 |
| 2 | EtO ₂ CCH ₂ CN |  CHO |  (7) | 91 |
| 3 | EtO ₂ CCH ₂ CN |  CHO |  (8) | 98 |
| 4 | EtO ₂ CCH ₂ CN |  CHO |  (9) | 95 |
| 5 | EtO ₂ CCH ₂ CN |  CHO |  (10) | 69 |
| 6 | EtO ₂ CCH ₂ CN |  =O |  (11) | 69 |
| 7 | NCCH ₂ CN |  =O |  (12) | 79 |
| 8 |  CN | CH ₃ CH ₂ CHO |  (5) | 97 ^c |


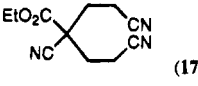
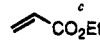
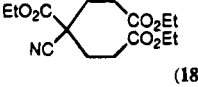
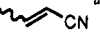
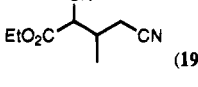
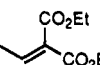
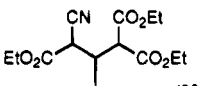

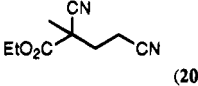
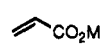
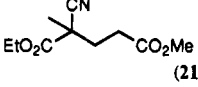

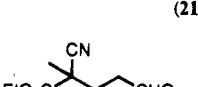
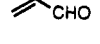
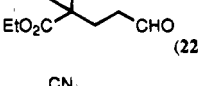

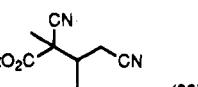

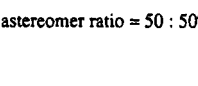
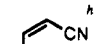
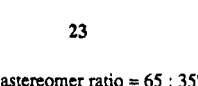

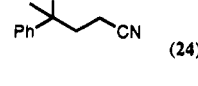
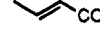
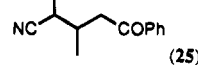
^aA mixture of nitrile (2.0 mmol), carbonyl compound (2.2 mmol), and RuH₂(PPh₃)₄ (3) (0.06 mmol) in dry THF (0.5 mL) was stirred at room temperature for 24 h under argon. ^bIsolated yield based on the starting nitrile.

^c1,3-Bis(diphenylphosphino)propane (0.12 mmol) was added.

(dppm), 1,2-bis(diphenylphosphino)ethane (dppe), or 1,3-bis(diphenylphosphino)propane (dppp) raised the conversion to 96–98%, although addition of PPh₃ (68%) or triethyl phosphite (62%) promoted the reaction moderately.

The present condensation can be applied to the reaction of nitriles with other electrophiles such as imines. Thus, the RuH₂(PPh₃)₄-catalyzed reaction of ethyl cyanoacetate with *N*-benzylideneaniline at room temperature gave ethyl benzylidenecyanoacetate (7) in 82% yield along with aniline. Similarly, the reaction of 4-(methoxycarbonyl)-*N*-(4'-methylbenzylidene)-aniline (14) with 2-methylmalononitrile (13) gave 4-[4'-(methoxycarbonyl)phenylamino]-2-cyano-2-methyl-3-*p*-tolylpropanenitrile (15) in 91% yield. Similar aldol-type reaction of *N*-tosyl- and *N*-(alkoxycarbonyl)imines by using RhH(CO)(PPh₃)₃ catalyst has been reported.¹⁷

**Table 2.** Ruthenium-Catalyzed Michael Addition of Nitriles with Olefins^a

| entry | nitrile | olefin | product | yield, ^b % |
|-------|--|---|---|-----------------------|
| 1 | EtO ₂ CCH ₂ CN |  |  (17) | 85 |
| 2 | EtO ₂ CCH ₂ CN |  |  (18) | 95 |
| 3 | EtO ₂ CCH ₂ CN |  |  (19) diastereomer ratio = 54 : 46 ^e | 51 |
| 4 | EtO ₂ CCH ₂ CN |  |  (30b) diastereomer ratio = 69 : 31 ^e | 90 |
| 5 | EtO ₂ CCH(CH ₃)CN |  |  (20) | 71 |
| 6 | EtO ₂ CCH(CH ₃)CN |  |  (21) | 77 ^f |
| 7 | EtO ₂ CCH(CH ₃)CN |  |  (22) | 99 |
| 8 | EtO ₂ CCH(CH ₃)CN |  |  (23) | 85 ^f |
| 9 | EtO ₂ CCH(CH ₃)CN |  |  (22) | 72 |
| 10 | EtO ₂ CCH(CH ₃)CN |  |  (23) diastereomer ratio = 50 : 50 ^e | 82 |
| 11 | EtO ₂ CCH(CH ₃)CN |  |  (23) diastereomer ratio = 65 : 35 ^e | 90 |
| 12 | PhCH ₂ CN |  |  (24) | 50 ^f |
| 13 | NCCH ₂ CN |  |  (25) | 68 |

^aA mixture of nitrile (2.0 mmol), olefin (2.2 mmol), and RuH₂(PPh₃)₄ (3) (0.06 mmol) in dry THF (0.5 mL) was stirred at room temperature for 24 h under argon. ^bIsolated yield based on the starting nitrile. ^c6.0 mmol. ^d*E*/*Z* = 1/8.

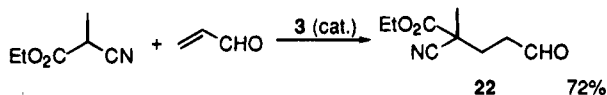
^eDetermined by ¹H NMR analysis. ^fRuH(C₂H₄)(PPh₃)₂(PPh₂C₆H₄) (4) (0.06 mmol) was used instead of 3. ^g*E*/*Z* = 100/0. ^h*E*/*Z* = 0/100. ⁱ1,4-Bis(diphenylphosphino)butane (0.12 mmol) was added.

Catalytic Michael Addition of Nitriles to Olefins. The reaction of nitriles with olefins bearing electron-withdrawing groups proceeds highly efficiently to give the corresponding Michael adducts. The catalytic activity of various group 8 metal complex catalysts has been examined also for the reaction of benzyl cyanide with crotononitriles (*E*/*Z* = 61:39, 1.1 equiv) in dry THF at room temperature under an argon atmosphere. Low-valent ruthenium hydride complexes, RuH₂(PPh₃)₄ (3) and

(17) Yamamoto, Y.; Kubota, Y.; Honda, Y.; Fukui, H.; Asao, N.; Nemoto, H. *J. Am. Chem. Soc.* **1994**, *116*, 3161.

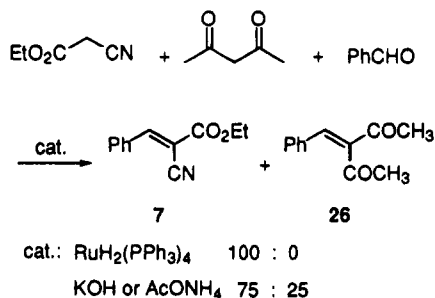
$\text{RuH}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2(\text{PPh}_2\text{C}_6\text{H}_4)$ (**4**), and rhodium hydride complex $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ have proven to be effective catalysts for the reaction;¹⁴ however, other transition metal complexes such as $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ and $\text{IrH}(\text{CO})(\text{PPh}_3)_3$ require higher reaction temperatures (60 °C) to complete the reaction. $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$, which is reported to be an effective catalyst for the addition of nitriles to allenes,¹⁸ is inactive for the Michael reactions. The remarkable effect of electron-donating phosphine ligands was also observed. Addition of a catalytic amount of **dppp** gave the best results, while other bidentate phosphine ligands such as **dppm**, **dppe**, **dppb**, 1,4-bis(diphenylphosphino)pentane, PPh_2Et , and PPhMe_2 also accelerate the reaction considerably.

Table 2 summarizes the representative results of the $\text{RuH}_2\text{-(PPh}_3)_4$ -catalyzed addition of nitriles to olefins. Various olefins bearing electron-withdrawing groups undergo addition of activated nitriles under neutral and mild conditions. Dialkylation of cyanoacetates proceeds efficiently upon treatment with 2–3 equiv of olefins (entries 1 and 2). Importantly, the addition to α,β -unsaturated aldehydes proceeds chemoselectively without contamination of the condensation product of the aldehyde (entry 9), although such a contamination is often observed by using conventional bases.

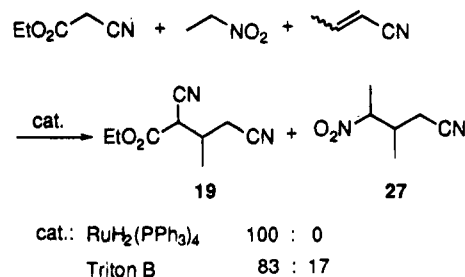


The reaction is catalyzed by ruthenium ethylene complex **4** efficiently (entries 6 and 8). The reaction of less reactive benzyl cyanides is enhanced by addition of a catalytic amount of dppb (entry 12).

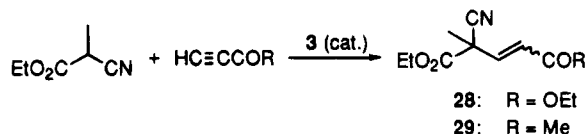
An important feature of the reaction is the chemoselective reaction of nitriles with either carbonyl compounds or Michael acceptors in the presence of other active methylene compounds. Typically, the $\text{RuH}_2(\text{PPh}_3)_4$ -catalyzed reaction of benzaldehyde with an equimolar mixture of ethyl cyanoacetate and 2,4-pentanedione, which has a similar pK_a value ($\text{pK}_\text{a} = 9.0$),¹⁹ gave (*E*)-ethyl 2-cyano-3-phenyl-2-propanoate (**7**) (80%) exclusively. In contrast, the same reaction in the presence of a catalytic amount of a conventional base such as AcONH_4 gave a mixture (75:25) of **7** and 3-benzylidene-2,4-pentanedione (**26**). Similar



selectivity has been observed in the catalytic additions. Thus, the $\text{RuH}_2(\text{PPh}_3)_4$ -catalyzed reaction of crotononitrile ($E:Z = 1:8$) with an equimolar mixture of ethyl cyanoacetate and nitroethane ($\text{p}K_a = 8.6$)¹⁹ gave ethyl 2,4-dicyano-3-methylbutanoate (**19**) chemoselectively, while similar treatment with Triton B (benzyltrimethylammonium hydroxide aqueous solution) catalyst afforded an 83:17 mixture of **19** and 3-methyl-4-nitropentanenitrile (**27**).



Importantly, addition of nitriles to acetylenic compounds proceeds with high chemoselectivity. Generally, such an addition to acetylenic compounds is very difficult, because competitive 1,2-addition,²⁰ polycondensation,²¹ and nucleophilic reactions of the acetylide anion²² give complex products. Successful addition reactions reported are limited to few cases which include additions of organocuprates²³ and TiCl₄-promoted addition of silyl enolates.²⁴ The RuH₂(PPh₃)₄-catalyzed reaction of ethyl cyanoacetate with ethyl propiolate at room temperature gives diethyl 2-cyano-2-methyl-3-pentenedioate (**28**) in 90% (*E*:*Z* = 1:1) isolated yield. Similar treatment with 3-butyne-2-one gives ethyl 2-cyano-2-methyl-5-oxo-3-hexenoate (**29**) in 81% (*E*:*Z* = 65:35) isolated yield. These reactions proceed cleanly without contamination of the coupling products, although it is well-known that terminal acetylenic compounds undergo dimerization reaction²⁵ or codimerization with olefins²⁶ in the presence of ruthenium catalysts. This indicates that the activation of the α -C-H bond of nitriles proceeds much faster than that of an acetylenic C-H bond.



The efficiency of the present method is highlighted by high diastereoselectivity of addition arising from specific chelation control. Thus, the ruthenium-catalyzed addition of cyano ester **30** bearing a malonate moiety proceeds with high diastereoselectivity as depicted in eq 5. Many methods for diastereoselective Michael reactions have been reported by using stoichiometric amount of lithium enolates,²⁷ silyl enolates,²⁸ tin enolates,²⁹ and enamines.³⁰ However, catalytic Michael reactions reported are limited to few reactions which include SbCl_5 -

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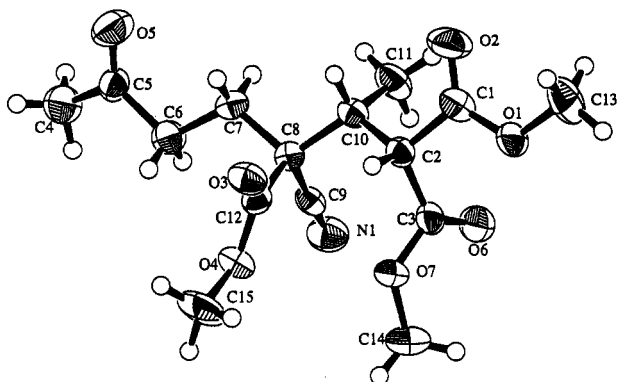
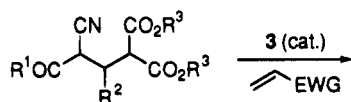
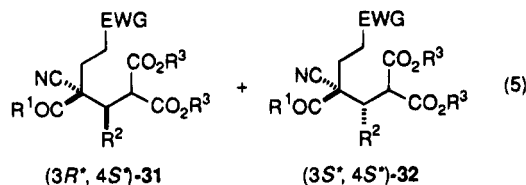


Figure 1. Molecular structure of cyano ester (3*R**,4*S**)-31a.

$\text{Sn}(\text{OTf})_2^{31}$ and trityl salts catalyzed reactions.³² In most of the reported methods stereocontrol is observed at only the two reacting carbon centers. This method presents a rare example of the diastereoselection control of the stereochemistry of α - and β -positions of the starting mixture of nitriles.



- 30a: $\text{R}^1 = \text{OMe}$, $\text{R}^2 = \text{R}^3 = \text{Me}$
 30b: $\text{R}^1 = \text{OEt}$, $\text{R}^2 = \text{Me}$, $\text{R}^3 = \text{Et}$
 30c: $\text{R}^1 = \text{OEt}$, $\text{R}^2 = \text{Et}$, $\text{R}^3 = \text{Et}$
 30d: $\text{R}^1 = \text{O}-i\text{-Bu}$, $\text{R}^2 = \text{Me}$, $\text{R}^3 = \text{Et}$
 30e: $\text{R}^1 = \text{NH}_2$, $\text{R}^2 = \text{Me}$, $\text{R}^3 = \text{Et}$



When a diastereomeric mixture of cyano ester 30a ($\text{R}^1 = \text{OMe}$, $\text{R}^2, \text{R}^3 = \text{Me}$, diastereomer ratio = 68:32), which can be readily obtained by the catalytic addition of dimethyl ethylenemalonate to methyl cyanoacetate, was allowed to react with methyl vinyl ketone at -78°C in the presence of catalyst 3, a mixture of (3*R**,4*S**)-31a and (3*S**,4*S**)-32a was obtained in 77% yield. The diastereomer ratio of 31a:32a was determined to be 96:4 by means of ^1H NMR analysis. The stereochemistry of 31a was unequivocally established by X-ray crystal structure analysis as shown in Figure 1. Crystallographic data including fractional coordinates, molecular distances, and angles are given as supporting information. Similar treatment of cyano ester 30b ($\text{R}^1 = \text{OEt}$, $\text{R}^2 = \text{Me}$, $\text{R}^3 = \text{Et}$, diastereomer ratio = 60:40) with either methyl vinyl ketone or acrylonitrile gave (3*R**,4*S**)-31b or (3*R**,4*S**)-31c selectively ((3*R**,4*S**)-31b:(3*S**,4*S**)-32b = 97:3, 73%; (3*R**,4*S**)-31c:(3*S**,4*S**)-32c = 90:10, 41%). In contrast, the reactions of 30b in the presence of a base catalyst such as Triton B gave 31 non-selectively (31b:32b = 75:25, 89%; 31c:32c = 44:56, 37%). Representative results of diastereoselective reactions of 30 are summarized in Table 3.

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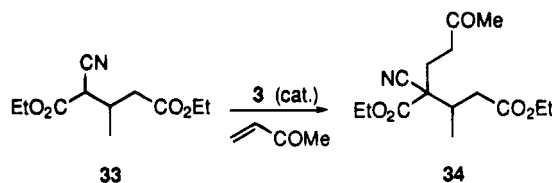
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Table 3. Diastereoselective Michael Reaction of Cyano Ester 30^a

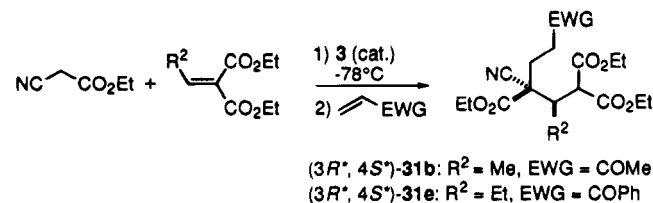
| entry | cyano ester 30 ^b | | | | product (yield, ^c %) | diastereomer ratio of 31:32 ^b |
|-------|-----------------------------|----------------|-----------------------|------|---------------------------------|--|
| | R ¹ | R ² | R ³ | EWG | | |
| 1 | OMe | Me | Me (30a) ^d | COMe | 31a:32a (77) | 96:4 |
| 2 | OEt | Me | Me (30b) ^e | COMe | 31b:32b (73) | 97:3 |
| 3 | OEt | Me | Et (30b) | CN | 31c:32c (41) ^h | 90:10 |
| 4 | OEt | Me | Et (30b) | COPh | 31d:32d (77) | 97:3 |
| 5 | OEt | Me | Et (30b) | COPh | 31d:32d (62) ⁱ | 96:4 |
| 6 | OEt | Et | Et (30c) ^f | COPh | 31e:32e (87) | 90:10 |
| 7 | O- <i>i</i> -Bu | Me | Et (30d) ^g | COMe | 31f:32f (77) | 98:2 |
| 8 | NH ₂ | Me | Et (30e) ^e | COPh | 31g:32g (63) ^h | 96:4 |

^a A mixture of cyano ester 30 (1.0 mmol), olefin (1.0 mmol), and $\text{RuH}_2(\text{PPh}_3)_4$ (3) (0.03 mmol) in dry THF (0.25 mL) was stirred at -78°C for 6 h under argon. ^b Diastereomer ratio was determined by 270 MHz ^1H NMR analysis. ^c Isolated yield based on 30. ^d Diastereomer ratio = 60:40. ^e Diastereomer ratio = 77:23. ^f Diastereomer ratio = 60:40. ^g Diastereomer ratio = 77:23. ^h The reaction was carried out at room temperature. ⁱ $\text{RuH}(\text{C}_2\text{H}_4)(\text{PPh}_2\text{C}_6\text{H}_4)$ (4) (0.03 mmol) was used instead of 3.

The cyano esters derived from alkylidenemalonate diesters and activated nitriles undergo addition reactions to various electron-deficient olefins with high diastereoselectivity. When the ruthenium ethylene complex 4 is used as a catalyst, similar high diastereoselectivity was obtained (entry 5). The observed high diastereoselectivity is due to the malonate moiety of the nitrile substrates. Indeed, the $\text{RuH}_2(\text{PPh}_3)_4$ -catalyzed reaction of diethyl 2-cyano-3-methylpentanedioate (33) (diastereomer ratio = 50:50) with methyl vinyl ketone at -78°C gave a diastereomeric mixture (66:34) of 34 in 60% yield, indicating that the chelation of the malonate moiety of 30 plays an important role for the present diastereoselection which we discuss latter.



Tandem addition reactions of α -cyano carboxylic acid derivatives can be performed conveniently. Typically, the $\text{RuH}_2(\text{PPh}_3)_4$ -catalyzed reaction of ethyl cyanoacetate with diethyl ethylenemalonate and subsequent addition of methyl vinyl ketone at -78°C gave 31b in 75% isolated yield ((3*R**,4*S**)-31b:(3*S**,4*S**)-32b = 97:3). Similar treatment of ethyl cyanoacetate with diethyl propylenemalonate followed by treatment with phenyl vinyl ketone gave (3*R**,4*S**)-31e in 62% yield ((3*R**,4*S**)-31e:(3*S**,4*S**)-32e = 90:10).



The adducts thus obtained undergo Claisen-type condensation, giving functionalized cyclohexene derivatives. Typically, the reaction of (3*R**,4*S**)-31b with sodium ethoxide in ethanol at 0°C gave cyclohexenol derivative (1*S**,2*R**,3*R**)-35b in 52% yield as a sole product. Similarly, cyano ester (3*R**,4*S**)-31f can be converted stereoselectively to (1*S**,2*R**,3*R**)-35f in

Table 4. IR and NMR Data of Hydrido(enolato)ruthenium Complexes

| | IR ^a (cm ⁻¹) | | | ¹ H NMR ^b (ppm) | | |
|---------------------|-------------------------------------|---|--------------------|---|---|------------------|
| | $\nu(\text{CN})$ | $\nu(\text{CO})$ | $\nu(\text{Ru-H})$ | Ru-H | others | PPh ₃ |
| 41a | 2191 | 1749 1602 | 1963 | -13.0 (br, 1H) | 2.8–3.1 (br, 3H, CH + CH ₂) 3.14 (s, 3H, OMe) 3.67 (s, 3H, OMe) | 6.8–7.7 (m) |
| 41b | 2185 | 1746 1598 | 1950 | -13.0 (br, 1H) | 0.83 (t, $J = 7.4$ Hz, 3H, CH ₃) 1.18 (t, $J = 7.4$ Hz, 3H, CH ₃) 2.94 (br, 1H, CH) 3.16 (s, 2H, CH ₂) 3.78 (q, $J = 7.4$ Hz, 2H, OCH ₂) 4.23 (q, $J = 7.4$ Hz, 2H, OCH ₂) | 6.8–7.7 (m) |
| 41c | 2183 | 1745 1601 | 1940 | -12.9 (br, 1H) | 0.6–1.7 (m, 14 H, CH ₂ CH ₂ CH ₃) 2.9–3.2 (br, 3 H, CH + CH ₂) 3.8–4.2 (br, 4 H, OCH ₂) | 6.8–7.7 (m) |
| 42a | | 1586 | 1941 | -16.6 (dt, $J_{\text{HP}} = 26.9, 22.0$ Hz, 1H) | 0.83 (s, 3 H, Me) 1.91 (s, 3 H, Me) 4.86 (s, 1 H, -CH=) | 6.8–7.7 (m) |
| 42b | | 1629 | 2020 | -17.8 (q, $J_{\text{HP}} = 24.8$ Hz, 1H) | 1.93 (s, 3 H, Me) 3.84 (s, 3 H, Me) 4.59 (s, 1 H, -CH=) | 6.8–7.7 (m) |
| 42c isomer A | | 1611 ^c | 1975 ^c | -17.8 (dt, $J_{\text{HP}} = 25.6, 23.2$ Hz, 1H) | 0.83 (s, 3 H, Me or OMe) 3.71 (s, 3 H, OMe or Me) 4.72 (s, 1 H, -CH=) | 6.8–7.7 (m) |
| isomer B | | 1611 | | -16.6 (dt, $J_{\text{HP}} = 25.6, 23.2$ Hz, 1H) | 1.98 (s, 3 H, OMe or Me) 2.04 (s, 3 H, Me or OMe) 4.79 (s, 1 H, -CH=) | 6.8–7.7 (m) |
| 44a isomer A | 2170 ^c | 2045 ^{c,d} 1893 ^c 198 ^{c,d} | -4.22 (t, | 3.05 (s, 1H, CH) $J_{\text{P-H}} = 18.4$ Hz, 1H) | 6.8–7.7 (m) 3.68 (s, 3H, OMe) | |
| isomer B | | 1655 ^c | | -4.28 (t, $J_{\text{P-H}} = 18.4$ Hz, 1H) | 2.77 (s, 1H, CH) 3.58 (s, 3H, OMe) | 6.8–7.7 (m) |
| 44b isomer A | 2159 ^c | 2044 ^{c,d} 1993 ^{c,d} 1641 ^c | 1893 ^c | -4.22 (t, $J_{\text{P-H}} = 18.4$ Hz, 1H) | 1.71 (t, $J = 7.4$ Hz, 3H, Me) 3.01 (s, 1H, CH) | 6.8–7.7 (m) |
| isomer B | | | | -4.28 (t, $J_{\text{P-H}} = 18.4$ Hz, 1H) | 4.24 (q, $J = 7.4$ Hz, 2H, OCH ₂) 1.01 (t, $J = 7.4$ Hz, 3H, Me) 2.77 (s, 1H, CH) 4.14 (q, $J = 7.4$ Hz, 2H, OCH ₂) | 6.8–7.7 (m) |

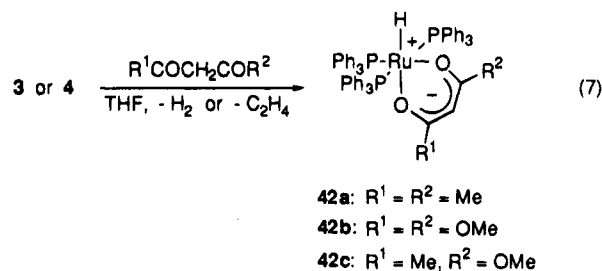
^a KBr disk. ^b 200 MHz ¹H NMR in C₆D₆. Numbers in parentheses indicate coupling constants hertz. ^c Mixture of isomers of A and B. ^d Absorbance of carbonyl ligands.

elimination of ethyl α -cyanoacetate from **41** is negligible compared to the oxidative addition of the nitrile to ruthenium.

The molecular structure of **41b** is depicted in Figure 2. Essentially the same molecular geometry is observed for **41a**, which has been reported in a preliminary form.¹² In both cases three phosphine ligands coordinate to ruthenium in meridional positions around the octahedron and the hydrido ligand is considered to occupy the site *cis* to the three P ligands. The structure is consistent with all the NMR and IR data. The ethyl cyanoacetate coordinates *trans* to the hydride and the enolato ligand *cis* to the hydride. An interesting feature in the structures of **41a** and **41b** is the coordination mode of the enolato ligand. The cyano group directly bonds to ruthenium, and π electrons are considered to be delocalized along the C(2)–C(3)–O(1) linkage to increase the nucleophilicity of the enolato ligand (*vide infra*). The dihedral angle of C(1)–C(2)–C(3)–O(1) (5°) is very small, showing the planarity for these four atoms. In contrast, the C(6)–C(7)–C(8)–O(3) linkage of coordinated ethyl cyanoacetate is tilted by the dihedral angle of 27°. A similar structural feature is also found in **41a**. This may be due to the contribution of the increased oxo π -allyl anionic character along the C(2)–C(3)–O(1) bond, making the zwitterionic bond in **41a** and **41b**. An alternative representation such as an azaallene-type bond is possible from the linear structure of the N(1)–C(1)–C(2) bond (178°), but this is not the case here, since the dihedral angle Ru–N(1)–C(1)–C(2)–C(3) is very small (9°). The relatively short interatomic distance (3.17 Å) between C(7) and O(1) atoms suggests an intramolecular nonbonding interaction probably by the hydrogen bonding of the enolato oxygen with one of the methylene

protons of the coordinated ethyl cyanoacetate (3.26 Å for **41a**), since the C–O bond distance due to the hydrogen bonding of C···H···O has been observed in a range of 3.0–4.0 Å.³⁶

Similarly, hydrido(enolato)ruthenium(II) complexes RuH(R¹-COCHCOR²)(PPh₃)₃ (R¹ = R² = Me (**42a**); R¹ = R² = OMe (**42b**); R¹ = Me, R² = OMe (**42c**)) were also obtained by the reactions of **4** with diketones and keto esters such as 2,4-pentanedione, dimethyl malonate, and methyl acetoacetate (eq 7). The reactions of **3** with these active methylene compounds gave the same products.



Spectroscopic analysis of **42a–c** reveals that these also have octahedral structures. An important structural difference between **41a** and **42a** is found in the enolato moiety. The IR spectrum of **42a** shows a $\nu(\text{Ru-H})$ band at 1941 cm⁻¹ and a

(36) (a) Desiraju, G. R. *Acc. Chem. Res.* **1991**, *24*, 290 and references cited therein. (b) Pimentel, G. C.; McClellan, A. L. *The Hydrogen Bond*; W. H. Freeman: San Francisco, 1960. (c) Schuster, P.; Zundel, G.; Sandorfy, C.; Eds. *The Hydrogen Bond II. Structure and Spectroscopy*; North-Holland: Amsterdam, 1976.

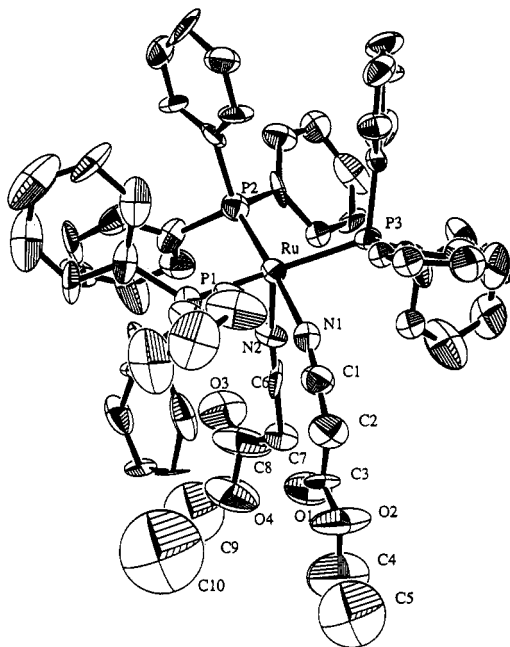


Figure 2. Molecular structure of **41b**. Selected bond lengths (Å): Ru–P(1), 2.358 (7); Ru–P(2), 2.319 (6); Ru–P(3), 2.373 (6); Ru–N(1), 2.10(2); N(1)–C(1), 1.17 (3); C(1)–C(2), 1.36 (3); C(2)–C(3), 1.4 (3); O(1)–C(3), 1.10(3); O(2)–C(3), 1.41 (3); Ru–N(2), 2.16 (2); N(2)–C(6), 1.16 (2); C(6)–C(7), 1.44 (3); C(7)–C(8), 1.47 (4); O(3)–C(8), 1.18(3); O(4)–C(8), 1.31 (3). Selected bond angles (deg): P(1)–Ru–P(2), 97.3 (2); P(1)–Ru–P(3), 158.6 (2); P(1)–Ru–N(1), 82.7 (5); P(1)–Ru–N(2), 91.3 (5); P(2)–Ru–P(3), 97.5 (2); P(2)–Ru–N(1), 170.9 (5); P(2)–Ru–N(2), 90.5 (5); P(3)–Ru–N(1), 103.9 (5); N(1)–Ru–N(2), 80.4 (7); Ru–N(1)–C(1), 166 (2); N(1)–C(1)–C(2), 178 (3); C(1)–C(2)–C(3), 121 (3); O(1)–C(3)–O(2), 121 (3); O(1)–C(3)–O(2), 130 (3); O(2)–C(3)–C(2), 101 (3); C(3)–O(2)–C(4), 114 (3); Ru–N(2)–C(6), 160 (2); N(2)–C(6)–C(7), 174 (3); C(6)–C(7)–C(8), 106 (2); O(3)–C(8)–O(4), 112 (4); O(3)–C(8)–O(7), 135 (4); O(4)–C(8)–C(7), 112 (3); C(8)–O(4)–C(9), 123 (3).

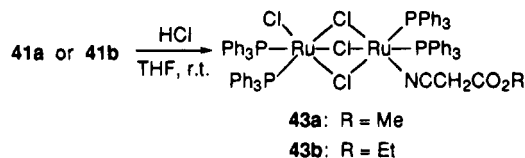
$\nu(\text{C}=\text{O})$ band at 1586 cm^{-1} . The relatively low value of the latter for the carbonyl group suggests the chelating coordination mode of the diketonato ligand.³⁷ The ^1H NMR spectrum of **42a** shows a double triplet at $\delta -16.6$ assignable to a hydrido ligand which is coupled with two magnetically equivalent and a unique P nuclei, all *cis* to the hydride. The 2,4-pentanedionato ligand is considered to coordinate to ruthenium by a bidentate *O*-enolato ligand form, since the methine proton resonates at relatively lower field and has no coupling with P nuclei.³⁸ Observation of two kinds of methyl signals indicates that they are inequivalent to each other and the *trans* positions of the chelating 2,4-pentanedionato ligand are occupied by the hydrido and triphenylphosphine ligands. Similar spectroscopic results were obtained for **42b** and **42c**. It should be noted that **42c** is a configurational isomeric mixture due to unsymmetry of the enolato ligand.

Reactions of Hydrido(enolato)ruthenium(II) Complexes. Protonolysis of **41a** and **41b** with hydrogen chloride in THF

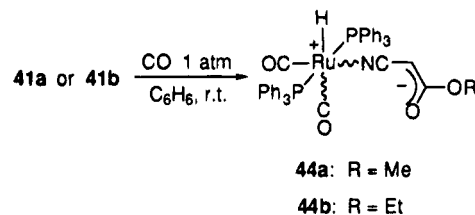
(37) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd. ed.; John Wiley & Sons: New York, 1977.

(38) (a) Thompson, D. W. *Structure Bonding* **1971**, 9, 27. (b) Block, B.; Flatau, K.; Junge, H.; Kuhr, M.; Musso, H. *Angew. Chem.* **1971**, 83, 239. (c) Gibson, D. *Coord. Chem. Rev.* **1969**, 4, 225. (d) Baba, S.; Ogura, S.; Kawaguchi, S. *Bull. Chem. Soc. Jpn.* **1974**, 47, 665. (e) Gibson, D.; Johnson, B. F. G.; Lewis, J. J. *Chem. Soc. A* **1970**, 367. (f) Hall, J. R.; Swie, J. J. *Organomet. Chem.* **1973**, 47, 195. (g) Hall, J. R.; Swie, J. *Ibid.* **1974**, 67, 455. (h) Dietrich, K.; Musso, H. *Ibid.* **1975**, 93, 15. (i) Mc Candish, L. E.; Macklin, J. W. *Ibid.* **1975**, 99, 31. (j) Nakamura, Y.; Nakamoto, K. *Inorg. Chem.* **1975**, 14, 63. (k) Allmann, R.; Flatau, K.; Musso, H. *Chem. Ber.* **1972**, 105, 3067. (l) Komiya, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1977**, 99, 3695.

liberated methyl cyanoacetate in 124% yield per ruthenium, giving $\text{Ru}_2\text{Cl}_4(\text{PPh}_3)_4(\text{NCCCH}_2\text{CO}_2\text{R})$ ($\text{R} = \text{Me}$ (**43a**), $\text{R} = \text{Et}$ (**43b**)). The enolato ligand seems to be completely hydrolyzed to alkyl cyanoacetate, and a part of the cyanoacetate ligand coordinates to ruthenium to form dimeric complexes **43a** or **43b**.

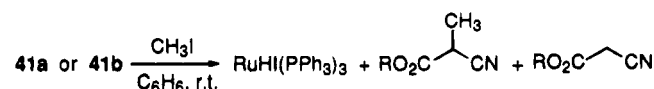


Treatment of **41a** or **41b** with carbon monoxide in benzene gave light yellow hydrido(carbonyl)(enolato)ruthenium(II) complex $\text{RuH}(\text{NCCCHCO}_2\text{R})(\text{CO})_2(\text{PPh}_3)_2$ ($\text{R} = \text{Me}$ (**44a**), $\text{R} = \text{Et}$ (**44b**)). Electron withdrawal by the carbonyl ligands probably weakened the $\text{Ru}-\text{H}$ bond to give a decrease in the stretching frequency. In contrast, a slight increase in the carbonyl stretching band in the enolato ligand is observed. This may be due to redistribution of electrons into the $\text{Ru}-\text{N}-\text{C}-\text{C}$ linkage from the oxo- π -allylic moiety to make the carbonyl group a more nonconjugated structure. However, the total nucleophi-



licity of the enolato ligand should decrease by strong electron withdrawal from π -accepting CO ligands. Complexes **44a** and **44b** are found to be isomeric mixtures, since their ^1H NMR spectra show two sets of signals of products in a 1:2 ratio. One is considered to contain the hydride *trans* to the enolato ligand and the other *trans* to the unique carbonyl ligand. These two geometries are exchanging with each other at 70 °C to give a thermodynamic mixture, because two sets of signals in the ^1H NMR spectrum collapsed with increasing the temperature. Protonolysis of **44b** released ethyl cyanoacetate accompanied by evolution of hydrogen gas. The resulting complex was the known carbonyl complex *cis*- $\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2$.³⁹

Reaction of **41a** with excess methyl iodide in benzene at room temperature gave methyl 2-cyanopropanoate and methyl cyanoacetate in 96% and 84% yields, respectively. The former is considered to be formed by methylation of the enolato ligand, while the latter by simple dissociation of the methyl cyanoacetate ligand. The resulting ruthenium product was hydridoiodotris-(triphenylphosphine)ruthenium(II), which was confirmed by spectroscopy and elemental analysis.⁴⁰ The reaction of **41b** with methyl iodide proceeded similarly. In contrast, the reaction of



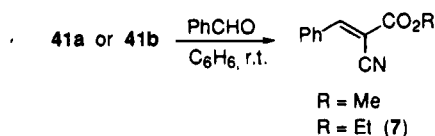
42a with methyl iodide in benzene did not produce 3-methyl 2,4-pentanedione at all at room temperature for 1 week. Only a small amount of methane (9%) and methyltriphenylphosphonium iodide was detected. This fact indicates that the enolato moiety in **41a** and **41b** is highly nucleophilic, whereas the 2,4-

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(40) Ito, T.; Kitazume, S.; Yamamoto, A.; Ikeda, S. *J. Am. Chem. Soc.* **1970**, *92*, 3011.

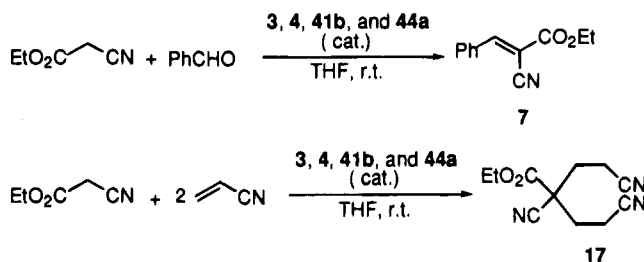
pentanedionato ligand in **42a** is inactive, probably because of stability of the Ru–acac bond by the chelation effect.

In relation to the catalytic chemoselective aldol-type reactions, the reactions of these complexes **41a** and **41b** with benzaldehyde in benzene at room temperature were performed. Alkyl 2-cyano-3-phenylpropenoates were obtained in 108% and 161% yields per ruthenium, respectively. Similar treatment of



44b gave **7** in 78% yield. On the other hand, **42a** showed no reactivity toward benzaldehyde. The reaction of **41b** with acrylonitrile affords ethyl 2-(2'-cyanoethyl)-2,4-dicyanobutanoate (**17**) in 45% yield per ruthenium, while no reaction occurred upon similar treatment with **44b**. These results are consistent with the fact that the highly chemoselective aldol reactions of alkyl cyanoacetate with aldehydes are catalyzed by ruthenium complexes even in the presence of 2,4-pentanedione, which has approximately the same $\text{p}K_a$ value ($\text{p}K_a = 9.0$) as that of alkyl cyanoacetate.¹⁹

The catalytic activity of the isolated hydrido(enolato)-ruthenium(II) complexes **41** was examined for aldol and Michael reactions in comparison with **3** or **4**. In the case of aldol reactions of ethyl cyanoacetate with benzaldehyde, complexes **3**, **4**, and **41b** showed similar catalytic activity, and **7** was obtained in 50–70% yields. A similar trend was also observed in the catalytic Michael addition reaction to acrylonitrile. In the presence of **3**, **4**, and **41b** catalysts, a double Michael addition product (**17**) was obtained in excellent yield. It is noteworthy that carbonyl-substituted complex **44a** shows low catalytic activity to both reactions.



Kinetics of the Catalytic Aldol-Type Reaction of Ethyl Cyanoacetate with Benzaldehyde. In order to obtain further insight into the mechanism of the ruthenium-catalyzed aldol reaction, kinetic experiments on the reaction of ethyl cyanoacetate with benzaldehyde were carried out by using hydrido(enolato)ruthenium(II) catalyst **41b**. The time–yield dependence of formation of **7** was periodically followed by gas chromatography. In order to keep the pseudo-first-order reaction conditions, a large excess amount of ethyl cyanoacetate was employed in these reactions. The rate was first order in the concentration of benzaldehyde (Figure 3). The first-order rate constant increases with an increase in the concentration of **41b** (Figure 4) but is independent of the concentration of ethyl cyanoacetate (Figure 5). Thus, the rate law for the reaction is expressed by eq 8.

$$\frac{d[\text{NC}(\text{EtO}_2\text{C})\text{C}=\text{CHPh}]}{dt} = k[\mathbf{41b}][\text{PhCHO}] \quad (8)$$

On the basis of these results, the aldol reaction can be rationalized by assuming the mechanism as shown in Scheme

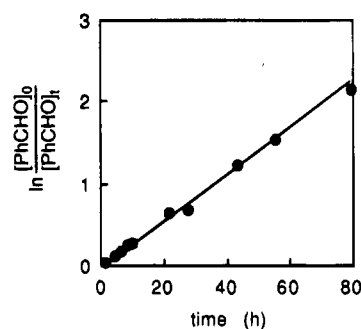


Figure 3. First-order plot of the aldol reaction of ethyl cyanoacetate with benzaldehyde catalyzed by **41b** in THF at 50 °C. [**41b**] = 0.418 mM; [NCCH₂CO₂Et] = 188 mM; [PhCHO] = 22.8 mM. $k_{\text{obs}} \times 10^6 = 8.26 \pm 0.25 \text{ s}^{-1}$.

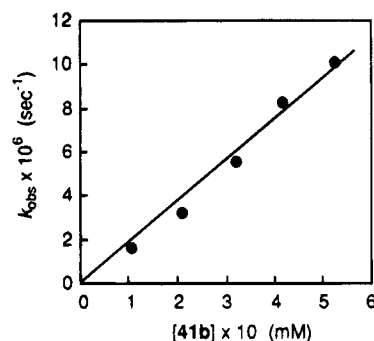


Figure 4. Dependence of the first order rate constants k_{obs} on the concentration of **41b**. Solvent, THF; temp = 50 °C; $k_{\text{obs}} \times 10^6$ (**41b**) = 1.61 ± 0.63 (0.105 mM), 3.22 ± 0.98 (0.210 mM), 5.57 ± 0.45 (0.320 mM), 8.26 ± 0.25 ($\times 0.418$ mM), $10.1 \pm 0.33 \text{ s}^{-1}$ (0.523 mM); [NCCH₂CO₂Et] = 188 mM; [PhCHO] = 22.2 ± 2 mM; $k \times 10^2$ ($k = k_{\text{obs}}/[\mathbf{41b}]$) = $1.74 \pm 0.19 \text{ s}^{-1} \text{ M}^{-1}$.

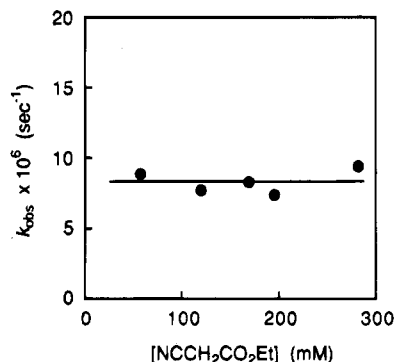
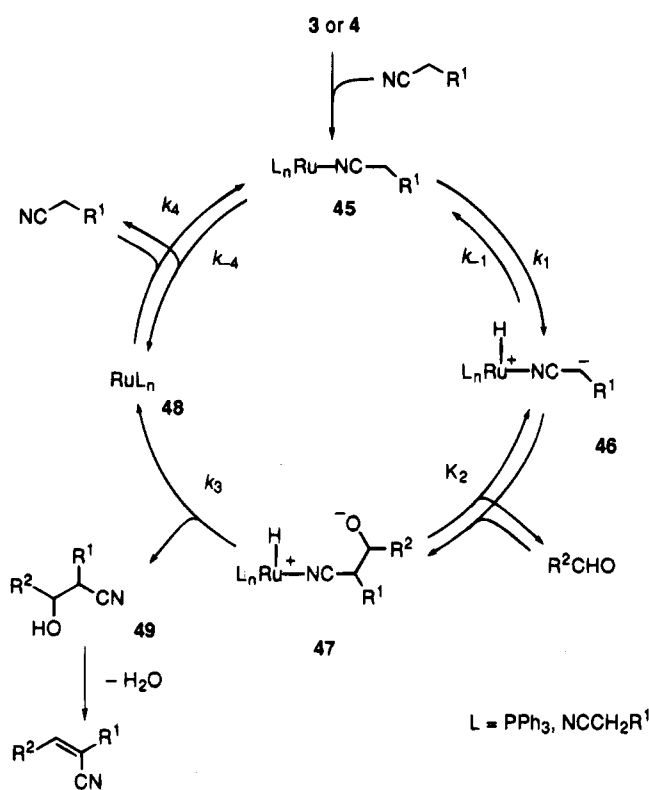


Figure 5. Dependence of the first order rate constants k_{obs} on the concentration of ethyl cyanoacetate. Solvent, THF; temp = 50 °C; [**41b**] = 0.426 ± 0.008 mM; $k_{\text{obs}} \times 10^6$ ([NCCH₂CO₂Et]) = 8.88 ± 0.43 (57.0 mM), 7.77 ± 0.37 (119 mM), 8.26 ± 0.25 (169 mM), 7.43 ± 0.47 (195 mM), $9.43 \pm 0.62 \text{ s}^{-1}$ (282 mM); [PhCHO] = 22.5 ± 0.8 mM.

1. The catalytically active species seems to be the zerovalent ruthenium complex **45**, which is formed by coordination of nitrile to dihydridoruthenium complex **3** and subsequent reductive elimination of molecular hydrogen. When ruthenium ethylene complex **4** was used as a catalyst, dissociation of ethylene would occur upon coordination of the nitrile to **4** to give **45**. Oxidative addition of the ruthenium to the α -C–H bond of the nitrile³³ affords a hydrido α -cyanoalkylruthenium complex, which is converted into stable hydrido(enolato)-ruthenium complex **46**. Direct interaction of the enolato ligand with an aldehyde takes place to give hydrido(alldolato)ruthenium(II) intermediate **47**, which undergoes elimination of aldol product **49** to give a coordinatively unsaturated ruthenium

Scheme 1



complex. Coordination of the nitrile to **48** regenerates **45** to complete the catalytic cycle. Alternatively, complex **45** can be formed directly upon coordination of the nitrile to **47** with dissociation of **49**. Dehydration of **49** may proceed under the reaction conditions.

The rate law is derived by assuming the equilibrium for the oxidative addition of ruthenium to the α -C-H bond of the nitrile, the association of aldehyde to **46** (K_2), and the coordination of the nitrile to **48** as shown in Scheme 1. If $K_2 \ll 1$, the rate is expressed by eq 9, where $[\text{Ru}]_{\text{total}}$ is the same as the initial catalyst concentration. If $k_1 \gg k_{-1}$ and $k_4 \gg k_{-4}$, the equation should be as eq 10. Thus, the equation is in accord with the kinetic data, which supports the proposed mechanism.

$$\frac{d[\text{NCR}^1\text{C}=\text{CHR}^2]}{dt} = \frac{k_3 K_2 [\text{Ru}]_{\text{total}} [\text{NCCH}_2\text{R}^1] [\text{R}^2\text{CHO}]}{(k_{-1}/k_1 + 1) [\text{NCCH}_2\text{R}^1] + (k_{-1}/k_1)(k_{-4}/k_4)} \quad (9)$$

if $k_1 \gg k_{-1}$ and $k_4 \gg k_{-4}$

$$\begin{aligned} \frac{d[\text{NCR}^1\text{C}=\text{CHR}^2]}{dt} &= k_3 K_2 [\text{Ru}]_{\text{total}} [\text{R}^2\text{CHO}] \\ &= k_{\text{obs}} [\text{R}^2\text{CHO}] \end{aligned} \quad (10)$$

The electronic properties of benzaldehydes were systematically altered with a series of para substituents. The rate constants for the ruthenium-catalyzed aldol reactions k ($k = k_{\text{obs}}/[\text{Ru}]_{\text{total}}$) shows a reasonably linear Hammett correlation as shown in Figure 6. The ρ value of +1.6 indicates that the electron-deficient benzaldehydes are more effective in catalytic aldol reactions.

The formation of **41** from the reaction of **3** or **4** suggests the alternative non-redox mechanism as shown in Scheme 2. That is, the reaction of **41** with aldehyde gives hydrido(alcolato)-ruthenium(II) **50**. Intramolecular hydrogen abstraction from the coordinated alkyl cyanoacetate gives enolato complex **51**. Dissociation of product followed by coordination of alkyl cyanoacetate regenerates **41** to complete the catalytic cycle.

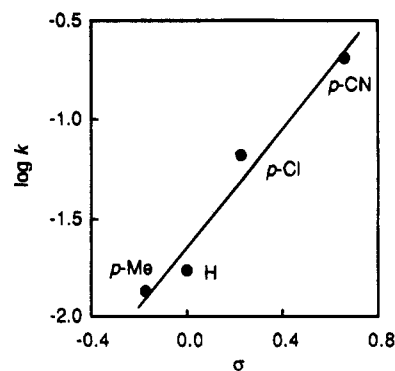
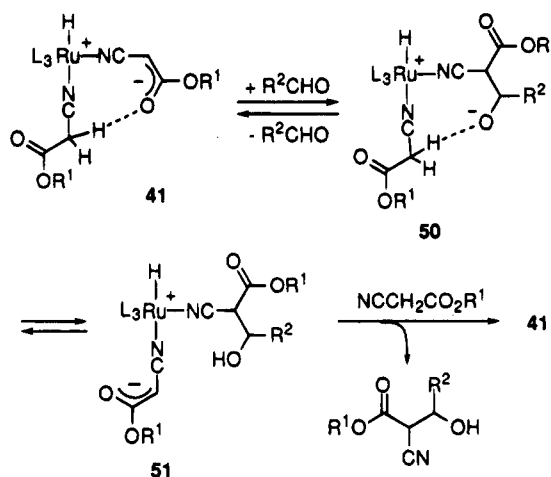
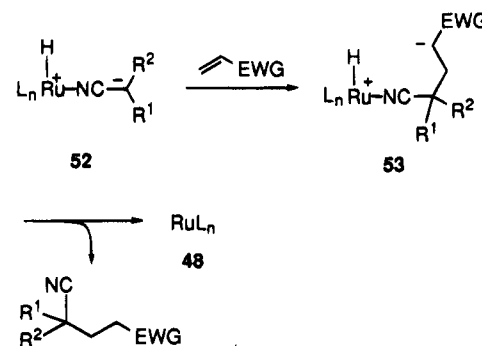


Figure 6. Hammett correlation of ruthenium-catalyzed aldol reaction of ethyl cyanoacetate with para-substituted benzaldehydes. Solvent, THF; temp = 50 °C; $[\text{41b}] = 0.388\text{--}0.600$ mM, $[\text{p-X-C}_6\text{H}_4\text{CHO}] = 19.8 \pm 1.8$ mM, $[\text{NCCH}_2\text{CO}_2\text{Et}] = 188$ mM; $\log k$ (X, σ), -1.87 (Me, -0.17), -1.76 (H, 0.00), -1.18 (Cl, 0.23), -0.688 (CN, 0.66); $\rho = +1.6 \pm 0.8$.

Scheme 2



Scheme 3



Michael reaction of nitriles with olefins bearing electron-withdrawing groups can be rationalized by the pathway shown in Scheme 3, which is similar to the mechanism of aldol reactions (Scheme 1). The addition of hydrido(enolato)-ruthenium **52** to an olefin bearing an electron-withdrawing group gives complex **53** which undergoes reductive elimination of Michael adducts and **48** to complete the catalytic cycle.

The highly diastereoselective Michael reaction of cyano ester **30** can be rationalized by assuming intermediate **54**, where chelation of the malonate moiety to the ruthenium plays an important role. Reaction of **3** or **4** with a diastereomeric mixture of cyano ester **30** gives enolato complex **54**, in which the cyano group and one carbonyl group of the malonate moiety coordinate to the ruthenium and the other alkoxy carbonyl groups are located at pseudoequatorial positions. Complex **54** is attacked

Calcd for $C_{12}H_{11}NO_3$: C, 66.35; H, 5.10; N, 6.45. Found: C, 66.17; H, 5.03; N, 6.45.

(E)-Ethyl 2-cyano-3-(4-methoxyphenyl)-2-propenoate (9): mp 80–81 °C; IR (KBr) 2994 (w), 2284 (m, CN), 1914 (w), 1717 (s, C=O), 1586 (s), 1563 (s), 1514 (s), 1433 (s), 1366 (s), 1321 (s), 1264 (s), 1211 (s), 1190 (s), 1184 (s), 1019 (s), 839 (m), 627 (w), 588 (w), 554 (s) cm^{-1} ; 1H NMR ($CDCl_3$, 270 MHz) δ 1.39 (t, J = 7.1 Hz, 3 H), 3.89 (s, 3 H), 4.36 (q, J = 7.1 Hz, 2 H), 6.99 (ddd, J = 5.0, 2.9, 2.9 Hz, 2 H), 7.99 (ddd, J = 5.0, 2.9, 2.9 Hz, 2 H), 8.16 (s, 1 H). Anal. Calcd for $C_{13}H_{13}NO_3$: C, 67.52; H, 5.67; N, 6.06. Found: C, 67.22; H, 5.64; N, 6.01.

(E)-Ethyl 3-(3'-cyclohexenyl)-2-cyano-2-propenoate (10): IR (neat) 3031 (m), 2986 (m), 2920 (s), 2841 (m), 2232 (m, CN), 1734 (s, C=O), 1624 (s), 1437 (m), 1385 (m), 1294 (s), 1265 (s), 1245 (s), 1217 (s), 1082 (s), 1053 (m), 1016 (m), 762 (s) cm^{-1} ; 1H NMR ($CDCl_3$, 270 MHz) δ 1.36 (t, J = 7.3 Hz, 3 H), 1.54–2.29 (m, 6 H), 2.94–3.08 (m, 1 H), 4.32 (q, J = 7.3 Hz, 2 H), 5.64–5.71 (m, 1 H), 5.74–5.81 (m, 1 H), 7.56 (d, J = 10.5 Hz, 1 H); HRMS calcd for $C_{12}H_{13}NO_2$ 205.1103, found 205.1107.

Ethyl cyclohexylidenecyanoacetate (11): IR (neat) 2982 (m), 2940 (s), 2863 (s), 2224 (m, CN), 1730 (s, C=O), 1601 (s), 1449 (s), 1368 (m), 1289 (s), 1269 (s), 1237 (s), 1217 (s), 1140 (m), 1100 (s), 1028 (s), 858 (m), 779 (m) cm^{-1} ; 1H NMR ($CDCl_3$, 270 MHz) δ 1.34 (t, J = 7.1 Hz, 3 H), 1.60–1.85 (m, 6 H), 2.66 (dd, J = 7.0, 6.8 Hz, 2 H), 2.97 (dd, J = 6.4, 5.0 Hz, 2 H), 4.28 (q, J = 7.1 Hz, 2 H). Anal. Calcd for $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82; N, 7.25. Found: C, 68.15; H, 7.76; N, 7.43.

Cyclohexylidenemalononitrile (12): IR (neat) 2948 (s), 2864 (s), 2232 (s, CN), 1598 (s), 1449 (s), 1352 (m), 1316 (m), 1291 (w), 1258 (w), 1130 (w), 1028 (w), 1005 (m), 895 (w), 858 (m), 706 (w) cm^{-1} ; 1H NMR ($CDCl_3$, 270 MHz) δ 1.63–1.74 (m, 2 H), 1.76–1.85 (m, 4 H), 2.66 (dd, J = 6.1, 6.1 Hz, 4 H). Anal. Calcd for $C_9H_{10}N_2$: C, 71.60; H, 5.51; N, 6.96. Found: C, 71.89; H, 5.41; N, 7.18.

Ruthenium-Catalyzed Reaction of Ethyl Cyanoacetate with *N*-Benzylideneaniline. A mixture of ethyl cyanoacetate (0.226 g, 2.00 mmol), *N*-benzylideneaniline (0.402 g, 2.22 mmol), and $RuH_2(PPh_3)_4$ (0.069 g, 0.06 mmol) in dry THF (0.5 mL) was stirred at room temperature for 24 h under argon. After removal of the solvent, the brown residue was purified by column chromatography (SiO_2 , AcOEt: hexane = 1:5) to afford **7** (0.331 g, 82%) as a light yellow solid.

4-[[4'-(Methoxycarbonyl)phenyl]amino]-2-cyano-2-methyl-3-p-tolylpropanenitrile (15). The $RuH_2(PPh_3)_4$ -catalyzed reaction of 4-(methoxycarbonyl)-*N*-(4-methylbenzylidene)aniline (**14**) (0.097 g, 0.39 mmol) with 2-methylmalononitrile (**13**) (0.048 g, 0.57 mmol) in dry THF (1.0 mL) at room temperature for 48 h gave **15** (116.6 g, 91%) as a colorless oil. After 14 h, the yield of **15** was determined to be 45% by means of NMR analysis, while similar treatment with $RhH(CO)(PPh_3)_3$ catalyst¹⁷ gave **15** in 36% NMR yield. **15**: IR (KBr) 3380 (s), 2999 (s), 2251 (CN, w), 1920 (br, w), 1701 (C=O, s), 1606 (s), 1525 (s), 1435 (s), 1314 (s), 1287 (s), 1181 (s), 1113 (s), 967 (w), 911 (s), 841 (s), 772 (s) cm^{-1} ; 1H NMR ($CDCl_3$, 270 MHz) δ 1.81 (s, 3 H, $CCH_3(CN)_2$), 2.35 (s, 3 H, $C_6H_4CH_3$), 3.83 (s, 3 H, CO_2CH_3), 4.77 (d, J = 9.1 Hz, 1 H), 4.84 (d, J = 9.1 Hz, 1 H), 6.67 (ddd, J = 7.0, 1.7, 1.7 Hz, 2 H, C_6H_4Me), 7.22 (ddd, J = 9.0, 2.4, 2.4 Hz, 2 H, $C_6H_4CO_2Me$), 7.36 (ddd, J = 7.0, 1.7, 1.7 Hz, 2 H, C_6H_4Me), 7.85 (ddd, J = 9.0, 2.4, 2.4 Hz, 2 H, $C_6H_4CO_2Me$).

Catalytic Activity of Metal Complexes and Phosphine Effect for the Reaction of Benzyl Cyanide with Crotononitrile. A mixture of benzyl cyanide (2.00 mmol), crotononitrile (2.20 mmol; *E*:*Z* = 61:39) and catalyst (0.06 mmol) in dry THF (3.0 mL) was stirred at room temperature for 1 h under argon. The conversions of benzyl cyanide and the yields of 2-phenyl-3-methyl-4-cyanobutanenitrile (**16**) were determined by GLC analysis (DB-1, 60–250 °C) using an internal standard (dodecane). The results with various catalysts are as follows: $RuH_2(PPh_3)_4$ (**3**) (convn 89%, yield of **16** 97%), $RuH(C_2H_4)(PPh_3)_2$ ($PPh_2C_6H_4$) (**4**) (93%, 90%), $RhH(CO)(PPh_3)_3$ (56%, 98%). Other complexes such as $RuH_2(CO)(PPh_3)_3$, $IrH(CO)(PPh_3)_3$, $Pd(PPh_3)_4$, $Pd_2(dba)_3 \cdot CHCl_3$, $Ru(OCOCF_3)_2(CO)(PPh_3)_2$,⁴⁹ $RuCl_2(PPh_3)_3$, $RhCl(PPh_3)_3$, $RhCl(CO)(PPh_3)_2$,⁵⁰ $RhCl_3 \cdot nH_2O$, and $PdCl_2$ show no catalytic activity.

The effect of phosphines was also examined under similar conditions by adding a phosphine (monophosphine 0.08 mmol, diphosphine 0.04

mmol). The results are as follows: PPh_2Et (85%, 82%), $PPhMe_2$ (45%, 89%), $Ph_2PCH_2PPh_2$ (dppm) (convn 59%; yield of **16** >99%), dppe (50%, 96%), dppp (76%, >99%), $Ph_2P(CH_2)_4PPh_2$ (dppb) (34%, >99%), $Ph_2P(CH_2)_5PPh_2$ (39%, >99%), none (20%, >99%).

General Procedure for the Ruthenium-Catalyzed Reaction of Nitriles with Olefins. A mixture of nitrile (2.00 mmol), olefin (2.20 mmol), and $RuH_2(PPh_3)_4$ (0.06 mmol) in dry THF (0.5 mL) was stirred at room temperature for 24 h under argon. After removal of the solvent, the residue was purified by Kugelrohr distillation and thin layer or column chromatography (SiO_2) to give the Michael adduct. The results are summarized in Table 2.

Ethyl 2-(2'-cyanoethyl)-2,4-dicyanobutanoate (17): IR (neat) 2980 (m), 2250 (CN, s), 1740 (C=O, s), 1450 (m), 1425 (m), 1280 (m), 1220 (m), 1095 (m), 1010 (m), 855 (m) cm^{-1} ; 1H NMR ($CDCl_3$, 60 MHz) δ 1.43 (t, J = 7.0 Hz, 3 H, CH_3), 1.80–2.80 (m, 8 H, CH_2), 4.42 (q, J = 7.0 Hz, 4 H, OCH_2CH_3); HRMS calcd for $C_{11}H_{14}N_3O_2$ (M + 1) 220.1086, found 220.1086.

Diethyl 4-cyano-4-(ethoxycarbonyl)heptanedioate (18): IR (neat) 3000 (s), 2265 (CN, m), 1745 (C=O, s), 1460 (s), 1380 (s), 1100 (s), 1030 (s), 935 (m), 865 (s), 795 (m), 765 (m) cm^{-1} ; 1H NMR ($CDCl_3$, 60 MHz) δ 1.23 (t, J = 7.2 Hz, 6 H, CH_3), 1.31 (t, J = 7.2 Hz, 3 H, CH_3), 1.90–2.72 (m, 8 H, CH_2), 4.16 (q, J = 7.2 Hz, 4 H, OCH_2CH_3), 4.28 (q, J = 7.2 Hz, 2 H, OCH_2CH_3); HRMS calcd for $C_{15}H_{23}NO_6$ 313.1525, found 313.1526.

Ethyl 2,4-Dicyano-3-methylbutanoate (19). 1H NMR (500 MHz) analysis showed that the diastereomeric ratio of **19** is 54:46: bp 150 °C; IR (neat) 3005 (s), 2260 (CN, m), 1755 (C=O, s), 1475 (m), 1440 (m), 1405 (m), 1385 (m), 1260 (s), 1110 (m), 1040 (s), 865 (m) cm^{-1} ; 1H NMR ($CDCl_3$, 500 MHz) δ 1.27 (d, J = 6.9 Hz, 3 H, $CHCH_3$ (major diastereomer)), 1.32 (d, J = 6.9 Hz, 3 H, OCH_3 (minor diastereomer)), 1.35 (t, J = 7.1 Hz, 3 H, OCH_2CH_3 (major and minor)), 2.47–2.72 (m, 3 H, $CHCH_2$ (major and minor)), 3.59 (d, J = 5.3 Hz, 1 H, $CH(CN)CO_2Et$ (minor)), 3.71 (d, J = 5.3 Hz, 1 H, $CH(CN)CO_2Et$ (major)), 4.31 (q, J = 7.1 Hz, 2 H, OCH_2CH_3 (major and minor)).

Diethyl 4-Cyano-2-(ethoxycarbonyl)-3-methylpentanedioate (30b). 1H NMR (500 MHz) analysis focused on C^3 -Me protons showed that the diastereomeric ratio of **30b** is 69:31: IR (neat) 3000 (s), 2275 (CN, w), 1750 (C=O, s), 1480 (s), 1400 (s), 1380 (s), 1200 (s), 1080 (m), 1030 (s), 865 (m), 765 (m) cm^{-1} ; 1H NMR ($CDCl_3$, 500 MHz) δ 1.15 (d, J = 6.9 Hz, 3 H, $CHCH_3$), 1.19 (d, J = 6.9 Hz, 3 H, $CHCH_3$), 1.28 (t, J = 7.1 Hz, 6 H, $C(CO_2CH_2CH_3)_2$), 1.29 (t, J = 7.0 Hz, 6 H, $C(CO_2CH_2CH_3)_2$), 1.33 (t, J = 7.2 Hz, 3 H, $C(CN)CO_2CH_2CH_3$), 1.33 (t, J = 7.1 Hz, 3 H, $C(CN)CO_2CH_2CH_3$), 2.94 (ddq, J = 8.5, 6.0, 6.9 Hz, 1 H, $CHCH_3$), 3.03 (ddq, J = 9.6, 4.1, 6.9 Hz, 1 H, $CHCH_3$), 3.45 (d, J = 9.6 Hz, 1 H, $CH(CO_2Et)_2$), 3.68 (d, J = 8.5 Hz, 1 H, $CH(CO_2Et)_2$), 3.94 (d, J = 6.0 Hz, 1 H, $CH(CN)CO_2Et$), 4.15 (d, J = 4.1 Hz, 1 H, $CH(CN)CO_2Et$), 4.22 (q, J = 7.1 Hz, 2 H, $C(CO_2Et)CO_2CH_2CH_3$), 4.24 (q, J = 7.1 Hz, $C(CO_2CH_2CH_3)CO_2Et$), 4.29 (q, J = 7.1 Hz, $C(CN)CO_2CH_2CH_3$). Anal. Calcd for $C_{14}H_{21}NO_6$: C, 56.18; H, 7.07; N, 4.68. Found: C, 56.14; H, 7.00; N, 4.41.

Ethyl 2,4-dicyano-2-methylbutanoate (20): IR (neat) 2995 (s), 2250 (CN, w), 1745 (C=O, s), 1450 (m), 1425 (m), 1390 (m), 1370 (m), 1220 (m), 1010 (s), 860 (s), 765 (m) cm^{-1} ; 1H NMR ($CDCl_3$, 270 MHz) δ 1.35 (t, J = 7.1 Hz, 3 H, CH_3), 1.65 (s, 3 H, CH_3), 2.15 (ddd, J = 14.0, 9.2, 6.2 Hz, 1 H, CH_2CN), 2.37 (ddd, J = 14.0, 9.2, 6.2 Hz, 1 H, CH_2CN), 2.54 (ddd, J = 13.4, 9.0, 7.1 Hz, 1 H, CH_2CH_2CN), 2.63 (ddd, J = 13.4, 9.0, 7.1 Hz, 1 H, CH_2CH_2CN), 4.31 (q, J = 7.1 Hz, 2 H, OCH_2CH_3). Anal. Calcd for $C_9H_{12}N_2O_2$: C, 59.98; H, 6.71; N, 15.54. Found: C, 59.72; H, 6.72; N, 15.44.

Ethyl 2-cyano-2-methyl-4-(methoxycarbonyl)butanedioate (21): IR (neat) 3467 (m), 2940 (s), 2930 (s), 2238 (CN, m), 1744 (C=O, s), 1439 (s), 1436 (s), 1300 (s), 1253 (s), 1203 (s), 1126 (s), 1080 (m), 935 (w), 865 (s), 795 (w), 765 (w) cm^{-1} ; 1H NMR ($CDCl_3$, 270 MHz) δ 1.33 (t, J = 7.1 Hz, 3 H, CH_3), 1.62 (s, 3 H, CH_3), 2.13 (ddd, J = 15.9, 9.1, 6.5 Hz, 1 H, $CH_2CH_2CO_2Me$), 2.30 (ddd, J = 15.9, 9.1, 6.5 Hz, 1 H, $CH_2CH_2CO_2Me$), 2.51 (ddd, J = 15.9, 9.1, 6.5 Hz, 2 H, $CH_2CH_2CO_2Me$), 3.70 (s, 3 H, OCH_3), 4.27 (q, J = 7.1 Hz, 2 H, CO_2CH_2); HRMS calcd for $C_{10}H_{12}NO_4$ 210.0766, found 210.0768.

Ethyl 2-cyano-4-formyl-2-methylbutanoate (22): IR (neat) 3000 (s), 2260 (CN, m), 1735 (C=O, s), 1450 (m), 1420 (m), 1390 (s), 1110 (s), 1020 (s), 860 (s), 775 (m), 735 (m) cm^{-1} ; 1H NMR ($CDCl_3$, 60

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MHz) δ 1.28 (t, J = 7.0 Hz, 3 H, CH₃), 1.75 (s, 3 H, CH₃), 1.94–2.91 (m, 4 H, CH₂), 4.23 (q, J = 7.0 Hz, 2 H, OCH₂CH₃), 9.67 (s, 1 H, CHO). Anal. Calcd for C₉H₁₃NO₃: C, 59.33; H, 7.19; N, 7.68. Found: C, 59.63; H, 7.11; N, 7.32.

Ethyl 2,4-dicyano-2,3-dimethylbutanoate (23): IR (neat) 3010 (s), 2280 (m, CN), 1755 (s, C=O), 1470 (m), 1435 (w), 1400 (w), 1380 (w), 1265 (s), 1210 (s), 1110 (m), 1035 (m), 865 (m) cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 1.27 (d, J = 6.7 Hz, 3 H, CHCH₃ (major diastereomer)), 1.32 (d, J = 6.8 Hz, 3 H, CHCH₃ (minor diastereomer)), 1.35 (t, J = 7.1 Hz, 3 H, OCH₂CH₃ (major and minor)), 1.62 (s, 3 H, C(CN)CH₃ (minor)), 1.63 (s, 3 H, C(CN)CH₃ (major)), 2.31–2.52 (m, 3 H, CHCH₂ (major and minor)), 4.32 (q, J = 7.1 Hz, 2 H, OCH₂CH₃ (major and minor)). Diastereomer ratio was determined by ¹H NMR (270 MHz) analysis. Anal. Calcd for C₁₀H₁₄N₂O₂: C, 61.84; H, 7.27; N, 14.42. Found: C, 61.71; H, 7.22; N, 14.42.

2-Methyl-2-phenylpentanedinitrile (24): IR (neat) 3010 (s), 2960 (s), 2270 (CN, s), 1615 (m), 1505 (s), 1460 (s), 1435 (m), 1400 (m), 1090 (m), 1040 (m), 770 (s), 700 (s) cm⁻¹; ¹H NMR (CDCl₃, 60 MHz) δ 1.80 (s, 3 H, CH₃), 2.13–2.67 (m, 4 H, CH₂CH₂), 7.23–7.70 (m, 5 H, ArH). Anal. Calcd for C₁₂H₁₂N₂: C, 78.23; H, 6.56; N, 15.20. Found: C, 78.26; H, 6.49; N, 15.04.

2-Cyano-3-methyl-5-oxo-5-phenylpentanenitrile (25): IR (neat) 3050 (m), 3000 (m), 2310 (w, CN), 1740 (s), 1715 (s, C=O), 1680 (m), 1630 (m), 1610 (m), 1515 (w), 1475 (s), 1440 (w), 1400 (s), 1320 (m), 1250 (s), 1210 (m), 1100 (m), 1030 (m), 980 (w), 930 (m), 780 (s), 710 (s) cm⁻¹; ¹H NMR (CDCl₃, 270 MHz) δ 1.40 (d, J = 6.8 Hz, 3 H, CH₃), 2.89 (dtq, J = 6.8, 6.8, 4.5 Hz, 1 H, CHCH₃), 3.22 (d, J = 6.8 Hz, 2 H, CH₂COPh), 4.41 (d, J = 4.5 Hz, 1 H, CH(CN)₂), 7.46–7.54 (m, 2 H, ArH (meta)), 7.63 (tt, J = 6.6, 1.4 Hz, 1 H, ArH (para)), 7.90–7.99 (m, 2 H, ArH (ortho)); HRMS calcd for C₁₃H₁₂N₂O 212.0950, found 212.0963.

Reaction of Ethyl Cyanoacetate with Benzaldehyde in the Presence of 2,4-Pentanedione Catalyzed by RuH₂(PPh₃)₄ or AcONH₄. The RuH₂(PPh₃)₄-catalyzed reaction of ethyl cyanoacetate (0.236 g, 2.09 mmol), 2,4-pentanedione (0.209 g, 2.09 mmol), and benzaldehyde (0.228 g, 2.15 mmol) was carried out at room temperature for 17 h under argon. GLC analysis showed that cyano ester **7** was obtained as the sole product. After removal of the solvent, the residue was purified by thin layer chromatography (SiO₂, AcOEt:hexane = 1:4), affording **7** (0.350 g, 83%) as a colorless solid.

When an equimolar mixture of ethyl cyanoacetate (5.65 g, 50 mmol) and 2,4-pentanedione (5.00 g, 50 mmol) was allowed to react with benzaldehyde (5.31 g, 50 mmol) in the presence of AcONH₄ (0.150 g, 1.95 mmol) and pyridine (5.5 mL) in boiling toluene (10 mL) for 6 h, cyano ester **7** and 3-benzylidene-2,4-pentanedione (**26**) were obtained in a ratio of 75:25 (GLC analysis).

Reaction of Ethyl Cyanoacetate with Crotononitrile in the Presence of Nitroethane Catalyzed by RuH₂(PPh₃)₄ or Triton B. The RuH₂(PPh₃)₄-catalyzed reaction of ethyl cyanoacetate (0.226 g, 2.0 mmol), nitroethane (0.150 g, 2.0 mmol), and crotononitrile ($E:Z$ = 1:8) (0.148 g, 2.2 mmol) was carried out at room temperature for 24 h under argon. GLC analysis of the reaction mixture showed that ethyl 2,4-dicyano-3-methylbutanoate (**19**) was obtained as the sole product. After removal of the solvent, the residue was purified by thin layer chromatography (SiO₂, CHCl₃) to give **19** (0.232 g, 38%) as a colorless oil.

When an equimolar mixture of ethyl cyanoacetate (0.119 g, 1.0 mmol) and nitroethane (0.081 g, 1.0 mmol) was allowed to react with crotononitrile ($E:Z$ = 1:8) (0.075 g, 1.1 mmol) in the presence of Triton B (benzyltrimethylammonium hydroxide 40% aqueous solution) (0.010 g, 0.03 mmol) in 1,4-dioxane (0.25 mL) at room temperature for 24 h, cyano ester **19** and 3-methyl-4-nitropentanenitrile (**27**) were obtained in a ratio of 5:1 (GLC analysis).

Diethyl 2-Cyano-2-methyl-3-pentenedioate (28). GLC analysis of the reaction mixture showed that the $E:Z$ ratio of **28** is 65:35. Thin layer chromatography (SiO₂, CHCl₃:ether = 5:3) gave (*E*)-**28** (53%) and (*Z*)-**28** (28%) as a yellow oil. (*E*)-**28**: IR (neat) 3005 (s), 2260 (CN, w), 1740 (C=O, s), 1665 (m), 1460 (m), 1380 (m), 1220 (m), 1240 (m), 1130 (m), 980 (m), 860 (m) cm⁻¹; ¹H NMR (CDCl₃, 60 MHz) δ 1.28 (t, J = 7.0 Hz, 3 H, CH₃), 1.31 (t, J = 7.0 Hz, 3 H, CH₃), 1.91 (s, 3 H, CH₃), 4.22 (q, J = 7.0 Hz, 2 H, CH₂), 4.28 (q, J = 7.0 Hz, 2 H, CH₂), 6.24 (d, J = 15 Hz, 1 H, $-CH=C-$), 6.87 (d, J = 15 Hz, 1 H, $-CH=C-$). (*Z*)-**28**: IR (neat) 3000 (s), 2260 (CN, w), 1750 (C=O, s), 1720 (C=O, s), 1650 (w), 1455 (m), 1380 (m), 1220 (s),

1135 (s), 1030 (s), 980 (w), 860 (m), 840 (m), 760 (m) cm⁻¹; ¹H NMR (CDCl₃, 60 MHz) δ 1.25 (t, J = 7.0 Hz, 3 H, CH₃), 1.30 (t, J = 7.0 Hz, 3 H, CH₃), 1.85 (s, 3 H, CH₃), 4.23 (q, J = 7.0 Hz, 2 H, CH₂), 4.28 (q, J = 7.0 Hz, 2 H, CH₂), 6.11 (s, 2 H, $-CH=CH-$).

Ethyl 2-Methyl-2-cyano-5-oxo-3-hexenoate (29). ¹H NMR (60 MHz) analysis of the reaction mixture showed that the $E:Z$ ratio of **29** is 50:50. Thin layer chromatography (SiO₂, CH₂Cl₂) gave (*E*)-**29** (46%) and (*Z*)-**29** (44%) as a yellow oil. (*E*)-**29**: IR (neat) 3000 (s), 2950 (m), 2255 (CN, w), 1750 (C=O, s), 1710 (C=O, s), 1690 (C=O, s), 1635 (s), 1460 (s), 1430 (m), 1370 (s), 1250 (s), 1125 (s), 1020 (s), 980 (s), 860 (s), 780 (m) cm⁻¹; ¹H NMR (CDCl₃, 60 MHz) δ 1.33 (t, J = 7.0 Hz, 3 H, OCH₂CH₃), 1.78 (s, 3 H, C(CN)CH₃), 2.32 (s, 3 H, COCH₃), 4.28 (q, J = 7.0 Hz, 2 H, OCH₂CH₃), 6.45 (d, J = 16.0 Hz, 1 H, CH=CHCOMe), 6.76 (d, J = 16.0 Hz, 1 H, CH=CHCOMe); HRMS calcd for C₁₀H₁₃NO₃ 195.0895, found 195.0887. (*Z*)-**29**: IR (neat) 3000 (s), 2255 (CN, m), 1740 (C=O, s), 1700 (m), 1620 (m), 1460 (m), 1410 (m), 1380 (m), 1250 (s), 1190 (s), 1135 (s), 1020 (s), 980 (m), 850 (m), 780 (m), 760 (m), 730 (m), 700 (m) cm⁻¹; ¹H NMR (CDCl₃, 60 MHz) δ 1.33 (t, J = 7.0 Hz, 3 H, OCH₂CH₃), 1.83 (s, 3 H, C(CN)CH₃), 2.27 (s, 3 H, COCH₃), 4.25 (q, J = 7.0 Hz, 2 H, OCH₂CH₃), 5.94 (d, J = 11.2 Hz, 1 H, CH=CHCOMe), 6.48 (d, J = 11.2 Hz, 1 H, CH=CHCOMe); HRMS calcd for C₁₀H₁₃NO₃ 195.0895, found 195.0895.

General Procedure for Diastereoselective Michael Reaction of cyano Esters. A mixture of cyano ester **30** (1.0 mmol), olefin (1.1 mmol), and RuH₂(PPh₃)₄ (0.03 mmol) in dry THF (0.25 mL) was stirred at -78 °C for 6 h under argon. The diastereomeric ratio of the product mixture of **31** and **32** was determined by ¹H NMR (500 MHz) analysis focused on the H² protons, which were observed as a diastereomeric pair of doublets. The mixture was purified by thin layer chromatography (SiO₂) to give the Michael adduct. The results are summarized in Table 3.

Methyl (3*R,4*S**)-2,4-Bis(methoxycarbonyl)-4-cyano-3-methyl-7-oxooctanoate (31a).** The relative stereochemical configuration of **31a** was established unequivocally by X-ray crystallographic analysis of crystals grown in diisopropyl ether (see supporting information). **31a**: mp 107.2 °C; IR (KBr) 2961 (w), 2317 (CN, w), 1740 (C=O, s), 1439 (m), 1377 (m), 1323 (m), 1286 (m), 1259 (m), 1209 (m), 1170 (m), 1124 (w), 1032 (m), 1095 (w), 1003 (w), 935 (w), 837 (w), 781 (w) cm⁻¹; ¹H NMR (CDCl₃, 270 MHz) δ 1.29 (d, J = 7.1 Hz, 3 H, C(CO₂Me)CO₂CH₃), 2.11–2.30 (m, 2 H, CH₂CH₂COMe), 2.17 (s, 3 H, COCH₃), 2.46 (ddd, J = 6.1, 10.0, 17.8 Hz, 1 H, CH₂CHCOMe), 2.71 (ddd, J = 6.1, 10.0, 17.8 Hz, 1 H, CH₂CHCOMe), 2.94 (dq, J = 5.1, 7.1 Hz, 1 H, CHCH₃), 3.58 (d, J = 5.1 Hz, 1 H, CH(CO₂Me)₂), 3.75 (s, 3 H, C(CO₂Me)CO₂CH₃), 3.77 (s, 3 H, C(CO₂CH₃)CO₂Me), 3.83 (s, 3 H, C(CN)CO₂CH₃); ¹³C NMR (CDCl₃, 67.9 MHz) δ 205.2 (COMe), 168.1 (C(CO₂Me)CO₂Me), 168.0 (C(CO₂Me)CO₂Me), 167.4 (C(CN)CO₂Me), 117.0 (CN), 53.5 (C(CO₂Me)₂), 53.1 (C(CN)CO₂Me), 52.8 (C(CO₂CH₃)CO₂Me), 52.4 (C(CO₂Me)CO₂CH₃), 52.3 (C(CN)CO₂CH₃), 39.0 (CH₂COMe), 38.6 (CHCH₃), 29.8 (COCH₃), 29.4 (CH₂CH₂COMe), 12.8 (CHCH₃). Anal. Calcd for C₁₅H₂₂NO₇: C, 54.87; H, 6.75; N, 4.27. Found: C, 54.95; H, 6.55; N, 4.16.

Ethyl (3*R,4*S**)-2,4-bis(ethoxycarbonyl)-4-cyano-3-methyl-7-oxooctanoate (31):** IR (neat) 3000 (s), 2250 (CN, w), 1740 (C=O, s), 1480 (s), 1450 (s), 1420 (s), 1380 (s), 1100 (s), 1030 (s), 900 (w), 860 (s), 765 (m) cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 1.27 (d, J = 7.1 Hz, 3 H, CHCH₃), 1.30 (t, J = 7.1 Hz, 3 H, C(CO₂Et)CO₂CH₂CH₃), 1.30 (t, J = 7.1 Hz, 3 H, C(CO₂CH₂CH₃)CO₂Et), 1.36 (t, J = 7.1 Hz, 3 H, C(CN)CO₂CH₂CH₃), 2.16 (ddd, J = 5.5, 10.5, 14.0 Hz, 1 H, CHCH₂COMe), 2.16 (s, 3 H, COCH₃), 2.24 (ddd, J = 4.8, 10.5, 14.0 Hz, 1 H, CHCH₂COMe), 2.47 (ddd, J = 5.5, 10.5, 17.9 Hz, 1 H, CH₂CHCOMe), 2.72 (ddd, J = 4.8, 10.5, 17.9 Hz, 1 H, CH₂CHCOMe), 2.93 (dq, J = 4.8, 7.1 Hz, 1 H, CHCH₃), 3.55 (d, J = 4.8 Hz, 1 H, CH(CO₂Et)₂), 4.15–4.26 (m, 4 H, C(CO₂Et)CO₂CH₂CH₃), 4.28 (dq, J = 1.8, 7.1 Hz, 1 H, C(CN)CO₂CH₂CH₃), 4.28 (dq, J = 1.8, 7.1 Hz, 1 H, C(CN)CO₂CH₂CH₃); ¹³C NMR (CDCl₃, 67.9 MHz) δ 205.4 (COMe), 167.7 (C(CO₂Et)CO₂Et), 167.1 (C(CN)CO₂Et), 117.1 (CN), 63.1 (C(CN)CO₂CH₂CH₃), 61.9 (C(CO₂CH₂CH₃)CO₂Et), 61.6 (C(CO₂Et)CO₂CH₂CH₃), 53.2 (C(CO₂Et)₂), 52.5 (C(CN)CO₂Et), 39.0 (CH₂COMe), 38.5 (CHCH₃), 29.9 (COCH₃), 29.3 (CH₂CH₂COMe), 13.89 (C(CO₂CH₂CH₃)CO₂Et), 13.85 (C(CO₂Et)CO₂CH₂CH₃), 13.8 (C(CN)CO₂CH₂CH₃), 12.7 (CHCH₃). Anal. Calcd for C₁₈H₂₇NO₇: C, 58.53; H, 7.31; N, 3.90. Found: C, 58.33; H, 7.31; N, 3.90.

Ethyl (3*R,4*S**)-2,4-bis(ethoxycarbonyl)-4,6-dicyano-3-methylhexanoate (31c):** IR (neat) 3000 (s), 2260 (CN, m), 1750 (C=O, s), 1480 (s), 1455 (s), 1400 (s), 1380 (s), 1100 (s), 1030 (s), 905 (w), 860 (m), 785 (w) cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) δ 1.28 (t, J = 7.1 Hz, 3 H, $\text{C}(\text{CO}_2\text{Et})\text{CO}_2\text{CH}_2\text{CH}_3$), 1.29 (d, J = 7.1 Hz, 3 H, CHCH_3), 1.31 (t, J = 7.1 Hz, $\text{C}(\text{CO}_2\text{CH}_2\text{CH}_3)\text{CO}_2\text{Et}$), 1.38 (t, J = 7.1 Hz, 3 H, $\text{C}(\text{CN})\text{CO}_2\text{CH}_2\text{CH}_3$), 2.28 (ddd, J = 5.5, 10.1, 13.7 Hz, 1 H, CHCH_2CN), 2.33 (ddd, J = 6.4, 9.5, 13.7 Hz, 1 H, CHCH_2CN), 2.44 (ddd, J = 6.4, 10.1, 16.7 Hz, 1 H, CH_2CHCN), 2.64 (ddd, J = 5.5, 9.5, 16.7 Hz, 1 H, CH_2CHCN), 2.95 (dq, J = 5.0, 7.1 Hz, 1 H, CHCH_3), 3.54 (d, J = 5.0 Hz, 1 H, $\text{CH}(\text{CO}_2\text{Et})_2$), 4.18–4.28 (m, 4 H, $\text{C}(\text{CO}_2\text{Et})\text{CO}_2\text{CH}_2\text{CH}_3$), 4.32 (dq, J = 2.5, 7.3 Hz, 1 H, $\text{C}(\text{CN})\text{CO}_2\text{CH}_2\text{CH}_3$), 4.33 (dq, J = 2.5, 7.3 Hz, 1 H, $\text{C}(\text{CN})\text{CO}_2\text{CH}_2\text{CH}_3$); ^{13}C NMR (CDCl_3 , 67.9 MHz) δ 167.6 ($\text{C}(\text{CN})\text{CO}_2\text{Et}$), 166.9 ($\text{C}(\text{CO}_2\text{Et})\text{CO}_2\text{CH}_2\text{CH}_3$), 166.8 ($\text{C}(\text{CO}_2\text{CH}_2\text{CH}_3)\text{CO}_2\text{Et}$), 117.4 (CH_2CN), 116.2 ($\text{C}(\text{CO}_2\text{Et})\text{CN}$), 63.9 ($\text{C}(\text{CN})\text{CO}_2\text{CH}_2\text{CH}_3$), 62.2 ($\text{C}(\text{CO}_2\text{CH}_2\text{CH}_3)\text{CO}_2\text{Et}$), 61.9 ($\text{C}(\text{CO}_2\text{Et})\text{CO}_2\text{CH}_2\text{CH}_3$), 53.1 ($\text{C}(\text{CO}_2\text{Et})_2$), 52.5 ($\text{C}(\text{CN})\text{CO}_2\text{Et}$), 38.7 (CHCH_3), 31.1 ($\text{CH}_2\text{CH}_2\text{CN}$), 14.0 (CH_2CN), 13.9 ($\text{CO}_2\text{CH}_2\text{CH}_3$), 12.9 (CHCH_3); HRMS calcd for $\text{C}_{17}\text{H}_{24}\text{N}_2\text{O}_6$ 352.1634, found 352.1579.

Ethyl (3*R,4*S**)-2,4-bis(ethoxycarbonyl)-4-cyano-3-methyl-7-oxo-7-phenylheptanoate (31d):** IR (neat) 3000 (s), 2250 (CN, w), 1750 (C=O, s), 1695 (s), 1590 (w), 1475 (m), 1455 (s), 1410 (w), 1400 (m), 1380 (s), 1360 (m), 1115 (s), 1100 (s), 1065 (m), 1030 (m), 970 (m), 860 (m), 745 (s), 690 (s), 665 (w) cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) δ 1.28 (t, J = 7.1 Hz, 3 H, $\text{C}(\text{CO}_2\text{Et})\text{CO}_2\text{CH}_2\text{CH}_3$), 1.31 (t, J = 7.1 Hz, 3 H, $\text{C}(\text{CO}_2\text{CH}_2\text{CH}_3)\text{CO}_2\text{Et}$), 1.34 (d, J = 7.1 Hz, 3 H, CHCH_3), 1.35 (t, J = 7.1 Hz, 3 H, $\text{C}(\text{CN})\text{CO}_2\text{CH}_2\text{CH}_3$), 2.38 (ddd, J = 5.7, 10.2, 14.0 Hz, 1 H, CHCH_2COPh), 2.42 (ddd, J = 5.0, 10.1, 14.0 Hz, 1 H, CHCH_2COPh), 3.00 (ddd, J = 5.7, 10.1, 17.4 Hz, 1 H, CH_2CHCOPh), 3.01 (dq, J = 5.0, 7.1 Hz, 1 H, CHCH_3), 3.27 (ddd, J = 5.0, 10.1, 17.4 Hz, 1 H, CH_2CHCOPh), 3.60 (d, J = 5.0 Hz, 1 H, $\text{CH}(\text{CO}_2\text{Et})_2$), 4.22 (dq, J = 7.3, 2.5 Hz, 1 H, $\text{C}(\text{CO}_2\text{CH}_2\text{CH}_3)\text{CO}_2\text{Et}$), 4.21 (dq, J = 7.3, 2.5 Hz, 1 H, $\text{C}(\text{CO}_2\text{CH}_2\text{CH}_3)\text{CO}_2\text{Et}$), 4.25 (dq, J = 7.3, 2.5 Hz, 2 H, $\text{C}(\text{CO}_2\text{Et})\text{CO}_2\text{CH}_2\text{CH}_3$), 4.25 (dq, J = 7.3, 2.5 Hz, 2 H, $\text{C}(\text{CO}_2\text{Et})\text{CO}_2\text{CH}_2\text{CH}_3$), 4.30 (dq, J = 2.3, 7.1 Hz, 2 H, $\text{C}(\text{CN})\text{CO}_2\text{CH}_2\text{CH}_3$), 4.30 (dq, J = 2.3, 7.1 Hz, 2 H, $\text{C}(\text{CN})\text{CO}_2\text{CH}_2\text{CH}_3$), 7.25–7.95 (m, 5 H, ArH); HRMS calcd for $\text{C}_{23}\text{H}_{29}\text{NO}_7$ 431.1944, found 431.1930.

Ethyl (3*R,4*S**)-2,4-bis(ethoxycarbonyl)-4-cyano-3-ethyl-7-oxo-7-phenylheptanoate (31e):** IR (neat) 2982 (s), 2245 (CN, w), 1742 (C=O, s), 1687 (m), 1599 (w), 1466 (m), 1369 (m), 1300 (m), 1238 (s), 1188 (m), 1157 (m), 1113 (m), 1030 (m), 744 (w), 690 (w) cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) δ 1.05 (t, J = 6.8 Hz, 3 H, CHCH_2CH_3), 1.24 (t, J = 7.2 Hz, 3 H, $\text{C}(\text{CO}_2\text{Et})\text{CO}_2\text{CH}_2\text{CH}_3$), 1.26 (t, J = 7.0 Hz, 3 H, $\text{C}(\text{CO}_2\text{CH}_2\text{CH}_3)\text{CO}_2\text{Et}$), 1.30 (t, J = 7.1 Hz, 3 H, $\text{C}(\text{CN})\text{CO}_2\text{CH}_2\text{CH}_3$), 1.56–2.08 (m, 2 H, CHCH_2CH_3), 2.08–2.65 (m, 2 H, CH_2CHCOPh), 2.65–3.27 (m, 2 H, CH_2COPh), 3.61 (d, J = 4.4 Hz, 1 H, $\text{CH}(\text{CO}_2\text{Et})_2$), 4.18 (q, J = 7.2 Hz, 2 H, $\text{C}(\text{CO}_2\text{Et})\text{CO}_2\text{CH}_2\text{CH}_3$), 4.21 (q, J = 7.0 Hz, 2 H, $\text{C}(\text{CO}_2\text{CH}_2\text{CH}_3)\text{CO}_2\text{Et}$), 4.26 (q, J = 7.1 Hz, 2 H, $\text{C}(\text{CN})\text{CO}_2\text{CH}_2\text{CH}_3$), 7.45–7.50 (m, 2 H, ArH (meta)), 7.56–7.60 (m, 1 H, ArH (para)), 7.93–7.98 (m, 2 H, ArH (ortho)); HRMS calcd for $\text{C}_{24}\text{H}_{31}\text{NO}_7$ 445.2101, found 445.2071. Anal. Calcd for $\text{C}_{24}\text{H}_{31}\text{NO}_7$: C, 64.70; H, 7.01; N, 3.14. Found: C, 65.57; H, 6.73; N, 3.32.

Ethyl (3*R,4*S**)-4-(*tert*-butoxycarbonyl)-4-cyano-2-(ethoxycarbonyl)-3-methyl-7-oxooctanoate (31f):** IR (neat) 2984 (m), 2243 (CN, w), 1736 (C=O, s), 1460 (m), 1394 (m), 1371 (s), 1302 (s), 1255 (s), 1226 (s), 1157 (s), 1095 (m), 1030 (m), 837 (w) cm^{-1} ; ^1H NMR (CDCl_3 , 270 MHz) δ 1.27 (t, J = 7.1 Hz, 3 H, $\text{C}(\text{CO}_2\text{Et})\text{CO}_2\text{CH}_2\text{CH}_3$), 1.30 (d, J = 7.3 Hz, 3 H, CHCH_3), 1.32 (t, J = 7.1 Hz, 3 H, $\text{C}(\text{CO}_2\text{CH}_2\text{CH}_3)\text{CO}_2\text{Et}$), 1.54 (s, 9 H, $\text{C}(\text{CH}_3)_3$), 2.09 (ddd, J = 5.4, 11.2, 13.8 Hz, 1 H, CHCH_2COMe), 2.18 (s, 3 H, COCH_3), 2.23 (ddd, J = 4.4, 11.2, 13.8 Hz, 1 H, CHCH_2COMe), 2.45 (ddd, J = 5.4, 11.2, 17.6 Hz, CHCOMe), 2.75 (ddd, J = 4.4, 11.2, 17.6 Hz, 1 H, CHCOMe), 2.88 (dq, J = 3.9, 7.3 Hz, 1 H, CHCH_3), 3.54 (d, J = 3.9 Hz, 1 H, $\text{CH}(\text{CO}_2\text{Et})_2$), 4.15–4.30 (m, 4 H, $\text{CO}_2\text{CH}_2\text{CH}_3$); ^{13}C NMR (CDCl_3 , 67.9 MHz) δ 205.6 (COMe), 168.0 ($\text{CO}_2\text{-}t\text{-Bu}$), 167.2 (CO_2Et), 166.7 (CO_2Et), 117.4 (CN), 85.1 ($\text{CO}_2\text{C}(\text{CH}_3)_3$), 62.0 ($\text{CO}_2\text{CH}_2\text{CH}_3$), 61.6 ($\text{CO}_2\text{CH}_2\text{CH}_3$), 53.1 ($\text{C}(\text{CN})\text{CO}_2\text{-}t\text{-Bu}$), 52.9 ($\text{C}(\text{CO}_2\text{Et})_2$), 39.1 (CHCH_3), 38.7 (CH_2COMe), 30.0 ($\text{CH}_2\text{CH}_2\text{COMe}$), 29.6 (COCH_3), 27.8 ($\text{C}(\text{CH}_3)_3$), 14.0 ($\text{CO}_2\text{CH}_2\text{CH}_3$), 13.9 ($\text{CO}_2\text{CH}_2\text{CH}_3$), 12.5 (CHCH_3). Anal. Calcd for $\text{C}_{20}\text{H}_{31}\text{NO}_7$: C, 60.44; H, 7.86; N, 3.52. Found: C, 60.16; H, 7.72; N, 3.60.

Ethyl (3*R,4*S**)-4-carbamoyl-4-cyano-2-(ethoxycarbonyl)-3-methyl-7-oxo-7-phenylheptanoate (31g):** IR (neat) 3420 (NH, s), 3000 (s),

2250 (CN, w), 1740 (C=O, s), 1685 (C=O, s), 1600 (m), 1475 (m), 1455 (s), 1420 (m), 1375 (s), 1280 (s), 1245 (s), 1220 (s), 1125 (s), 1095 (s), 1040 (s), 975 (m), 860 (w), 750 (s), 690 (m) cm^{-1} ; ^1H NMR (CDCl_3 , 270 MHz) δ 1.26 (t, J = 7.3 Hz, 3 H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 1.32 (t, J = 7.3 Hz, 3 H, CHCH_3), 2.30–2.50 (m, 2 H, $\text{CH}_2\text{CH}_2\text{CO}$), 2.90 (dq, J = 3.4, 7.3 Hz, 1 H, CHCH_3), 3.02–3.27 (m, 2 H, CH_2COPh), 3.64 (d, J = 3.4 Hz, 1 H, $\text{CH}(\text{CO}_2\text{Et})_2$), 4.22 (dq, J = 7.3, 12.4 Hz, 2 H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 4.24 (dq, J = 7.3, 17.6 Hz, 2 H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 7.43–7.99 (m, 5 H, ArH); ^{13}C NMR (CDCl_3 , 67.9 MHz) δ 197.5 (COPh), 168.6 (CONH_2), 167.8 (CO_2Et), 167.6 (CO_2Et), 136.3 (Ph (para)), 133.5 (Ph (ipso)), 128.7 (Ph (ortho)), 128.1 (Ph (meta)), 119.0 (CN), 62.0 ($\text{CO}_2\text{CH}_2\text{CH}_3$), 61.8 ($\text{CO}_2\text{CH}_2\text{CH}_3$), 53.2 ($\text{C}(\text{CO}_2\text{Et})_2$), 52.4 ($\text{C}(\text{CN})\text{CO}_2\text{Et}$), 38.7 (CHCH_3), 34.3 (CH_2COPh), 30.7 ($\text{CH}_2\text{CH}_2\text{COPh}$), 14.0 ($\text{CO}_2\text{CH}_2\text{CH}_3$), 13.9 ($\text{CO}_2\text{CH}_2\text{CH}_3$), 12.7 (CHCH_3).

Triton B-Catalyzed Reaction of 30 with Olefin. A mixture of 30 (1.0 mmol), olefin (1.1 mmol), and Triton B (0.01 mL) in 1,4-dioxane (0.25 mL) was stirred at room temperature for 24 h under argon. The reaction mixture was acidified with 2 N HCl (20 mL) and extracted with ether. The combined organic layers were washed successively with 2 N HCl solution, water, and saturated NaHCO_3 aqueous solution and dried over MgSO_4 . Removal of the solvent gave the Michael adduct as a colorless oil. The diastereomeric ratio of the product was determined by ^1H NMR analysis.

Ethyl 4-Cyano-4-(ethoxycarbonyl)-3-methyl-7-oxooctanoate (34). The $\text{RuH}_2(\text{PPh}_3)_4$ -catalyzed reaction of diethyl 2-cyano-3-methylpentanedioate (33, diastereomer ratio 50:50) with methyl vinyl ketone was carried out at -78°C . ^1H NMR (270 MHz) analysis of the reaction mixture showed that the diastereomeric ratio of 34 was 66:34. IR (neat) 3000 (m), 2255 (CN, w), 1740 (C=O, s), 1475 (m), 1450 (m), 1380 (m), 1255 (s), 1190 (s), 1105 (s), 1030 (s), 860 (m) cm^{-1} ; ^1H NMR (CDCl_3 , 60 MHz) δ 1.17 (d, J = 6.6 Hz, 3 H, CHCH_3), 1.27 (t, J = 7.2 Hz, 3 H, $\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_3$), 1.34 (t, J = 7.1 Hz, 3 H, $\text{C}(\text{CN})\text{CO}_2\text{CH}_2\text{CH}_3$), 2.18 (s, 3 H, COCH_3), 1.97–2.97 (m, 7 H, $\text{CH}_2\text{CH}_2\text{COMe}$, $\text{CH}(\text{Me})\text{CH}_2$), 4.21 (q, J = 7.2 Hz, 2 H, $\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_3$), 4.33 (q, J = 7.1 Hz, 2 H, $\text{C}(\text{CN})\text{CO}_2\text{CH}_2\text{CH}_3$).

General Procedure for the Ruthenium-Catalyzed Sequential Michael Reaction. A mixture of nitrile (1.0 mmol), dialkyl alkylidene-cyanomalonate (1.0 mmol), and $\text{RuH}_2(\text{PPh}_3)_4$ (0.03 mmol) in dry THF (0.25 mL) was stirred at room temperature for 2 h under argon. The solution was cooled to -78°C , and the second olefin (1.0 mmol) was added dropwise over a period of 1 min. The solution was stirred at -78°C for 6 h. After removal of the solvent, the residue was purified by thin layer chromatography (SiO_2) to give the Michael adduct. The diastereomeric ratio of the product was determined by ^1H NMR analysis.

Diethyl (1*S,2*R**,3*R**)-5-Acetyl-1-cyano-4-hydroxy-2-methyl-4-cyclohexene-1,3-dicarboxylate (35b).** To a solution of 31b (0.375 g, 1.02 mmol) in absolute ethanol (2 mL) was added a solution of sodium ethoxide in ethanol (2.5 M, 0.44 mL) at 0°C , and the mixture was stirred for 3 h. After usual workup, 35b (0.170 g, 52%) was obtained as a yellow oil: IR (neat) 2984 (s), 2247 (CN, w), 1740 (C=O, s), 1631 (w), 1466 (s), 1392 (s), 1369 (s), 1248 (s), 1182 (s), 1119 (s), 1026 (s), 949 (w), 912 (w), 856 (m), 806 (w) cm^{-1} ; ^1H NMR (CDCl_3 , 270 MHz) δ 1.11 (d, J = 6.3 Hz, 3 H, CHCH_3), 1.32 (t, J = 7.8 Hz, 3 H, $\text{CHCO}_2\text{CH}_2\text{CH}_3$), 1.38 (t, J = 7.1 Hz, 3 H, $\text{C}(\text{CN})\text{CO}_2\text{CH}_2\text{CH}_3$), 2.19 (s, 3 H, COCH_3), 2.72 (dq, J = 6.3, 11.7 Hz, 1 H, CHCH_3), 2.91 (dd, J = 1.5, 15.1 Hz, 1 H, $\text{C}(\text{CN})\text{CH}$), 3.05 (dd, J = 1.5, 15.1 Hz, 1 H, $\text{C}(\text{CN})\text{CH}$), 3.42 (dd, J = 1.5, 11.7 Hz, 1 H, CHCO_2Et), 4.28 (q, J = 7.1 Hz, 2 H, $\text{CHCO}_2\text{CH}_2\text{CH}_3$), 4.36 (dq, J = 2.0, 7.1 Hz, 2 H, $\text{C}(\text{CN})\text{CO}_2\text{CH}_2\text{CH}_3$), 15.8 (s, 1 H, OH); ^{13}C NMR (CDCl_3 , 67.9 MHz) δ 198.5 (C=O), 175.5 (C=COH), 169.5 (CO_2Et), 167.7 (CO_2Et), 116.6 (CN), 102.6 (C=COH), 63.5 ($\text{CO}_2\text{CH}_2\text{CH}_3$), 62.1 ($\text{CO}_2\text{CH}_2\text{CH}_3$), 53.4 ($\text{C}(\text{CN})\text{CO}_2\text{Et}$), 36.8 (CHCH_3), 34.2 ($\text{C}(\text{CN})\text{CH}_2$), 25.3 (CHCH_3), 15.9 (COCH_3), 14.2 ($\text{CO}_2\text{CH}_2\text{CH}_3$), 14.1 ($\text{CO}_2\text{CH}_2\text{CH}_3$); HRMS calcd for $\text{C}_{16}\text{H}_{21}\text{NO}_6$ 323.1369, found 323.1369.

***tert*-Butyl (1*S**,2*R**,3*R**)-5-Acetyl-1-cyano-3-(ethoxycarbonyl)-4-hydroxy-2-methyl-4-cyclohexene-1-carboxylate (35f).** To a solution of 31f (0.137 g, 0.35 mmol) in absolute ethanol (0.6 mL) was added sodium ethoxide in ethanol (2.0 M, 0.2 mL) at 0°C , and the mixture was stirred for 5 h. After usual workup, 35f (0.075 g, 62%) was obtained as a yellow oil: ^1H NMR (CDCl_3 , 60 MHz) δ 1.26 (d, J = 7.0 Hz, 3 H, CHCH_3), 1.30 (t, J = 7.0 Hz, 3 H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 1.55 (s, 9 H, $\text{CO}_2\text{C}(\text{CH}_3)_3$), 2.17 (s, 3 H, COCH_3), 2.16–2.85 (m, 1 H, CHCH_3),

2.85–3.17 (m, 2 H, C(CN)CH₂), 3.56 (d, $J = 11.6$ Hz, 1 H, CHCO₂-Et), 4.40 (q, $J = 7.0$ Hz, 2 H, CO₂CH₂CH₃), 15.90 (s, 1 H, C=COH); HRMS calcd for C₁₈H₂₅NO₆ 351.1682, found 351.1682.

Triethyl (2*S,3*S**,6*R**)-3-Cyano-6-hydroxy-2-methyl-1,1,3-cyclohexanetricarboxylate (36).** A mixture of **30b** (0.299 g, 1.00 mmol), acrolein (0.067 g, 1.19 mmol), and RuH₂(PPh₃)₄ (0.035 g, 0.03 mmol) in dry THF (0.25 mL) was stirred at -78 °C for 6 h under argon. ¹H NMR (500 MHz) analysis focused on H² protons showed that the diastereomeric ratio of **36** (2*S**,3*S**,6*R**):**37** (2*R**,3*S**,6*R**) was 95:5. After removal of the solvent, the residue was purified by thin layer chromatography (SiO₂, CHCl₃) to give **36** (0.191 g, 54%) as a yellow oil. **36**: IR (neat) 3520 (OH, s), 3000 (s), 2250 (CN, w), 1750 (C=O, s), 1455 (s), 1400 (s), 1380 (s), 1240 (s), 1135 (s), 1100 (s), 1080 (s), 1030 (s), 930 (m), 910 (w), 885 (s), 775 (w), 730 (w) cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 1.30 (t, $J = 7.1$ Hz, 3 H, OCH₂CH₃), 1.31 (t, $J = 7.1$ Hz, 3 H, OCH₂CH₃), 1.35 (t, $J = 7.1$ Hz, 3 H, OCH₂CH₃), 1.37 (d, $J = 7.1$ Hz, 3 H, CHCH₃), 1.93–2.00 (m, 2 H, H⁴(ax) and H⁵(eq)), 2.16–2.30 (m, 1 H, H³(ax)), 2.46 (ddd, $J = 12.1, 5.5, 4.8$ Hz, 1 H, H⁴(eq)), 2.92 (br. q, $J = 7.1$ Hz, 1 H, H²), 3.84 (br, 1 H, OH), 4.11 (br, 1 H, H⁶), 4.17 (dq, $J = 10.8, 7.0$ Hz, 1 H, OCHH), 4.25 (dq, $J = 7.1, 2.2$ Hz, 2 H, OCH₂), 4.25 (dq, $J = 7.1, 2.2$ Hz, 2 H, OCH₂), 4.27 (dq, $J = 7.2, 3.7$ Hz, 2 H, OCH₂), 4.33 (dq, $J = 10.9, 7.1$ Hz, 1 H, OCHH); ¹³C NMR (CDCl₃, 67.9 MHz) δ 170.0 (C=O), 169.1 (C=O), 167.2 (C=O), 119.7 (CN), 73.0 (C⁶OH), 62.8 (OCH₂), 62.5 (OCH₂), 61.9 (OCH₂), 61.8 (C¹), 46.5 (C³), 41.7 (C²), 29.7 (C⁴), 27.3 (C⁵), 14.5 (C²CH₃), 13.9 (CH₃), 13.8 (CH₃); HRMS calcd for C₁₇H₂₅NO₇ 355.1631; found 355.1640. **37**: IR (neat) 2984 (m), 2245 (CN, w), 1744 (C=O, s), 1466 (m), 1390 (m), 1259 (s), 1219 (s), 1138 (m), 1114 (m), 1060 (m), 1026 (m), 963 (w), 860 (w) cm⁻¹; ¹H NMR (CDCl₃, 270 MHz) δ 1.28 (t, $J = 7.3$ Hz, 3 H, OCH₂CH₃), 1.30 (d, $J = 7.3$ Hz, 3 H, CHCH₃), 1.32 (t, $J = 7.3$ Hz, 3 H, OCH₂CH₃), 1.33 (t, $J = 7.3$ Hz, 3 H, OCH₂CH₃), 1.82–1.99 (m, 1 H, H⁵(eq)), 2.10–2.22 (m, 2 H, H⁵(ax) and H⁴(eq)), 2.23–2.36 (m, 1 H, H⁴(ax)), 3.20 (q, $J = 7.3$ Hz, 1 H, CHCH₃), 3.25 (br, OH), 4.26 (q, $J = 7.3$ Hz, 4 H, OCH₂), 4.29 (q, $J = 7.3$ Hz, 2 H, OCH₂); ¹³C NMR (CDCl₃, 67.9 MHz) δ 170.7 (C=O), 168.1 (C=O), 167.0 (C=O), 119.6 (CN), 68.1 (C⁶OH), 62.8 (OCH₂), 62.2 (OCH₂), 61.7 (OCH₂), 60.3 (C¹), 47.0 (C³), 37.0 (C²), 27.2 (C⁴), 26.7 (C⁵), 13.9 (OCH₂CH₃), 13.8 (OCH₂CH₃), 13.7 (C²CH₃).

mer-Hydrido[(methoxycarbonyl)methyl]cyano[(methyl cyanoacetate)tris(triphenylphosphine)ruthenium(II) (41a). RuH(C₂H₄)(PPh₃)₂(PPh₂C₆H₄) (**4**) (0.116 g, 0.126 mmol) was treated with methyl cyanoacetate (0.639 mmol) in THF (1 mL) at room temperature for 4 h to give a yellow solution. Evolution of ethylene (2.73 mL STP, 97% Ru) was observed. After removal of the solvents, the residual brown solid was recrystallized from THF/hexane to give yellow crystals (0.106 g, 69%) containing two molecules of THF. mp 110–115 °C dec. Anal. Calcd for C₇₀H₇₁N₂O₆P₃Ru: C, 68.34; H, 5.82; N, 2.28. Found: C, 67.75; H, 5.34; N, 2.34. The structure of **41a** was unequivocally determined by X-ray structure analysis.¹² Molar electric conductivity $\Lambda = 0.015$ S cm² mol⁻¹ in THF at 25 °C.

Reaction of RuH₂(PPh₃)₄ (**3**) (0.0682 g, 0.0592 mmol) with methyl cyanoacetate (0.0296 mmol) in THF (3 mL) was carried out at room temperature for 7 h. Workup of the solution gave a yellow solid of **41a** (0.0503 g, 72%) which was identified by IR and NMR analysis.

mer-Hydrido[(ethoxycarbonyl)methyl]cyano[(ethyl cyanoacetate)tris(triphenylphosphine)ruthenium(II) (41b). Complex **4** (0.150 g, 0.164 mmol) was allowed to react with ethyl cyanoacetate (0.840 mmol) in THF (1 mL) at room temperature for 6 h to give a yellow solution. Ethylene (3.25 mL STP, 89% Ru) was detected. Addition of hexane gave yellow plates at room temperature. Recrystallization from THF/hexane gave yellow crystals (0.155 g, 80%) containing one molecule of THF: mp 120–121 °C dec. Anal. Calcd for C₆₈H₆₇N₂O₅P₃Ru: C, 68.85; H, 5.69; N, 2.36. Found: C, 68.51; H, 5.48; N, 2.60. $\Lambda = 0.006$ S cm² mol⁻¹ in THF at 25 °C.

Reaction of **3** (0.352 g, 0.305 mmol) with ethyl cyanoacetate (2.99 mmol) in THF (2 mL) was carried out at room temperature for 26 h. A considerable amount of ethyl cyanoacetate (162% Ru) was consumed in the reaction. Workup of the solution gave yellow solid of **41b** (0.160 g, 44%). In the reactions of **3**, hydrogen gas was detected. However, the amount of H₂ varied in each experiment between 1–36% Ru. Hydrogenation of ethyl cyanoacetate did not take place even in the presence of hydrogen. At present, complete determination of the fate

of the hydrides is unsuccessful, but at least a part of the hydrides was converted to hydrogen gas, giving the product.

mer-Hydrido[(butoxycarbonyl)methyl]cyano[(butyl cyanoacetate)tris(triphenylphosphine)ruthenium(II) (41c). Complex **4** (0.183 g, 0.200 mmol) was treated with butyl cyanoacetate (0.992 mmol) in THF (1 mL) at room temperature for 6 h to give a yellow solution. Ethylene (4.38 mL STP, 98% Ru) was evolved. After removal of the solvent in vacuo, the residual solid was washed with hexane. Recrystallization from THF/hexane gave yellow crystals (0.217 g, 93%): mp 138–139 °C dec. Anal. Calcd for C₆₈H₆₇N₂O₄P₃Ru: C, 69.79; H, 5.77; N, 2.39. Found: C, 70.77; H, 5.71; N, 2.57. $\Lambda = 0.006$ S cm² mol⁻¹ in THF at 25 °C.

mer-Hydrido(2,4-pentanedionato)tris(triphenylphosphine)ruthenium(II) (42a). 2,4-Pentanedione (0.215 mmol) was added to a toluene solution (3 mL) of **4** (0.156 g, 0.170 mmol) at room temperature, and the solution was stirred for a day to give a homogeneous brown solution. Addition of hexane and cooling to -20 °C gave yellow needles which were washed with hexane (0.111 g, 66%): mp 220 °C dec. Anal. Calcd for C₅₉H₅₃O₂P₃Ru: C, 71.72; H, 5.41. Found: C, 71.36; H, 5.84.

Reaction of **3** (0.0183 g, 0.0159 mmol) with 2,4-pentanedione (0.048 mmol) in C₆D₆ for 2 days gave **42a** in ca. 100% yield. A small amount of hydrogen gas was detected but the amount was not measured. The hydrogenation product of 2,4-pentanedione (4-hydroxy-2-pentanone) was also detected in 80% yield by ¹H NMR analysis.

mer-Hydrido(dimethyl malonato)tris(triphenylphosphine)ruthenium(II) (42b). Dimethyl malonate (0.271 mmol) was added to a toluene solution (3 mL) of **4** (0.166 g, 0.181 mmol) at room temperature, and the solution was stirred for 18 h to give pale yellow precipitates. After filtration, the precipitates were washed with hexane. Recrystallization from toluene/hexane gave yellow fine needles (0.0384 g, 21%): mp 213–216 °C dec. Anal. Calcd for C₅₃H₅₃O₄P₃Ru: C, 69.47; H, 5.24. Found: C, 69.59; H, 5.60.

mer-Hydrido(methyl acetoacetato)tris(triphenylphosphine)ruthenium(II) (42c). Methyl acetoacetate (0.0240 mmol) was added to a C₆D₆ solution (0.3 mL) of **4** (0.022 g, 0.0240 mmol) at room temperature. After 18 h, ¹H NMR analysis showed the formation of **42c**. This complex is characterized by spectroscopy, consisting of two configurational isomers (see text and Table 4).

Hydrido[(methoxycarbonyl)methyl]cyano[dicarbonylbis(triphenylphosphine)ruthenium(II) (44a). A C₆D₆ solution (0.3 mL) of **41a** (0.0146 g, 0.0119 mmol) in the NMR tube was degassed. Then, carbon monoxide (1 atm) was introduced. After 1 h a pale yellow homogeneous solution was obtained. Formation of an isomeric mixture of **44a** (94%) was confirmed and free methyl cyanoacetate (103%) was detected by ¹H NMR analysis. ³¹P{¹H} NMR showed the presence of an equimolar amount of free PPh₃ in solution. Complex **44a** was characterized by spectroscopic methods (Table 4). ³¹P{¹H} NMR (toluene-*d*₈, external 85% H₃PO₄) isomer A: δ 39.50 (s), isomer B: δ 40.48 (s).

Hydrido[(ethoxycarbonyl)methyl]cyano[dicarbonylbis(triphenylphosphine)ruthenium(II) (44b). Carbon monoxide (1 atm) was introduced into a THF solution (2 mL) of **41b** (0.131 g, 0.110 mmol). The solution was stirred at room temperature for 20 h to give a pale yellow homogeneous solution. After removal of all the volatile compounds, the residual solid was recrystallized from THF/hexane to give crystals of an isomeric mixture of **44b** (0.0367 g, 42%): mp 215–216 °C dec. Anal. Calcd for C₄₃H₃₇N₂O₄P₂Ru: C, 64.55; H, 4.72; N, 1.68. Found: C, 64.98; H, 4.69; N, 1.76. $\Lambda = 0.005$ S cm⁻¹ mol⁻¹. Complex **44b** was characterized by spectroscopic methods (Table 4). ³¹P{¹H} NMR (toluene-*d*₈, external 85% H₃PO₄) isomer A: δ 39.31 (s), isomer B: δ 40.27 (s).

Reaction of 41b with Ethyl Cyanoacetate-*d*₂. To a solution of **41b** (6.2 mg, 0.0052 mmol) in C₆D₆ was added ethyl cyanoacetate-*d*₂ (0.0147 mmol), which was prepared by the reaction of ethyl cyanoacetate with deuterium oxide in THF (yield 58%, deuterium content at methylene protons was 79%). The solution was left at room temperature for 24 h. ¹H NMR analysis of the solution revealed that 49% of the methine proton and 65% of the methylene protons were deuterated, while no hydride was deuterated under the reaction conditions.

Protonolysis of 41a with Hydrogen Chloride. Hydrogen chloride gas (0.81 mmol) was added to a THF solution (1 mL) of **41a** (0.0317

g, 0.0257 mmol), and the solution was stirred for 19 h at room temperature to give a homogeneous red solution. A quantitative amount of hydrogen gas (0.60 mL STP, 104% Ru) was evolved, and methyl cyanoacetate (0.0320 mmol, 124% Ru) was detected by GLC analysis. After removal of the solvent in vacuo, the residual red solid was recrystallized from THF/hexane to afford red crystals of $\text{Ru}_2\text{Cl}_4(\text{NCCH}_2\text{COOMe})(\text{PPh}_3)_4$ (**43a**) (0.0120 g, 60%); mp 250–251 °C; IR (KBr) 2269, 1753 cm^{-1} . Anal. Calcd for $\text{C}_{80}\text{H}_{73}\text{NO}_3\text{Cl}_4\text{P}_4\text{Ru}_2$: C, 61.42; H, 4.70; N, 0.90; Cl, 9.07. Found: C, 61.81; H, 5.06; N, 1.12; Cl, 9.89.

Protonolysis of 41b with Hydrogen Chloride. Hydrogen chloride gas (0.81 mmol) was added to a THF solution (1 mL) of **41b** (0.0388 g, 0.0327 mmol), and the solution was stirred for 21 h at room temperature to give a homogeneous red solution. A quantitative amount of hydrogen gas (0.58 mL STP, 79% Ru) was evolved, and ethyl cyanoacetate (0.0419 mmol, 128% Ru) was detected by GLC analysis. After removal of the solvent in vacuo, the residual yellow brown solid was recrystallized from THF/hexane to afford red crystals of $\text{Ru}_2\text{Cl}_4(\text{NCCH}_2\text{COOEt})(\text{PPh}_3)_4 \cdot \text{THF}$ (**43b**) (0.0232 g, 90%); mp 223–224 °C; IR (KBr) 2269, 1747 cm^{-1} . ^1H NMR spectrum of the crystals of **43b** indicated the presence of one THF molecule in **43b**; ^1H NMR (CDCl_3 , 200 MHz) δ 1.15 (t, J = 7.4 Hz, Me), 2.97, 3.10 (AB quartet, J = 18.4 Hz, CH_2), 4.12 (q, J = 7.4 Hz, OCH_2), 6.8–8.3 (m, PPh_3); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , external 85% H_3PO_4) δ 51.01 (d, J = 37.7 Hz) 47.46 (d, J = 29.1 Hz), 47.25 (d, J = 37.7 Hz), 44.29 (d, J = 29.1 Hz). Anal. Calcd for $\text{C}_{81}\text{H}_{75}\text{NO}_3\text{Cl}_4\text{P}_4\text{Ru}_2$: C, 61.64; H, 4.79; N, 0.89; Cl, 8.99. Found: C, 61.17; H, 5.00; N, 0.95; Cl, 9.54.

Protonolysis of 44b with Hydrogen Chloride. Hydrogen chloride gas (1.62 mmol) was added to a THF solution (1 mL) of **44b** (0.156 g, 0.197 mmol), and the solution was stirred for 19 h at room temperature to give a red homogeneous solution. Hydrogen gas (1.60 mL STP, 36% Ru) was evolved, and ethyl cyanoacetate (0.266 mmol, 135% Ru) was detected by GLC analysis. After removal of the solvent in vacuo, the residual colorless solid was recrystallized from THF/hexane to afford colorless crystals of *cis*- $\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2$ (0.0375 g, 25%); IR (KBr) 2042, 1978, (CHCl_3) 2059, 1996 cm^{-1} . Anal. Calcd for $\text{C}_{38}\text{H}_{30}\text{O}_2\text{Cl}_2\text{P}_2\text{Ru}$: C, 60.05; H, 4.02. Found: C, 60.01; H, 4.07.

Reaction of 41a or 41b with Methyl Iodide. Typically, methyl iodide (0.0225 mmol) was added to a C_6D_6 solution (0.3 mL) of **41a** (0.0112 g, 0.0091 mmol), and the solution was allowed to stand for 6 h at room temperature to give a homogeneous purple solution. Methyl cyanoacetate (0.0764 mmol, 84% Ru) and methyl 2-cyanopropanoate (0.0875 mmol, 96% Ru) were detected by ^1H NMR analysis. The resulting ruthenium product was found to be $\text{RuHI}(\text{PPh}_3)_3$ ⁴⁰ (8.8 mg, 95%). Similarly, the reaction of **41b** (0.0927 g, 0.0781 mmol) with methyl iodide (0.0964 mmol) in THF (2 mL) at room temperature for 4 h gave ethyl cyanoacetate (67% Ru) and ethyl 2-cyanopropanoate (0.0952 mmol, 122% Ru) along with $\text{RuHI}(\text{PPh}_3)_3$ (28%). IR (KBr): 2032 (ν_{RuH}) cm^{-1} ; ^1H NMR (C_6D_6 , 200 MHz): δ -14.6 (q, J = 24.5 Hz).

Reaction of 42a with Methyl Iodide. Methyl iodide (0.049 mmol) was added to a C_6D_6 solution (0.3 mL) of **42a** (9.8 mg, 0.0099 mmol), but no reaction took place after at least 10 h at room temperature. After 1 week a trace amount of methane was released, and in solution 2,4-pentanedione was detected in 48% yield. Colorless crystals were also formed during the reaction and were identified as methyltriphenylphosphonium iodide by its IR spectrum. Yield was not measured.

Reaction of 41a, 41b, 42a, or 44b with Benzaldehyde. Benzaldehyde (0.010 mmol) was added to a THF solution of **41b** (5.0 mg, 0.0020 mmol), and the solution was stirred at room temperature. The solution was periodically analyzed by GLC. After 1 h, benzaldehyde was consumed in 110% yield per mol of **41b**, and product **7** was detected in 8% yield. The yield of the latter gradually increased to 40% in 10 h. Addition of ethyl cyanoacetate to the resulting solution increased the yield of **7** to 79%.

The reaction of benzaldehyde (0.0139 mmol) with **41b** (7.0 mg, 0.0059 mmol) in C_6D_6 was monitored by measuring the NMR spectra periodically. After 7 days, product **7** was detected (0.00953 mmol, 161% Ru). The following reactions were performed analogously. From **41a** (6.3 mg, 0.0051 mmol) and benzaldehyde (0.012 mmol), 0.0055 mmol (108%) of (*E*)-methyl 2-cyano-3-phenyl-2-propenoate was obtained after 6 days. From **44b** (13.1 mg, 0.0165 mmol) and

benzaldehyde (0.325 mmol), 0.0129 mmol (78%) of **7** was obtained after 7 days. Complex **42a** did not react at all with benzaldehyde at room temperature.

Reaction of 41b or 44b with Acrylonitrile. Acrylonitrile (1.53 mmol) was added to a THF solution of complex **41b** (0.171 g, 0.144 mmol), and the solution was stirred for 18 h at room temperature. After removal of volatile compounds in vacuo, the residue was extracted with diethyl ether. Dryness of the solution gave ethyl 2-(2'-cyanoethyl)-2,4-dicyanobutanoate (**17**) (0.0650 mmol, 45% Ru). From **44b** (0.0192 g, 0.0242 mmol) and acrylonitrile (0.107 mmol), no product **17** was detected after a week.

Catalytic Aldol and Michael Reactions Promoted by Ruthenium Enolate Complexes. Ethyl cyanoacetate (0.654 mmol) was added to a solution of the catalyst (1–6 mol %) in THF (1.0 mL) under a nitrogen atmosphere. Then, benzaldehyde (1.1–1.2 equiv) was added using a microsyringe. After the reaction, the solution was evaporated to dryness and the residual oil was dissolved in C_6D_6 . The yields of **7** were determined by ^1H NMR analysis using an internal standard (dioxane). The results with various catalysts are as follows: **3** (52%), **4** (67%), **41b** (57%), **44b** (26%), PPh_3 (6%). The reaction of ethyl cyanoacetate with acrylonitrile (2.2–2.3 equiv) was carried out under similar reaction conditions. The yields of **17** are determined by ^1H NMR analysis. The results are as follows: **3** (86%), **4** (100%), **41b** (90%), **44b** (59%).

Kinetics. A settled amount of catalyst and ethyl cyanoacetate were placed in a 20 mL Schlenk tube under nitrogen and dissolved in THF (5.00 mL). Dibenzyl was added as an internal standard, and the solution was kept at 50 ± 1 °C by a thermostatted oil bath. Benzaldehyde was added by a microsyringe to start the reaction. The amounts of benzaldehyde employed were always smaller than one-tenth of ethyl cyanoacetate to ignore the concentration change of ethyl cyanoacetate during the reaction. Yields of **7** were estimated periodically by GLC using a PEG-20M capillary column. Though the reactions finally proceeded to 80–90% yields in most of the reactions, saturation of the time–yield curve was observed when the concentrations of the catalysts were very small. First-order plots of the reactions gave straight lines at least in the initial 20–50% of the reactions, where the first-order rate constants were estimated.

X-ray Structure Analysis of 41b. A crystal suitable for X-ray analysis was sealed in a thin glass capillary under nitrogen. Intensity data were collected at room temperature on a Rigaku AFC-SR four-circle diffractometer. The ω – 2θ data collection technique was used, and 15947 data were collected to a maximum 2θ of 50°. Absorption corrections were not applied. The structure was solved by a heavy atom method. The non-hydrogen atoms except for C(23), C(46), C(48), C(53), C(57), and C(58) were refined anisotropically. The structure was refined by full matrix least-squares techniques using the teXsan crystallographic software package. One THF molecule included in the crystal was not determined because of its high disorder of the atoms. Hydrogens were included in the calculation but they were not refined. The final R (R_w) factor is 9.9 (9.9)% for 5892 reflections ($|F_o| > 5\sigma|F_o|$), where $R = \sum[|F_o| - |F_c|] / \sum |F_o|$ and $R_w = \{\sum w[|F_o| - |F_c|]^2\} / \{\sum w|F_o|^2\}^{1/2}$. The highest peak in the final difference Fourier map had a height of 1.04 $\text{e}/\text{\AA}^3$. The structure factor table, final positional data, iso and anisotropic thermal parameters, bond distances and lengths with F_o/F_c Table are available as the supporting information.

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Supporting Information Available: Crystal structure data for **31a** and **41b** including the final positional data, iso- and anisotropic thermal parameters, and bond distances and lengths (29 pages); tables of observed and calculated structure factors (44 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.