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Synthesis of *N*-bonded enolatoruthenium(II) by oxidative addition of alkyl cyanocarboxylate to a ruthenium(0) complex

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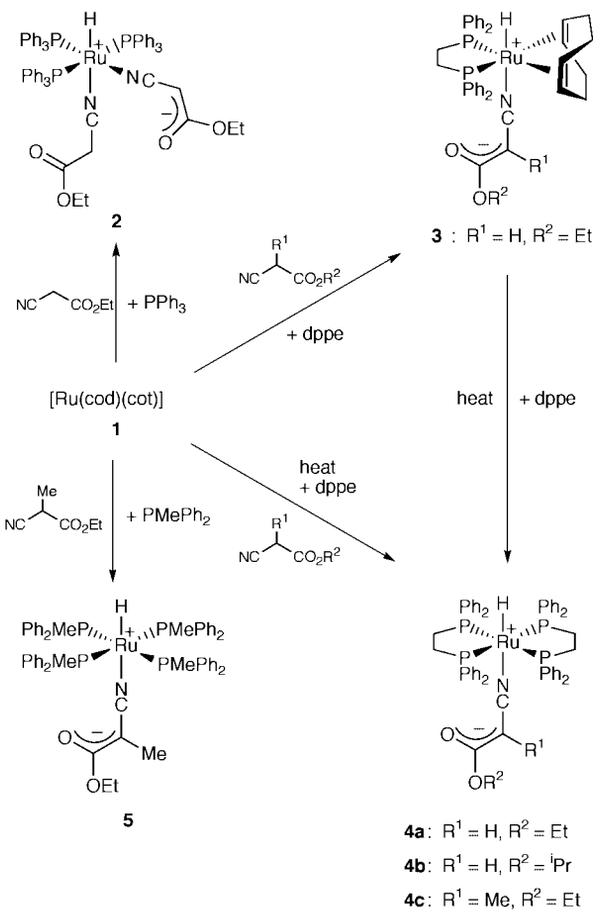
Reaction of a zero-valent ruthenium complex [Ru(cot)(cod)] **1** (cod = 1,5-cyclooctadiene; cot = 1,3,5-cyclooctatriene) with alkyl cyanoacetate in the presence of mono- and bi-dentate tertiary phosphines gave a series of hydrido(enolato)-ruthenium(II) complexes: *mer*-[RuH(NCCHCO$_2$Et)(NCCH$_2$CO$_2$Et)(PPh$_3$)$_3$] **2**; *trans*-[RuH(NCCHCO$_2$Et)(cod)-(dppe)] **3** (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$); *trans*-[RuH(NCCR^{1}CO$_2$R^2)(dppe)$_2$] (R^1 = H, R^2 = Et **4a**: or Pr^i **4b**; R^1 = Me, R^2 = Et **4c**) and *trans*-[RuH(NCCMeCO$_2$Et)(PMePh$_2$)$_4$] **5**. The molecular structure of **3** shows that the enolato ligand co-ordinates to the ruthenium centre *via* the cyano group in an octahedral geometry. These hydrido-(enolato)ruthenium(II) complexes catalyse Michael and Knöevenagel reactions under neutral and mild conditions.

Introduction

Transition-metal enolates have attracted considerable interest in relation to organic syntheses, since they are capable of providing regio-, chemo- and stereo-selective products under ambient conditions.[1–9] For example, Murahashi and co-workers[2,6] reported that *cis*-[RuH$_2$(PPh$_3$)$_4$] catalysed chemoselective aldol-type and Michael reactions, where nitriles exclusively react with electrophiles while 1,3-dicarbonyl compounds remained unreacted regardless of their pK_a values. We have independently isolated the zwitterionic *N*-bonded enolatoruthenium(II) complex *mer*-[RuH(NCCHCO$_2$R)(NCCH$_2$CO$_2$R)(PPh$_3$)$_3$] by the reaction of *cis*-[RuH$_2$(PPh$_3$)$_4$] or [RuH(C$_2$H$_4$){P(C$_6$H$_4$)Ph$_2$}-(PPh$_3$)$_2$] with alkyl cyanoacetate, which acts as an active key intermediate for catalytic aldol-type and Michael reactions.[3,6] Higher reactivity of the zwitterionic enolatoruthenium(II) complex toward electrophiles such as benzaldehyde and acrylonitrile than the chelating enolatoruthenium(II) species derived from 1,3-dicarbonyls is found to be responsible for Murahashi's chemoselectivity. Thus, the structure–reactivity relationship of the isolated enolatoruthenium complexes is considered to be very important to create new transition metal enolate catalysts. In this context, the supporting ligand is believed to play an important role in controlling the structure and reactivity of the enolato ligand. For example, addition of Ph$_2$PCH$_2$CH$_2$PPh$_2$ (dppe) to Murahashi's catalyst enhanced its activity.[2] The complexes [Ru(cod)(cot)] **1** (cod = 1,5-cyclooctadiene; cot = 1,3,5-cyclooctatriene) are known to be versatile ruthenium(0) starting materials for preparing various complexes by simple ligand exchange reactions.[10] We report the synthesis of *N*-bonded enolatoruthenium(II) complexes by oxidative addition of alkyl cyanoacetate to these ruthenium(0) complexes in the presence of PPh$_3$, dppe and PMePh$_2$ under ambient conditions, along with their catalytic Knöevenagel and Michael reactions.



Scheme 1

Results and discussion

Synthesis and molecular structure of *N*-bonded enolatoruthenium(II) complexes

Reaction of the zero-valent ruthenium complex [Ru(cod)-(cot)] **1** with ethyl cyanoacetate and PPh$_3$ at room temperature produced the enolatoruthenium(II) complex *mer*-[RuH-(NCCHCO$_2$Et)(NCCH$_2$CO$_2$Et)(PPh$_3$)$_3$] **2** as light yellow cubes in 45% yield (Scheme 1). All spectroscopic data are identical to those of **2** prepared by the method starting from *cis*-[RuH$_2$(PPh$_3$)$_4$] or [RuH(C$_2$H$_4$)(P(C$_6$H$_4$)Ph$_2$)(PPh$_3$)$_2$].[3,6] This result indicates that oxidative addition of ethyl cyanoacetate to ruthenium(0) does occur to give the *N*-bound enolatoruthenium(II) complex **2**.

Encouraged by this result, we attempted to prepare a series of enolatoruthenium(II) complexes with some tertiary phosphines. Reaction of **1** with ethyl cyanoacetate in the presence of 1 equivalent of dppe at room temperature resulted in the form-

Table 1 Selected bond distances (Å) and angles (°) of [RuH(NC-$CHCO_2Et$)(cod)(dppe)]·0.5 C_6H_6 **3**·0.5 C_6H_6

Ru(1)–P(1)	2.311(1)	Ru(1)–P(2)	2.309(1)
Ru(1)–N(1)	2.158(2)	Ru(1)–C(6)	2.261(3)
Ru(1)–C(7)	2.259(4)	Ru(1)–C(10)	2.256(4)
Ru(1)–C(11)	2.250(3)	N(1)–C(1)	1.146(4)
O(1)–C(3)	1.205(4)	O(2)–C(3)	1.376(4)
C(1)–C(2)	1.404(5)	C(2)–C(3)	1.390(5)
C(4)–C(5)	1.466(7)	C(6)–C(7)	1.390(5)
C(6)–C(13)	1.511(5)	C(7)–C(8)	1.511(6)
C(8)–C(9)	1.502(5)	C(8)–C(9)	1.502(5)
C(9)–C(10)	1.526(5)	C(10)–C(11)	1.383(5)
C(11)–C(12)	1.519(5)	C(12)–C(13)	1.513(5)
C(14)–C(15)	1.534(5)		
P(1)–Ru(1)–P(2)	83.42(3)	P(1)–Ru(1)–N(1)	84.63(7)
P(2)–Ru(1)–N(1)	87.09(7)	Ru(1)–N(1)–C(1)	171.0(3)
C(3)–O(2)–C(4)	120.0(3)	C(1)–C(2)–C(3)	120.3(3)
C(2)–C(3)–O(1)	128.1(4)	C(2)–C(3)–O(1)	128.1(4)
C(2)–C(3)–O(2)	119.8(3)	O(1)–C(3)–O(2)	112.0(3)
C(7)–C(6)–C(13)	122.3(4)	C(6)–C(7)–C(8)	127.4(3)
C(7)–C(8)–C(9)	115.9(3)	C(8)–C(9)–C(10)	115.8(6)
C(9)–C(10)–C(11)	124.6(3)	C(10)–C(11)–C(12)	125.5(3)
C(11)–C(12)–C(13)	114.7(3)	C(6)–C(13)–C(12)	117.2(3)

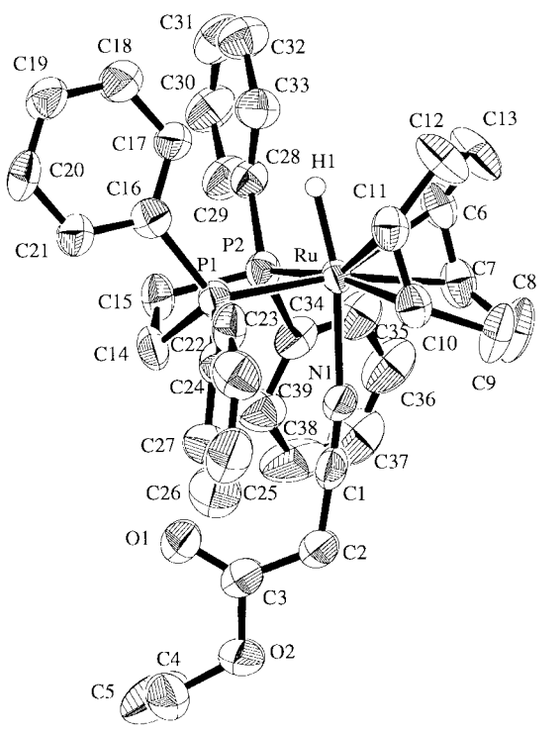


Fig. 1 An ORTEP drawing of [RuH(NCCHCO$_2$Et)(cod)(dppe)] **3**. Hydrogen atoms are omitted for clarity. Ellipsoids represent 50% probability.

ation of yellow crystals of *trans*-[RuH(NCCHCO$_2$Et)(cod)-(dppe)] **3** in 33% yield, which was characterised by structure analysis, IR and NMR spectroscopies, and elemental analysis. Light yellow cubes of compound **3**·0.5C_6H_6 suitable for X-ray crystallography were obtained from a mixture of benzene and hexane. The ORTEP[11] drawing is depicted in Fig. 1, and selected bond distances and angles are given in Table 1.

The overall structure is best regarded as an octahedron, where the enolato and hydrido ligands co-ordinate in the *trans* configuration and the cod and the dppe ligands lie on the equatorial plane. In accord with the structure of **2**,[3,6] the enolato group binds to ruthenium through the cyano group. The short N(1)–C(1) distance (1.146 Å) with almost linear Ru(1)–N(1)–C(1) (171.0°) indicates that the triple bond character of N(1)–C(1) remains intact. The relatively short C(2)–C(3) distance [1.390(5) Å], slightly long O(1)–C(3) [1.205(4) Å], and bond angles C(1)–C(2)–C(3) [120.3(3)°] and O(1)–C(3)–C(2) [128.1(4)°] support the contribution of an oxo π-allyl structure to the C(2)–C(3)–O(1) linkage. Although complex **2**,[6] the methyl ester analogue of **2**[3] and the related [Re(NCCHCO$_2$-Et)(NCCH$_2$CO$_2$Et)(PMe$_2$Ph)$_4$][4b] are found to have an intramolecular hydrogen bond between the enolato and the co-ordinated ester ligands, neither an intra- nor inter-molecular hydrogen bond has been found for **3**.

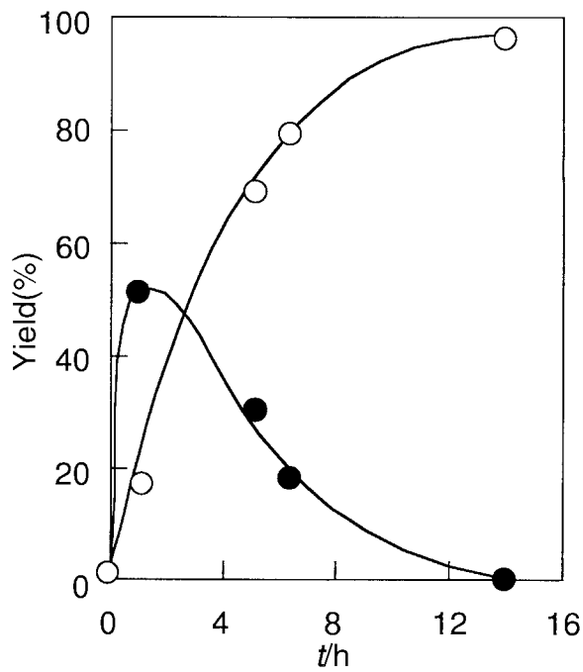


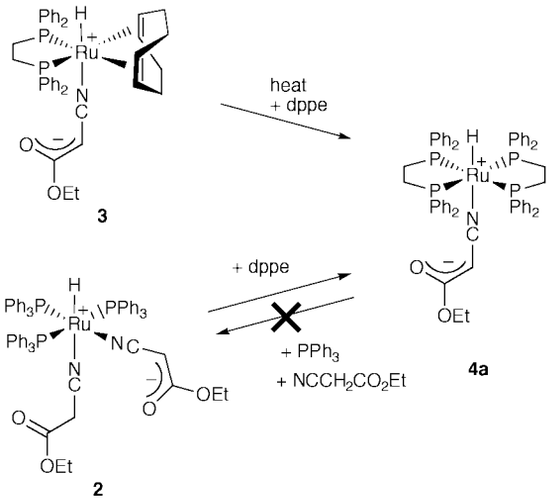
Fig. 2 Time–yield curves for formation of complexes **3** (●) and **4a** (○) in the reaction of **1** with ethyl cyanoacetate in the presence of dppe in benzene-d_6 at 60 °C.

Consistently, the IR spectrum of compound **3** shows characteristic absorption bands at 2180 and 2061 cm^{-1} assignable to ν(CN) and ν(Ru–H), respectively. An intense band at 1610 cm^{-1} is due to ν(C=O) of the enolato ligand. The ^{1}H NMR spectrum shows a triplet at δ −10.00 (J_{PH} = 20.2 Hz) due to the hydride ligand coupled to two equivalent P nuclei. Two broad signals at δ 2.3 and 3.4 are due to the aliphatic and olefinic protons of the cod ligand. A triplet at δ 1.47, a quartet at δ 4.62 and a singlet at δ 3.69 are assignable to the methyl, methylene and methine protons of the enolato ligand, where the methine proton has no coupling with P nuclei. These spectroscopic data suggest that the *N*-bonded enolate structure is kept in **3** in solution and the alternative *C*-bonded enolate is excluded.

When the reaction of complex **1** with ethyl cyanoacetate was performed in the presence of 2 equivalents of dppe at 55 °C for 32 h a similar ruthenium enolate complex *trans*-[RuH-(NCCHCO$_2$Et)(dppe)$_2$] **4a** having two dppe ligands was obtained. The ^{1}H NMR spectrum shows a quintet at δ −16.27 (J_{PH} = 18.31 Hz) which is assignable to the hydride ligand coupled to four equivalent P nuclei. The peaks at δ 1.47(t), 4.62(q) and 3.45(s) are assignable to the methyl, methylene and methine protons of the enolato ligand, respectively. The IR spectrum shows characteristic bands at 2179, 1953, and 1603 cm^{-1}, which are assigned as ν(CN), ν(Ru–H), and ν(CO), respectively. Analogously to **3**, the enolato ligand would also bind to the ruthenium through the cyano group.

While complex **4a** was obtained by the reaction of **1** with only twice the amount of dppe and ethyl cyanoacetate at 55 °C, **3** was exclusively formed at room temperature even in the presence of an excess of dppe. The time-course curve for the reaction of **1** with dppe and ethyl cyanoacetate at 60 °C is shown in Fig. 2, indicating a typical successive reaction pattern *via* **3**.

Consistently, the reaction of **3** with 1 equivalent of dppe at 50 °C in benzene-d_6 resulted in the facile formation of **4a** by releasing 1,5-cod (yield: 50% for 22 h, 100% for 118 h) (Scheme 2).

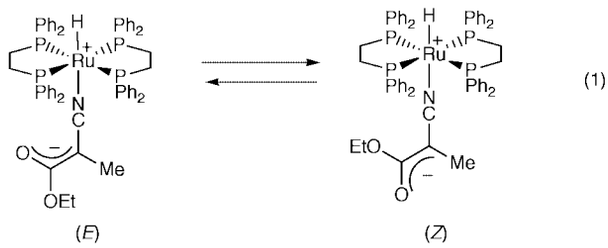


Scheme 2

Complex **4a** was also derived by ligand exchange of **2** with 2 equivalents of dppe in benzene-d_6 even at room temperature, by releasing PPh_3 and ethyl cyanoacetate (yield: 63% for 1 h, 82% for 3 h, 82% for 14 h). However, treatment of **4a** with PPh_3 at room temperature gave no reaction. These results are reflections of the strong co-ordination ability of the dppe ligand.

More detailed information about the oxidative addition of ethyl cyanoacetate to ruthenium(0) was obtained from the following experiment. Treatment of complex **1** with $NCCD_2$-CO_2Et (90% deuteriated) in the presence of 2 equivalents of dppe at 50 °C in benzene-d_6 resulted in the formation of *trans*-[RuD(NCCDCO$_2$Et)(dppe)$_2$] **4a**-d_2, where 80% of the hydride and the methine proton were deuteriated. The IR spectrum shows a new band at 1329 cm^{-1} assignable to ν(Ru–D). This fact indicates that the hydride ligand originated on the α-methylene protons of ethyl cyanoacetate, showing formal oxidative addition of the C–H bond to ruthenium(0). Although Chaudret and his co-workers[12] reported scrambling between Ru–H and protons of cyclo-olefins in [RuH(cod)(cot)][BF_4], such a process is negligible in our system.

The isopropyl analogue *trans*-[RuH(NCCHCO$_2$Pr^i)(dppe)$_2$] **4b** was also obtained in a similar way (see below). When ethyl 2-cyanopropionate was employed in this reaction with dppe or $PMePh_2$, *trans*-[RuH(NCCMeCO$_2$Et)(dppe)$_2$] **4c** and *trans*-[RuH(NCCMeCO$_2$Et)($PMePh_2$)$_4$] **5** were obtained, respectively. Of particular interest is that two sets of hydride and enolato ligands are observed for these complexes (see Experimental section). As a typical example, the ^{1}H NMR spectrum of **5** has two overlapped quintets at δ −15.32 (J_{PH} = 21 Hz) and −15.27 (J_{PH} = 21 Hz) in 2:1 ratio suggesting the presence of two hydride ligands coupled to four equivalent P nuclei. Two pairs of ethoxycarbonyl resonances at δ 4.6–4.8(m), 1.43(t) and 1.52(t) and two methyl protons at δ 2.80(s) and 2.75(s) were observed in 2:1 ratio at room temperature. The variable-temperature NMR experiments showed that these two sets of signals coalesced into a broad peak upon heating at 60 °C and recovered on cooling, suggesting that these two complexes are exchanging with each other. Compounds **4a**, **4b** and **4c** also have two isomers in 4:1, 4:1, and 1.5:1 ratios at 24 °C. Although a facile exchange between *cis* and *trans* isomers has been reported for [RuH_2(dmpe)$_2$][13] and [RuH(C_8H_6NH)-(dmpe)$_2$] (C_8H_6NH = indole),[14] this process is not operating in our system because two sets of quintet patterns for hydride ligands were observed throughout the variable temperature NMR experiments, showing *trans* configurations of both isomers. We believe that these isomers are most likely the (*E*) and (*Z*) conformers of the enolato ligands as shown in eqn. (1). A similar transformation process has been observed for the related rhenium complex *cis*-[Re(NCCRCO$_2$Et)(NCCHR-CO$_2$Et)(PMe_2Ph)$_4$].[4b]



(1)

Stoichiometric reactions of enolatoruthenium(II) complexes with electrophiles

To reveal the nucleophilic properties of the enolato ligand, reactions with some electrophiles were performed. As we previously reported, protonolysis of complex **2** with hydrogen chloride in thf liberated ethyl cyanoacetate giving the dinuclear complex [(Ph_3P)$_2$(Cl)Ru(μ-Cl)$_3$Ru(PPh_3)$_2$(NCCH$_2$CO$_2$Et)].[6] On exposure of **4a** and **4c** to hydrogen chloride gas, ethyl cyanoacetate and ethyl 2-cyanopropionate (53% from **4a**, 64% from **4c**) and molecular hydrogen (37% from **4a**, 87% from **4c**) were liberated to give a known dichlororuthenium complex, *trans*-[$RuCl_2$(dppe)$_2$].[15] Complexes **3** and **5** also reacted with hydrogen chloride gas to give ethyl cyanoacetate (46%) and ethyl 2-cyanopropionate (38%) with generation of molecular hydrogen in 7 and 87% yields, respectively. The fate of the ruthenium fragment is unclear to date.

Carbon electrophiles also reacted with the enolato ligand of complexes **3**, **4a**, and **4c** (Table 2). The reaction of complex **4a** with methyl iodide gave ethyl cyanoacetate (26%), ethyl 2-cyanopropionate (28%), and ethyl 2-cyanoisobutyrate (58%) and the novel hydrido(iodo)ruthenium(II) complex *trans*-[RuH(I)(dppe)$_2$] in 70% yield. Ethyl 2-cyanopropionate is considered to be formed by the simple methylation of the enolato ligand. In addition, dimethylation of the enolato ligand also took place giving ethyl 2-cyanoisobutyrate.† Similarly, **3** also reacted with methyl iodide to give ethyl cyanoacetate (16%), ethyl 2-cyanopropionate (15%), and ethyl 2-cyanoisobutyrate (47%). Formation of dimethylated products may be due to the high reactivity of alkyl cyanoacetate. In fact, reactions of **4c** with methyl, ethyl and isopropyl iodides gave corresponding ethyl α-alkylcyanopropionate and *trans*-[RuH(I)(dppe)$_2$] in almost quantitative yields. Contrary to these results, treatments of complex **4c** with neopentyl and phenyl iodides gave no reaction. Such a trend for tertiary and aryl halides is general in S_N2 type reactions. These data show that the enolatoruthenium(II) complexes have enough nucleophilicity for C–C bond formation reactions.

The investigation of the stoichiometric reaction of complex **4a** with benzaldehyde showed that no Knöevenagel product was formed at room temperature even after 9 d. However, a similar treatment in the presence of methanol as proton source gave ethyl 2-cyanocinnamate in 9.6% yield. Interestingly, when 10 equivalents of ethyl 2-cyanopropionate was added as a proton source to both systems, the yield of ethyl 2-cyanocinnamate increased to 55 and 48%, respectively.‡ These results show that **4a** is also susceptible to nucleophilic reactions and a suitable proton source is required to produce the Knöevenagel product.

† One of referees pointed out that the formation of ethyl 2-cyanoisobutyrate seems to indicate facile ligand exchange reaction between the enolate and ethyl 2-cyanopropionate. However, treatment of complex **4a** with ethyl 2-cyanopropionate resulted in no reaction. Although the detailed mechanism is not clear at present, this fact suggests that the formation of ethyl 2-cyanoisobutyrate takes place on the ruthenium complex.

‡ Ethyl 2-cyanopropionate only acts as a proton source and does not react with benzaldehyde at all (*cf.* Table 3). The most probable product after addition of ethyl 2-cyanopropionate to this reaction mixture is [RuH(NCCMeCO$_2$Et)(dppe)$_2$].

Table 2 Reactions of enolatoruthenium(II) complexes **3**, **4a** and **4c** with organo iodides

Complex	RI	Yield(%)		
		NC CO$_2$Et	Me NC CO$_2$Et	Me R NC CO$_2$Et
3	MeI	16	15	47
4a	MeI	26	28	58
4c	MeI	—	0	108
4c	EtI	—	0	90
4c	^{i}PrI[a]	—	0	96
4c	Me_3CCH_2I	—	0	0
4c	PhI[a]	—	0	0

Reaction conditions: enolatoruthenium complex, 0.1 mmol; organo iodide, 0.226–1.19 mmol; solvent, thf; room temperature. Yields were determined by GLC. [a] At 50 °C.

Catalytic Knöevenagel and Michael reactions by enolatoruthenium(II) complexes

Since these enolatoruthenium(II) complexes have shown considerable nucleophilicity, they were employed as catalysts for Michael and Knöevenagel reactions of alkyl cyanocarboxylates with acrylonitrile or benzaldehyde and the results are in Table 3. Results of the catalytic Knöevenagel reactions are summarised as follows: (*i*) dppe ligand itself has negligible activity under the reaction conditions (entry 1); (*ii*) catalytic activity increased in the order **1**, **1** + dppe and **2** < **3** < **4a** and **4c** (entries 2–7). It is worth noting that the triphenylphosphine ligands in **2** were easily displaced by dppe giving the catalytically more active complex **4**. The fact is in accord with the drastic improvement of Murahashi's aldol type reactions of nitriles catalysed by **2** by adding a bidentate ligand such as dppe;[2] (*iii*) Knöevenagel reaction of ethyl 2-cyanopropionate with benzaldehyde did not take place at all (entries 8–11). The results of catalytic Michael reactions are as follows: (*i*) dppe and **1** itself also had no catalytic activity (entries 12–14); (*ii*) when the concentration of **1**/dppe catalyst increased, the yield of the double Michael product was improved (entries 15–17); (*iii*) complexes **2**, **3** and **4c** had moderate catalytic activity (entries 18–20); (*iv*) catalytic Michael reactions of ethyl 2-cyanopropionate to give acrylonitrile smoothly proceeded with **4c** or **5**, while dppe, **1** and a mixture of **1** and dppe showed negligible activity (entries 21–25).

From the above results in combination with our previous mechanistic report on Murahashi's aldol reaction,[6] a possible mechanism for the present Knöevenagel reaction has been proposed as shown in Scheme 3. First of all complex **4a** is formed from **1** *via* **3** or **2** in the presence of dppe ligand under ambient conditions. The formal oxidative addition of the C–H bond of the α-methylene proton of ethyl cyanoacetate to ruthenium(0) takes place to give an hydrido(enolato)ruthenium(II) complex. The enolato ligand in **4a** is nucleophilic enough to react with benzaldehyde to give the aldolatoruthenium(II) intermediate **6**. Since ethyl 2-cyanopropionate showed no reactivity, this nucleophilic reaction step may be sensitive to the steric properties of the reaction centre. In the presence of an excess amount of ethyl cyanoacetate the incoming ethyl cyanoacetate would act as a proton source to give the product. The dehydration process proceeds rapidly and irreversibly to produce **4a**, liberating ethyl cyanocinnamate and water. This mechanism is similar to the one proposed for the reaction catalysed by **2**[3,6] or [Re(NCCHCO$_2$R)(NCCH$_2$CO$_2$R)(PMe$_2$Ph)$_4$],[4] but the nucleophilicity of the *N*-bonded enolato ligand would be much more enhanced by the loss of hydrogen bonding between it and the coordinated ester ligands.

Michael reactions are also considered to proceed in a similar way involving nucleophilic reaction of an enolatoruthenium(II) intermediate to give acrylonitrile. In this case, further Michael addition took place giving a double addition product as Murahashi and co-workers[2] reported. It is also worth noting that ethyl 2-cyanopropionate did react more smoothly with acrylonitrile in the presence of **4c** or **5**, while no Knöevenagel reaction took place with benzaldehyde in all cases. Interestingly, Ito and co-workers[16] also recently reported that alkyl 2-cyanopropionate did not react with benzaldehyde in the presence of a rhodium(I) catalyst. The reason for this selectivity is not clear and we should wait for further detailed mechanistic studies.

In summary, the present reaction provides a versatile method to give catalytically active *N*-bonded enolatoruthenium(II) complexes from the ruthenium(0) complex [Ru(cod)(cot)] **1** by oxidative addition of the C–H bond of the alkyl cyanocarboxylate.

Experimental

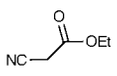
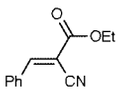
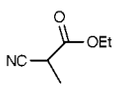
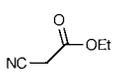
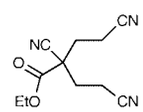
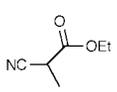
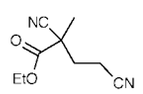
All manipulations were carried out under dry nitrogen using standard Schlenk and vacuum line techniques unless otherwise noted. All solvents were distilled from appropriate drying agents prior to use. The compound triphenylphosphine was donated by Hokko Chemical Co; 1,2-bis(diphenylphosphino)ethane (dppe)[17] and [Ru(cod)(cot)] **1**[18] were prepared according to the literature methods. Acrylonitrile and methyl iodide were dried over anhydrous magnesium sulfate and distilled under nitrogen. Benzaldehyde, ethyl cyanoacetate, and ethyl 2-cyanopropionate were dried with calcium chloride and distilled under reduced pressure. Dry hydrogen chloride was generated by the reaction of flame dried sodium chloride with concentrated sulfuric acid under vacuum. Deuteriated solvents for use in NMR experiments were dried with P_2O_5 for $CDCl_3$ or sodium wire for C_6D_6 and were vacuum-transferred from these drying agents.

Proton NMR spectra were recorded on JEOL FX-200, LA-300, or Bruker AM-400 spectrometers, ^{31}P-{^{1}H} NMR spectra on JEOL LA-300 (121.6 MHz) or Brucker AM-400 (161.5 MHz) spectrometers with chemical shifts reported in ppm downfield from 85% H_3PO_4 in D_2O. The IR spectra were obtained on a JASCO FT/IR-5M Fourier transform spectrometer using KBr disks. The catalytic reactions were monitored by a Shimadzu GC-8APF gas-liquid phase chromatograph using glass packed PEG-20M (5 mm × 4 m) or OV-1 (5 mm × 4 m) columns with flame ionisation detection (FID). The volumes of gases generated were measured by a Toepler pump. The GLC analyses of inorganic gases were performed with a Shimadzu GC-3 BT gas–liquid phase chromatograph using stainless-steel packed molecular sieves or active carbon with thermal conductivity detection (TCD). Melting points were estimated under nitrogen with a Yazawa MP-21 capillary melting apparatus and are uncorrected. Elemental analyses were performed by a YANACO CHN autocorder MT-2 or Perkin-Elmer 2400 Series II CHN analyzer. Molar electrical conductivities were measured on a TOA model CM-7B instrument.

Reactions of [Ru(cod)(cot)] 1 with ethyl cyanoacetate in the presence of tertiary phosphine ligand

With PPh_3. To a mixture of complex **1** (279.0 mg, 0.885 mmol) and PPh_3 (656.0 mg, 2.50 mmol) in thf (5 cm^3) was added ethyl cyanoacetate (260 μl, 2.44 mmol) by syringe under nitrogen. After stirring at room temperature for 45 h the resulting light yellow precipitate was separated by filtration. Recrystallisation from a mixture of benzene–hexane gave bright yellow cubes of [RuH(NCCHCO$_2$Et)(NCCH$_2$CO$_2$Et)(PPh$_3$)$_3$] **2** in 45% yield (436.8 mg, 0.392 mmol). All spectroscopic data were identical to those of **2** derived from the alternative method,[3,6] mp 120–121 °C (decomp.); $\tilde{\nu}_{max}$/cm^{-1} 3000m, 2184s, 1950w, 1746s, 1600s, 1574s, 1480s, 1434s, 1328m, 1187m, 1137m, 1090w, 743s, 697vs and 519vs; δ_H[200 MHz, C_6D_6, room

Table 3 Catalytic Knöevenagel and Michael reactions[a]

Entry	Catalyst	(mol%)	Active hydrogen compound	Electrophile	Product	Yield(%)
1	dppe	(1.0)				0.8
2	**1**	(1.0)				29
3	**1** + dppe	(1.0)				32
4	**2**	(1.0)				29
5	**3**	(1.0)				52
6	**4a**	(1.0)				76
7	**4c**	(1.0)				80
8[b]	dppe	(1.0)				No reaction
9[b]	**1**	(1.0)				No reaction
10[b]	**1** + dppe	(1.0)				No reaction
11	**5**	(1.0)				No reaction
12	dppe	(1.0)				0.2
13	dppe	(4.8)				2.1
14	**1**	(1.0)				0
15	**1** + dppe	(1.0)				0
16	**1** + dppe	(4.4)				8.1
17	**1** + dppe	(5.6)				22
18	**2**	(1.0)				29
19	**3**	(1.0)				29
20	**4c**	(1.0)				34
21	dppe	(1.0)				2.5
22	**1**	(1.0)				3.3
23	**1** + dppe	(1.0)				4.7
24	**4c**	(1.3)				61
25	**5**	(1.0)				77

[a] Conditions: solvent = tetrahydrofuran; 50 °C; 36 h. [b] In C_6D_6.

temperature (r.t.)] −12.9 (br, 1 H), 0.83 (br t, J = 7.3, 3 H), 1.17 (br t, J = 7.3, 3 H), 2.9 (br, 2 H), 3.1 (s, 2 H), 3.76 (br q, J = 7.3, 2 H), 4.22 (br q, J = 7.3 Hz, 2 H), 6.9 (br s, 27 H) and 7.6 (br s, 18 H).

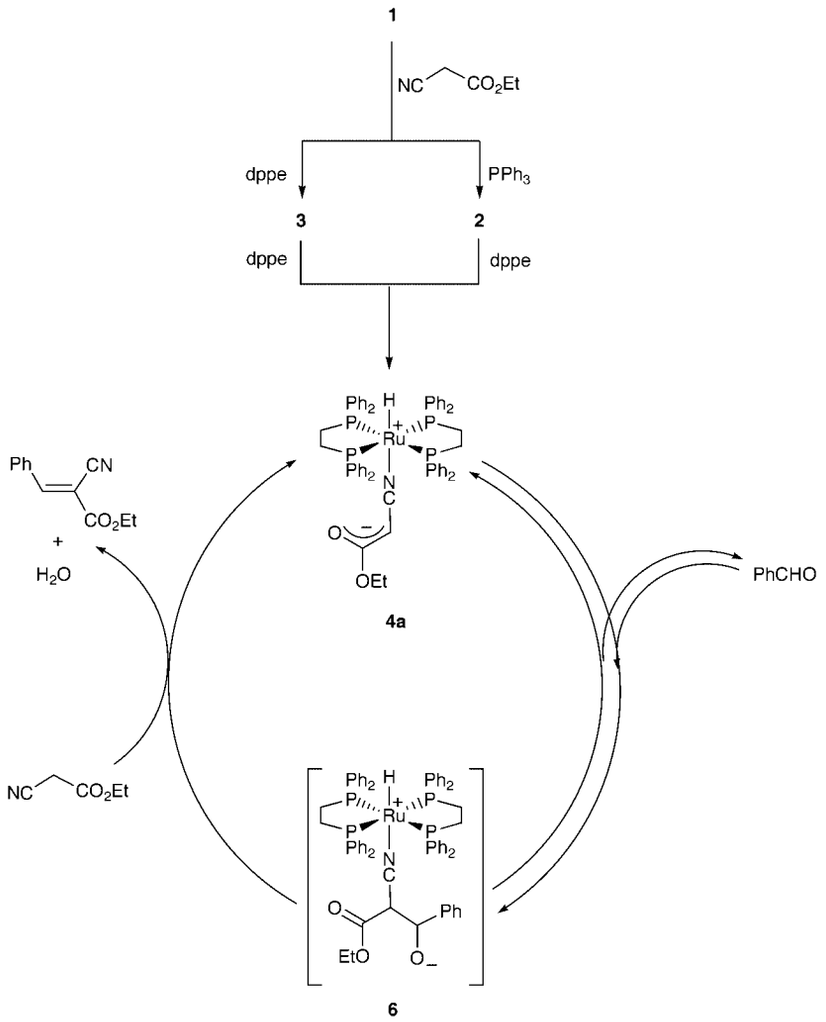
With dppe at room temperature. Ethyl cyanoacetate (190 μl, 1.79 mmol) was added to a benzene solution (3 cm^3) of compound **1** (279.0 mg, 0.885 mmol) and dppe (286.6 mg, 0.978 mmol) under nitrogen. The mixture was allowed to react at room temperature for 6 d. Addition of hexane (*ca.* 1 cm^3) to the mixture and slow diffusion of the hexane layer into the benzene phase in a refrigerator resulted in the formation of light yellow crystals of [RuH(NCCHCO$_2$Et)(cod)(dppe)] **3** in 33% yield (220.9 mg, 0.291 mmol), mp 166–169 °C (decomp.) (Found: C, 66.15; H, 6.69; N, 1.97. $C_{39}H_{43}NO_2P_2Ru{\cdot}0.5C_6H_6$ requires C, 66.40; H, 6.10; N, 1.84%); Λ = 0.002 9 S cm^2 mol^{-1} (thf, 25 °C); $\tilde{\nu}_{max}$/cm^{-1} 3090m, 2990m, 2180s, 2061w, 1610vs, 1420s, 1090s, 690vs and 515s (KBr, r.t.); δ_H(200 MHz, C_6D_6, r.t.) −10.00 (t, J_{PH} = 20.2, 1 H), 1.60 (m, 2 H), 1.47 (t, J = 7.3, 3 H), 2.0 (br, 2 H), 2.3 (br, 2 H), 3.4 (br, 2 H), 3.69 (s, 1 H), 4.4 (br, 1 H), 4.62 (q, J = 7.3, 2 H), 7.01 (br, 4 H), 7.09 (m, 4 H), 7.28 (t, J = 8.9, 4 H), 7.70 (t, J = 8.9, 4 H) and 7.93 (t, J = 8.9 Hz, 4 H).

With dppe at 55 °C. To a benzene solution (4 cm^3) of compound **1** (166.5 mg, 0.528 mmol) and dppe (462.2 mg, 1.16 mmol) was added ethyl cyanoacetate (110 μl, 1.03 mmol) under nitrogen. After stirring at 55 °C for 32 h a yellow powder was deposited by addition of hexane. Recrystallisation of the precipitate from benzene–hexane at 0 °C gave yellow crystals of [RuH(NCCHCO$_2$Et)(dppe)$_2$] **4a** in 65% isolated yield (348.9 mg, 0.345 mmol), mp 278–280 °C (decomp.) (Found: C, 69.02; H, 5.59; N, 1.31. $C_{57}H_{55}NO_2P_4Ru{\cdot}0.5C_6H_6$ requires C, 68.63; H, 5.57; N, 1.33%); Λ = 0.064 S cm^2 mol^{-1} (thf, at 25 °C); $\tilde{\nu}_{max}$/cm^{-1} 3100m, 3000m, 2179s, 1953w, 1603vs, 1375w, 1440s, 1100s, 690vs and 530s (KBr, r.t.). Compound **4a** has two isomers, which would be due to the (*E*) and (*Z*) isomers of the enolato ligand. The ratio of major : minor isomers is 4 : 1 at 24 °C. Major isomer: δ_H(200 MHz, C_6D_6, r.t.) −16.27 (qnt, J_{PH} = 18.31, 1 H), 1.47 (t, J = 7.3, 3 H), 1.98 (br, 2 H), 2.78 (br, 2 H), 3.45 (s, 1 H), 4.62 (q, J = 7.3 Hz, 2 H), 6.85 (br, 8 H), 7.08 (br, 8 H), 7.12 (br, 8 H), 7.31 (br, 8 H) and 7.50 (br, 8 H); δ_P (122.55 MHz, C_6D_6, 24 °C) 66.3 (s). Minor isomer (signals overlapped with the major ones preventing complete characterisation, only several peaks characterised.): δ_H(300 MHz, C_6D_6, 24 °C) −16.36 (qnt, J_{PH} = 19.8, 2 H), 1.38 (t, J = 7.8 Hz, 3 H), 2.56 (br, 4 H) and 3.25 (s, 1 H); δ_P(122.55 MHz, C_6D_6, 24 °C) 66.0 (s).

A similar treatment of complex **1** (13.4 mg, 0.0425 mmol) with dppe (34.4 mg, 0.0863 mmol) and NCCD$_2$CO$_2$Et (4.8 μl, 0.044 mmol, 90% deuteriated) gave [RuD(NCCDCO$_2$Et)(dppe)$_2$] **4a**-d$_2$ in 76% yield (32.8 mg, 0.0324 mmol). The ^{1}H NMR spectrum shows that the hydride and the methine proton were 80% deuteriated; $\tilde{\nu}_{max}$/cm^{-1} 3060m, 2174s, 1629s, 1605 (sh), 1585 (sh), 1483m, 1462s, 1434m, 1409w, 1373w, 1329w, 1133m, 1097s, 812m, 743s, 697vs, 669m, 530s, 507m and 491m.

Reaction of compound 1 with isopropyl cyanoacetate in the presence of dppe

A similar treatment of complex **1** (78.8 mg, 0.250 mmol) with dppe (202.2 mg, 0.507 mmol) and isopropyl cyanoacetate (68 μl, 0.54 mmol) as mentioned above resulted in the formation of [RuH(NCCHCO$_2$^{i}Pr)(dppe)$_2$] **4b** in 35% yield (90.1 mg, 0.088 mmol) (Found: C, 68.35; H, 6.21; N, 1.47. $C_{58}H_{57}NO_2P_4Ru$ requires C, 68.90; H, 6.36; N, 1.24%); $\tilde{\nu}_{max}$/cm^{-1} 3100m, 2174s, 1949w, 1603vs, 1483w, 1434s, 1403s, 1139m, 1112s, 1099s, 1071m, 978m, 875m, 811m, 743s, 695vs and 527vs (KBr, r.t.). Compound **4b** is found to have two isomers, due to (*E*) and (*Z*) isomers of the enolato ligand. The ratio of the major : minor isomers is 4 : 1 at 24.0 °C. Major isomer: δ_H(300 MHz, C_6D_6, 24 °C) −16.27 (qnt, J = 18, 1 H), 1.56 (d, J = 6.6, 6 H), 1.98 (m, 4 H), 2.62 (m, 4 H), 3.42 (s, 1 H), 5.69 (sept, J = 6.6 Hz, 1 H), 6.85 (m, 12 H), 7.09 (m, 12 H), 7.29 (br, 8 H) and 7.49 (br, 8 H);



Scheme 3

δ_P(121.55 MHz, C_6D_6, r.t.) 66.36 (s). Minor isomer (signals were overlapped with the major ones preventing complete characterisation, only several peaks characterised): δ_H(300 MHz, C_6D_6, 24.0 °C) −16.33 (qnt, J = 18, 1 H), 1.50 (d, J = 6.6, 6 H), 2.63 (m, 4 H), 3.22 (s, 1 H) and 5.84 (sept, J = 6.6 Hz); δ_P(121.55 MHz, C_6D_6, r.t.) 67.66 (s).

Reaction of compound 1 with ethyl 2-cyanopropionate in the presence of dppe

A similar treatment of complex **1** (85.9 mg, 0.272 mmol) with dppe (231.1 mg, 0.580 mmol) and ethyl 2-cyanopropionate (68 μl, 0.54 mmol) as described above resulted in the formation of [RuH(NCCMeCO$_2$Et)(dppe)$_2$] **4c** in 42% isolated yield (117.1 mg, 0.114 mmol); mp 279–282 °C (Found: C, 68.53; H, 5.92; 1.34%. $C_{58}H_{57}NO_2P_4Ru{\cdot}0.5C_6H_6$ requires C, 68.85; H, 5.68; N, 1.32%); Λ = 0.001 7 S cm^2 mol^{-1} (thf, 25 °C); $\tilde{\nu}_{max}$/cm^{-1} 2950w, 2183s, 2087w, 1605vs, 1440s, 1410s, 1160s, 730s and 700s. Compound **4c** also has two isomers, due to (*E*)- and (*Z*)-isomers of the enolato ligand. The ratio of major : minor isomers is 1.5 : 1 at r.t.. Major isomer: δ_H(200 MHz, C_6D_6, r.t.) −16.37 (qnt, J_{PH} = 19.6, 1 H), 1.39 (t, J = 7.3, 3 H), 1.98 (s, 3 H), 2.58 (br, 4 H), 2.92 (br, 4 H), 4.65 (q, J = 7.3 Hz), 6.78 (br, 8 H), 7.01 (br, 8 H), 7.10 (br, 8 H), 7.31 (br, 8 H) and 7.49 (br, 8 H); δ_P(161.5 MHz, C_6D_6, r.t.) 69.89 (s). Minor isomer (signals overlapped with the major ones preventing complete characterisation, only several peaks characterised): δ_H(200 MHz, C_6D_6, r.t.) −16.27 (qnt, J_{PH} = 19.6, 1 H), 1.54 (t, J = 7.3, 3 H), 2.08 (s, 3 H) and 4.69 (q, J = 7.3 Hz); δ_P(161.5 MHz, C_6D_6, r.t.) 70.76 (s).

Reaction of compound 1 with ethyl 2-cyanopropionate in the presence of PMePh$_2$

Ethyl 2-cyanopropionate (120 μl, 0.953 mmol) was added into a mixture of complex **1** (274.3 mg, 0.870 mmol) and 4 equivalents of PPh$_2$Me (690 μl, 3.67 mmol) in thf (5 cm^3) under nitrogen. After stirring at 55 °C for 30 h hexane was added to precipitate a pale yellow powder. This was washed with hexane and diethyl ether to give analytically pure [RuH(NCCMeCO$_2$Et)(PMePh$_2$)$_4$] **5** in 93% yield (821.3 mg, 0.810 mmol), mp 154–156 °C (Found: C, 69.53; H, 6.34; N, 1.43. $C_{58}H_{57}NO_2P_4Ru{\cdot}C_6H_6$ requires C, 69.42; H, 6.10; N, 1.27%); Λ = 0.002 2 S cm^2 mol^{-1}; $\tilde{\nu}_{max}$/cm^{-1} 3040w, 2159m, 2098w, 1968w, 1618vs, 1584w, 1479m, 1434s, 1324m,1090s, 889s, 742s, 696s, 678s and 505s. Compound **5** also has two isomers, which would be due to (*E*)- and (*Z*)-isomers of the enolato ligand. The ratio of these isomers is 2/1 at r.t.. Major isomer: δ_H(200 MHz, C_6D_6, r.t.) −15.32 (qnt., J_{PH} = 21 Hz, 1 H), 1.43 (t, J = 7 Hz, 3 H), 1.80 (s, 12 H), 2.80 (s, 3 H), 4.6–4.8 (m, 2 H), 6.83 (br, 24 H) and 7.38 (br, 16 H). Minor isomer: δ_H(200 MHz, C_6D_6, r.t.) −15.27 (qnt, J_{PH} = 21, 1 H), 1.52 (t, J = 7 Hz, 3 H), 1.84 (s, 12 H), 2.75 (s, 3 H), 4.6–4.8 (m, 2 H), 6.83 (br, 24 H) and 7.38 (br, 16 H).

Time-course of the reaction of compound 1 with ethyl cyanoacetate in the presence of dppe

Compound **1** (21.4 mg, 0.0678 mmol), dppe (53.6 mg, 0.135 mmol) and triphenylmethane as an internal standard (4.3 mg, 0.018 mmol) were dissolved in benzene-d_6 (600 μl) under nitrogen. Ethyl cyanoacetate (14.0 μl, 0.132 mmol) was added and

the mixture heated at 60 °C in a thermostatted oil-bath. The yields of **3** and **4a** were estimated by using the methine peak of triphenylmethane (δ 5.43) in the ^{1}H NMR spectra: 1.5 h, **3** (52%), **4a** (18%); 5 h, **3** (30%), **4a** (67%); 6.5 h, **3** (19%), **4a** (78%); 14 h, **3** (0%), **4a** (96%).

Reaction of compound 2 with dppe

Compound **2** (17.7 mg, 1.59 mmol) was treated with 2 equivalents of dppe (13.2 mg, 0.0331 mmol) in benzene-d_6 at room temperature. After reaction for 1 h **4a** and ethyl cyanoacetate were detected in 63 and 50% yields, respectively. After 3 h **2** had completely disappeared to give **4a** and ethyl cyanoacetate in 82 and 60% yields, respectively. These yields did not change for 14 h.

Reaction of compound 3 with dppe

Compound **3** (21.1 mg, 0.0293 mmol) was treated with dppe (12.2 mg, 0.0306 mmol) in a benzene-d_6 (600 μl). After reaction at 50 °C for 22 h 50% of **3** was converted into **4a** (yield 50%) with liberation of 1,5-cod (50%). After 118 h **3** was completely converted into **4a** (yield 100%) with liberation of 1,5-cod (100%).

Reaction of compound 4a with PPh_3 and ethyl cyanoacetate

Compound **4a** (10.9 mg, 0.0108 mmol) was treated with 3 equivalents of PPh_3 (8.7 mg, 0.033 mmol) and 1 equivalent of ethyl cyanoacetate (1.2 μl, 0.011 mmol) in benzene-d_6 at room temperature. There was no reaction.

Protonolyses of enolatoruthenium(II) complexes 3, 4a, 4c and 5 with hydrogen chloride

Complex 3. Tetrahydrofuran (*ca.* 2 cm^3) was introduced into a Schlenk tube (20 cm^3) containing compound **3** (58.8 mg, 0.0816 mmol) under vacuum by a trap-to-trap method. Dry hydrogen chloride gas (28.7 cm^3, 1.28 mmol) was added under vacuum by using a mercury manometer. The reaction mixture was stirred at room temperature for 24 h. The gas generated was collected by using a Toepler pump and characterised by GLC, giving molecular hydrogen (0.0056 mmol, 6.9%) and ethyl cyanoacetate (0.038 mmol, 46%).

Complex 4a. Compound **4a** (103.3 mg, 0.102 mmol) was dissolved in 1,2-dimethoxyethane (*ca.* 2 cm^3) in a Schlenk tube (20 cm^3) under vacuum and dry hydrogen chloride gas (23.5 cm^3, 0.971 mmol) introduced under vacuum. After stirring the solution at 50 °C for 25 h, molecular hydrogen (0.0373 mmol, 37%) and ethyl cyanoacetate (0.0541 mmol, 53%) were detected. The resulting precipitate was separated by filtration and washed with hexane. After drying under vacuum a yellow powder was obtained (153.8 mg). $\tilde{\nu}_{max}$/cm^{-1} 3040m, 1585w, 1571w, 1484m, 1433vs, 1097 (br), 874w, 824m, 744m, 697vs, 527s and 520s.

Complex 4c. Compound **4c** (152.0 mg, 0.148 mmol) was dissolved in thf (*ca.* 2 cm^3) and dry hydrogen chloride gas (30.3 cm^3, 1.35 mmol) introduced under vacuum. After 7 h at room temperature, molecular hydrogen (0.128 mmol, 87%) and ethyl 2-cyanopropionate (0.0902 mmol, 64%) were produced. A yellow powder was precipitated by addition of hexane. Recrystallisation of it from dichloromethane–hexane gave yellow crystals. $\tilde{\nu}_{max}$/cm^{-1} 3040w, 1485m, 1433vs, 1262w, 1096vs, 697vs and 527s. δ_H(200 MHz, $CDCl_3$, r.t.) 2.56–2.97 (m, 8 H), 6.7–7.0 (m, 32 H), 7.5 (m, 4 H) and 8.2 (m, 4 H).

Complex 5. Compound **5** (113.6 mg, 0.110 mmol) was dissolved in 1,2-dimethoxyethane (*ca.* 2 cm^3) and dry hydrogen chloride gas (26.8 cm^3, 1.10 mmol) introduced under vacuum. The solution turned to green from yellow within 10 min. After reaction at 50 °C for 16 h molecular hydrogen (0.0961 mmol, 87%) and ethyl 2-cyanopropionate (0.0422 mmol, 38%) were produced.

Reactions of enolatoruthenium(II) complexes 3, 4a and 4c with methyl iodide

Complex 3. Methyl iodide (74.0 μl, 1.19 mmol) was added to compound **3** (85.8 mg, 0.119 mmol) in dry thf (*ca.* 2 cm^3). After stirring the reaction mixture for 46 h at room temperature, ethyl cyanoacetate (0.0188 mmol, 16%), ethyl 2-cyanopropionate (0.0178 mmol, 15%), ethyl 2-cyanoisobutyrate (0.0564 mmol, 47%) and 1,5-cod (0.0126 mmol, 11%) were produced.

Complex 4a. Methyl iodide (48.0 μl, 0.771 mmol) was added to compound **4a** (77.8 mg, 0.0770 mmol) in dry thf (*ca.* 2 cm^3). After stirring the reaction mixture for 47 h at room temperature, ethyl cyanoacetate (0.0196 mmol, 26%), ethyl 2-cyanopropionate (0.0218 mmol, 28%) and ethyl 2-cyanoisobutyrate (0.0443 mmol, 58%) were produced. Then, all volatile materials were removed under vacuum to give a yellow solid, which was washed with ether giving analytically pure *trans*-[RuH(I)(dppe)$_2$] in 70% yield (55.1 mg, 0.0537 mmol) (Found: C, 60.02; H, 5.01; I, 11.16. $C_{52}H_{49}IP_4Ru$ requires C, 60.88; H, 4.81; N, 12.37%); $\tilde{\nu}_{max}$/cm^{-1} 3040w, 2068m, 1585w, 1572w, 1584m, 1432s, 1187w, 1154w, 1089s, 1066 (sh), 881m, 820s, 740s, 694vs, 648s, 529vs, 509s, 486s, 423s and 418m; δ_H(200 MHz, $CDCl_3$, r.t.) −16.23(qnt, J = 19.5 Hz, 1 H), 2.13 (br, 4 H), 2.76 (br, 4 H) and 6.94–7.26 (m, 40 H).

Complex 4c. Methyl iodide (30.0 μl, 0.480 mmol) was added to compound **4c** (145.9 mg, 0.133 mmol) in thf (*ca.* 2 cm^3). After reaction at room temperature for 18 h ethyl 2-cyanoisobutyrate (0.144 mmol, 108%) was produced. Hexane was added to give a precipitate. Recrystallisation of the powder from dichloromethane–hexane gave microcrystals, which were characterised as [RuH(I)(dppe)$_2$] by the following spectroscopic data (yield: 20%, 27.8 mg, 0.0271 mmol); $\tilde{\nu}_{max}$/cm^{-1} 3040w, 2067m, 1585w, 1572w, 1482m, 1432s, 1187w, 1153w, 1088s, 1073 (sh), 881m, 819s, 739s, 693vs, 648s, 529vs, 509s, 485s, and 417m; δ_H(200 MHz, $CDCl_3$, r.t.) −16.23(qnt, J = 19.5 Hz, 1 H), 2.14 (br, 4 H), 2.78 (br, 4 H) and 6.95–7.26 (m, 40 H).

Reactions of enolatoruthenium(II) complex 4c with alkyl iodides

Ethyl iodide. Ethyl iodide (30.0 μl, 0.380 mmol) was added to compound **4c** (116.6 mg, 0.114 mmol) in thf (*ca.* 2 cm^3). After stirring for 46 h at room temperature ethyl 2-cyano-2-methylbutyrate (0.102 mmol, 90%) was produced.

Isopropyl iodide. Isopropyl iodide (60.0 μl, 0.601 mmol) was added to compound **4c** (61.6 mg, 0.0601 mmol) in thf (*ca.* 2 cm^3). After stirring for 8 h at 50 °C ethyl 2-cyano-2,3-dimethylbutyrate (0.0576 mmol, 96%) was produced. The resulting precipitate was washed with ether and dried under vacuum to give *trans*-[RuH(I)(dppe)$_2$] in 81% yield (50.0 mg, 0.0487 mmol).

Neopentyl iodide. Neopentyl iodide (30.0 μl, 0.226 mmol) was added to complex **4c** (77.2 mg, 0.0753 mmol) in thf (*ca.* 2 cm^3). After stirring for 3 d at 30 °C no new products were observed by GLC analysis. Hexane was added to give a precipitate which was characterised as **4c** (55.2 mg, 0.0542 mmol, 72%).

Phenyl iodide. Phenyl iodide (50.0 μl, 0.450 mmol) was added to complex **4c** (159.6 mg, 0.156 mmol) in thf (*ca.* 2 cm^3). After stirring for 3 d at 50 °C no new products were observed by GLC analysis. All volatile materials were evaporated under vacuum and the resulting solid was washed with ether to recover **4c** (93.9 mg, 0.0920 mmol, 59%).

Stoichiometric reaction of compound 4a with benzaldehyde

Benzaldehyde (5.4 μl, 0.053 mmol) was added to a thf solution (3 cm^3) of complex **4a** (52.2 mg, 0.0516 mmol) and bibenzyl (11.5 mg, 0.0631 mmol) as an internal standard under nitrogen. After stirring for 9 d at 30 °C no Knöevenagel products were

observed by GLC analysis. Then, ethyl 2-cyanopropionate (66.0 μl, 0.524 mmol) was added and the mixture was kept at 30 °C. A Knöevenagel product, ethyl 2-cyanocinnamate, was detected in 30 and 55% yields after 1 h and 1 d, respectively.

Stoichiometric reaction of compound 4a with benzaldehyde in the presence of methanol

Benzaldehyde (5.4 μl, 0.053 mmol) was added to a thf solution (3 cm^3) of complex **4a** (52.7 mg, 0.0521 mmol) and bibenzyl (11.3 mg, 0.0620 mmol) as an internal standard under nitrogen. After stirring for 26 h at 30 °C no Knöevenagel product was detected. Then, methanol (22 μl, 0.054 mmol) was added and stirred at 30 °C for 9 d. A Knöevenagel product, ethyl 2-cyanocinnamate, was detected in 9.6% yield. Then, ethyl 2-cyanopropionate (66.0 μl, 0.524 mmol) was added and kept at 30 °C. Ethyl 2-cyanocinnamate increased to 22 and 48% after 1 h and 1 d, respectively.

Catalytic Michael reaction between ethyl cyanoacetate and acrylonitrile

As a typical example, the catalytic Michael reaction with complex **4a** is described. Ethyl cyanoacetate (185 μl, 1.74 mmol) and acrylonitrile (230 μl, 3.49 mmol) were added to a thf solution (2 cm^3) of **4a** (17.4 mg, 0.0172 mmol) under argon. The reaction mixture was stirred at room temperature for 36 h. All volatile materials were removed under reduced pressure and then benzene-d_6 (600 μl) and 1,4-dioxane (3.0 μl, 0.036 mmol) as internal standard were added to the residue. The conversion of ethyl cyanoacetate and the yield of the double Michael product were 95 and 75%, respectively. No mono Michael product was observed. NMR spectrum of the double Michael product $NCC(CH_2CH_2CN)_2CO_2Et$: δ_H(200 MHz, C_6D_6, r.t.) 1.75 (dt, J = 14.6, 7.2, 2 H, CH_2CH_2 CN), 1.96 (dt, J = 14.6, 7.2, 2 H, CH_2CH_2CN), 2.26 (t, J = 7.2, 4 H, CH_2CN) and 4.16 (q, J = 7.2 Hz, 2 H, OCH_2). Other catalytic Michael reactions of ethyl cyanoacetate and ethyl 2-cyanopropionate were performed analogously and the results are summarised in Table 3.

Catalytic Knöevenagel reaction between ethyl cyanoacetate and benzaldehyde

Ethyl cyanoacetate (170 μl, 1.60 mmol) and benzaldehyde (170 μl, 1.67 mmol) were added to a thf solution (2 cm^3) of complex **4a** (16.2 mg, 0.0160 mmol) under argon then stirred at room temperature for 36 h. After removal of all volatile materials, benzene-d_6 (600 μl) and 1,4-dioxane (3.0 μl, 0.036 mmol) as internal standard were added to the residue. The yield of the dehydrated Knöevenagel product was 66% based on ethyl cyanoacetate. NMR spectrum of (*E*)-CH(Ph)=C(CN)(CO_2Et): δ_H(200 MHz, C_6D_6, r.t.) 1.00 (t, J = 7.3, 3 H, OCH_2CH_3), 4.02 (q, J = 7.3 Hz, 2 H, OCH_2CH_3), 6.95–7.71 (m, 5 H, C_6H_5) and 8.03 (s, 1 H, CH=C). Other catalytic Knöevenagel reactions were performed analogously and the results are summarised in Table 3.

Crystallography

Yellow crystals of compound **3** were grown from a saturated solution of benzene–hexane. The crystallographic data were collected at 20 °C on a Rigaku AFC5R diffractometer using Mo-Kα radiation (λ = 0.710 69 Å). Using the criterion $|F_o| > 3.0\sigma|F_o|$, 6288 out of 9523 reflections were used for calculation. The structure was solved by Patterson methods using the R-CRYSTAN program.[19] The hydrogens H(4B), H(5C), H(8A), H(8B), H(9A), H(9B), H(12A), H(12B), H(13A), H(13B), H(26), H(37), H(40), H(41) and H(42) were located at the ideal positions and not refined. Others were found in the Fourier-difference map and refined isotropically. The final R (R') value was 0.0588 (0.0488). The crystallographic data are summarised in Table 4.

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Table 4 Crystallographic data for $[RuH(NCCHCO_2Et)(cod)(dppe)]\cdot 0.5C_6H_6$ **3**·$0.5C_6H_6$

Chemical formula	$C_{42}H_{46}NO_2P_2Ru$
Formula weight	759.86
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	19.055(3)
b/Å	10.080(2)
c/Å	19.720(4)
β/°	102.31(2)
V/Å^3	3700(1)
Z	4
μ(Mo-Kα)/cm^{-1}	1.511
No. data collected	9523
No. observed for refinement	6288 ($\|F_o\| > 3\sigma\|F_o\|$)
R	0.0588
R'	0.0488

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