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N-bonded enolatorhenium(I) complexes having dimethylphenylphosphine ligands as active key intermediates in catalytic Knoevenagel and Michael reactions[1]

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Abstract

Enolatorhenium(I) complexes *cis*-Re($NCCRCO_2R'$)($NCCHRCO_2R'$)(PMe_2Ph)$_4$ (R = H, R′ = Me (**2a**); R = H, R′ = Et (**2b**); R = H, R′ = *n*-Bu (**2c**); R = Me, R′ = Et (**2d**)) are prepared by the reaction of ReH(N_2)(PMe_2Ph)$_4$ (**1**) with alkyl cyanoalkyl carboxylate. X-ray structure analysis of **2b** shows that it has an octahedral Re geometry, where mutually *cis* enolato and ester ligands bind to the rhenium via cyano groups. Reaction of **2b** with benzaldehyde gives Re($NCCHCO_2Et$)[NC(EtO_2C)C=CHPh]–(PMe_2Ph)$_4$ (**4**), which is also derived from the ligand exchange reaction of **2b** with ethyl (*E*)-2-cyano-3-phenylpropenoate. These rhenium(I) complexes **1**, **2**, and **4** catalyze Knoevenagel and Michael reactions under neutral and mild conditions. A possible mechanism for the Knoevenagel reaction has been proposed. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Rhenium dinitrogen complex; Rhenium enolate complex; Crystal structure; Knoevenagel reaction; Michael reaction

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1. Introduction

Transition metal enolates have currently attracted considerable attention because they can act as active intermediates in stereo-, regio-, or chemoselective C–C bond formation reactions under neutral and ambient conditions. They are generally prepared by the metathetical reactions of transition metal halides with alkali–metal enolates or the reactions of metal anions with α-halocarbonyl compounds. Thus, a number of *C*- and *O*-bonded transition metal enolates of Mo, W, Re, Ru, Rh, Ni, and Pd have been prepared by these methods, showing the importance of these enolates in catalysis [1–5]. We recently showed formation of *C*-bonded gold(I) and -(III) enolates from gold alkoxides as active intermediates for catalytic Knoevenagel reactions [6]. In addition to these methods, oxidative addition of active methylene compounds to transition metal complexes is also a promising method for the synthesis of enolates [7–11]. For example, zwitterionic *mer*-RuH($NCCHCO_2R$)($NCCH_2CO_2R$)(PPh_3)$_3$ is isolated by the reaction of $RuH_2(PPh_3)_4$ or $RuH(C_2H_4)[P(C_6H_4)Ph_2](PPh_3)_2$ with cyanoalkyl carboxylates. This complex acts as an active intermediate in highly chemoselective Murahashi's aldol and Michael reactions [7]. In this case, nucleophilicity of the *N*-bonded enolato ligand significantly increased because of its non-chelating oxo-π-allyl character [8,9].

We previously reported synthesis and molecular structure of *cis*-ReH(N_2)(PMe_2Ph)$_4$ (**1**) [12], where the N_2 ligand is expected to be liberated in facile affording a reactive 16e species. Actually, complex **1** was found to

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[1] Dedicated to Professor Akira Nakamura upon his retirement from Osaka University and in honor of his numerous contributions to organometallic chemistry.

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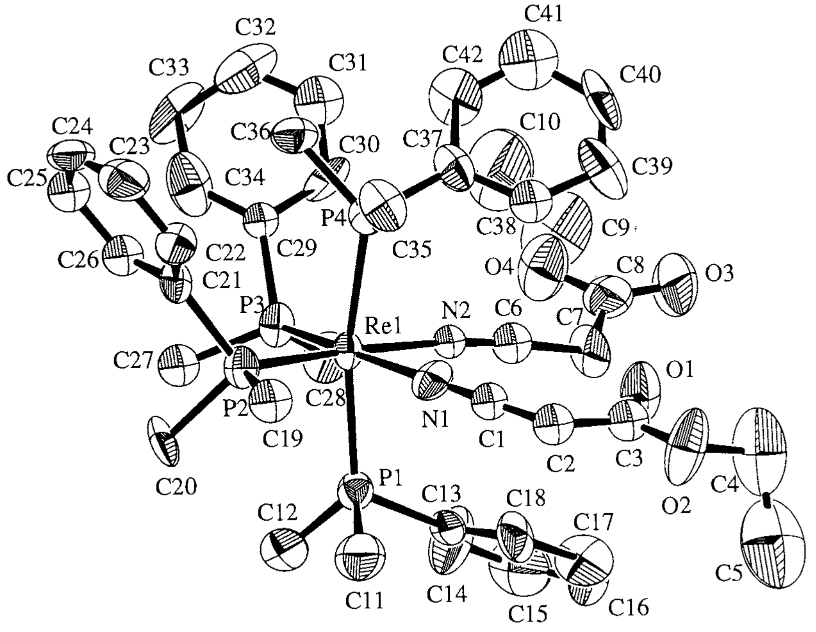


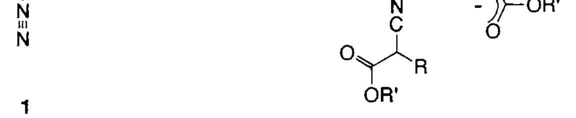
Fig. 1. ORTEP drawing of *cis*-Re(NCCHCO$_2$Et)(NCCH$_2$CO$_2$Et)(PMe$_2$Ph)$_4$ (**2b**). All hydrogen atoms are omitted for clarity.

catalyze Knoevenagel reactions and the zwitterionic enolatorhenium complexes, *cis*-Re(NCCHCO$_2$R)(NCCH$_2$CO$_2$R)(PMe$_2$Ph)$_4$ and *cis*-Re(NCCHCO$_2$R)[NC(RO$_2$C)C = CHPh](PMe$_2$Ph)$_4$, were isolated as active intermediates [13]. Herein we report the full account of the preparations and chemical reactions of the enolatorhenium(I) complexes.

2. Results and discussion

2.1. Reactions of ReH(N$_2$)(PMe$_2$Ph)$_4$ with active hydrogen compounds

Treatment of *cis*-ReH(N$_2$)(PMe$_2$Ph)$_4$ (**1**) with an excess amount of alkyl cyanoacetate or ethyl 2-cyanopropionate in Et$_2$O at room temperature gave novel enolatorhenium complexes, *cis*-Re(NCCRCO$_2$R′)(NCCHRCO$_2$R′)(PMe$_2$Ph)$_4$ (R = H, R′ = Me (**2a**); R = H, R′ = Et (**2b**); R = H, R′ = *n*-Bu (**2c**); R = Me, R′ = Et (**2d**)) accompanied by evolution of quantitative amount of molecular nitrogen and hydrogen (Eq. (1)).



(1)

1

L = PMe$_2$Ph

2a: R = H, R' = Me
2b: R = H, R' = Et
2c: R = H, R' = Bu
2d: R = Me, R' = Et

The enolatorhenium complexes **2a**–**d** were isolated as analytically pure yellow (**2a**, **2b** and **2d**) or green (**2c**) crystals from a mixture of Et$_2$O and hexane. These complexes are fairly air sensitive but thermally stable under an inert gas atmosphere.

The molecular structure of **2b** was unequivocally determined by the X-ray structure analysis. The ORTEP drawing is depicted in Fig. 1 and the crystallographic data, the selected bond distances and angles are summarized in Tables 1 and 2. The enolato, the ester and four PMe$_2$Ph ligands bind with the rhenium center consisting of an octahedral geometry, where the enolato and the ester ligands coordinate mutually *cis* via cyano groups. The bond angles of N(1)–Re(1)–N(2) (79.4(5)°), N(1)–Re(1)–P(1) (82.7(4)°), N(1)–Re(1)–P(2) (92.8(4)°), N(1)–Re(1)–P(3) (167.5(4)°), and N(1)–Re(1)–P(4) (83.9(4)°) show a slight distortion from an ideal octahedral geometry. Although both the enolate and the ester ligands are essentially isomorphic, relatively shorter C(2)–C(3) bond (1.41(2) Å), longer O(1)–C(3) bond (1.23(2) Å), and smaller C(1)–C(2)–C(3)–O(1) dihedral angle (3.5°) suggest that this *N*-bonded ligand is the enolato ligand and the other is the coordinated ester ligand. The planarity of the enolato ligand suggests delocalization of electrons along these bonds. This implies a strong oxo-π-allyl character of the enolato ligand, although the slightly distorted linear C(1)–N(1)–Re(1) linkage (168.2 (13)°) and the slightly longer N(1)–C(1) bond (1.22 (2) Å) in the enolato ligand may suggest small contribution of an alternative σ-azaallenyl structure. By analogy of the previously reported *N*-bonded enolatoruthenium complexes *fac*-RuH(NCCHCO$_2$R)-(NCCH$_2$CO$_2$R)(PPh$_3$)$_3$ (R = Me,

Table 1
Crystallographic data for *cis*-Re(NCCHCO$_2$Et)(NCCH$_2$CO$_2$Et)(PMe$_2$Ph)$_4$ (**2b**)

Formula	$C_{42}H_{57}N_2O_4P_4Re$
Space group	I_4 (#82)
Unit cell dimensions	
a (Å)	31.586(3)
c (Å)	9.583(5)
V (Å^3)	9560.4(54)
Z	8
$D_{calc.}$ (g cm^{-3})	1.339
μ (Mo–K$_\alpha$)	27.15
Monochrometer	Graphite
Temperature (K)	293
Absorption correction	Empirical (ψ-scan method)
Diffractometer	Rigaku AFC-5S
Scan method	ω–2θ
Data collected	$0 \leq h \leq 44$; $0 \leq k \leq 44$; $0 \leq l \leq 13$
2θ range (°)	3.0–60.0
Reflections collected	7366
Independent reflections	4085
R_F	0.066
	0.151
Goodness-of-fit	1.098

Et) [8,9], **2b** is the best regarded as a zwitterionic enolatorhenium(I) complex. In accordance with high nucleophilicity of the enolato ligand (vide infra), the non-bonding interaction between O(1) and C(7) (3.27 Å) is observed. This may probably be due to the intramolecular hydrogen bonding between O(1) and a hydrogen in the methylene group C(7), since typical C–O bond distances involving hydrogen bonding lie in the range 3.0–4.0 Å [14]. Such intramolecular hydrogen bonding has also been observed in the *N*-bonded enolatoruthenium analogues mentioned above [8,9]. This intramolecular hydrogen bonding may encourage (*E*)-enolato form as shown in the X-ray structure of **2b**.

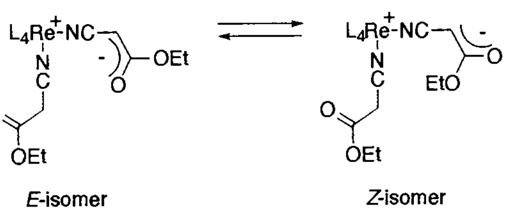
Table 2
Selected bond distances (Å) and angles (°) for Re(NC-CHCO$_2$Et)(NCCH$_2$CO$_2$Et)PMe$_2$Ph)$_4$ (**2b**)[a]

Re(1)–N(1)	2.13(2)	Re(1)–N(2)	2.057(12)
Re(1)–P(1)	2.402(5)	Re(1)–P(2)	2.350(4)
Re(1)–P(3)	2.330(4)	Re(1)–P(4)	2.419(5)
N(1)–C(1)	1.22(2)	N(2)–C(6)	1.18(2)
O(1)–C(3)	1.23(2)	O(2)–C(3)	1.34(2)
O(2)–C(4)	1.38(3)	O(3)–C(8)	1.19(2)
O(4)–C(8)	1.33(3)	O(4)–C(9)	1.45(3)
C(1)–C(2)	1.30(2)	C(2)–C(3)	1.41(2)
C(6)–C(7)	1.41(2)	C(7)–C(8)	1.56(3)
N(1)–Re(1)–N(2)	79.4(5)	N(1)–Re(1)–P(1)	82.7(4)
N(1)–Re(1)–P(2)	92.8(4)	N(1)–Re(1)–P(3)	167.5(4)
N(1)–Re(1)–P(4)	83.9(4)	C(1)–N(1)–Re(1)	168.2(13)
C(6)–N(2)–Re(1)	171.8(14)	N(1)–C(1)–C(2)	174.8(19)
C(1)–C(2)–C(3)	121.9(15)	O(1)–C(3)–O(2)	122.8(17)
O(1)–C(3)–C(2)	125.3(14)	O(2)–C(3)–C(2)	111.7(18)
N(2)–C(6)–C(7)	172.7(20)	C(6)–C(7)–C(8)	113.5(18)
O(3)–C(8)–O(4)	126.2(27)	O(3)–C(8)–C(7)	120.4(26)
O(4)–C(8)–C(7)	113.4(19)		

[a] Estimated standard deviations in the least significant figure are given in parentheses.

IR spectrum of **2b** shows characteristic two intensive peaks at 2236 and 2169 cm^{-1} which are assignable to the ν_{CN} bands of the coordinated ester and the enolato ligands, respectively. Two intensive peaks due to the ν_{CO} bands appear at 1745 and 1629 cm^{-1}. Observation of the latter lower bands is consistent with the presence of the highly delocalized oxo-π-allyl linkage. The low molar electric conductivity of **2b** in THF (0.035 S cm^2 mol^{-1}) indicates its non-ionic character, implying the zwitterionic structure.

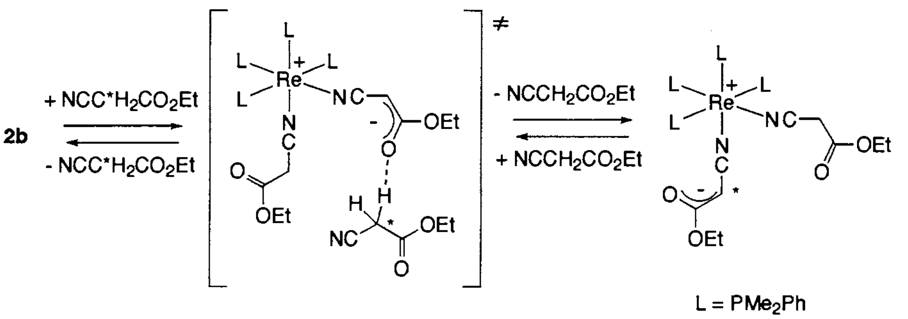
In ^{1}H-NMR spectrum of **2b**, no hydride signal was observed. A singlet at 3.75 ppm is assignable to the methine proton of the enolato ligand having no H–P coupling. This is consistent with the fact that the enolato ligand has a linkage to the rhenium center not by the methine carbon but by the nitrile group. A triplet at 1.33 ppm and a quartet at 4.39 ppm are due to an ethyl group of the enolato ligand. A broad peak at 2.69 ppm, a triplet at 0.91 ppm and a quartet at 3.71 ppm are assignable to the signals due to active methylene protons, and methylene and methyl protons of the ethyl group of the ester, respectively. A pair of virtual triplets are observed at 0.93 and 1.64 ppm being assignable to the methyl groups of PMe$_2$Ph ligands. This indicates that these two PMe$_2$Ph ligands are mutually *trans* having diastereotopic methyl groups, which lack a mirror plane of symmetry along these Re–P bonds. Thus, the enolato and coordinated ester ligands should locate in the *cis* configuration to each other. On the other hand, methyl groups of *cis*-PMe$_2$Ph ligands, which coordinate *trans* to the enolate and the ester ligands, appear close to each other as doublets at 1.68 and 1.72 ppm. This observation indicates a small difference in *trans* influence of the enolato and the ester ligands, where both ligands are coordinating to Re by the cyano group. These spectroscopic data are consistent with the X-ray structure of **2b**. ^{31}P{^{1}H}-NMR spectrum of **2b** in toluene-d$_8$ shows three broad peaks at -26.2, -22.0, and -20.1 ppm in approximately a 1:2:1 ratio at -40°C, which merge into two broad peaks at -26.9 and -22.6 ppm at room temperature. The observed three signals are consistent with the structure, where two magnetically equivalent *trans* and two unique *cis* P nuclei are present in **2b**, although fine splittings of the signals are not resolved due to extensive broadening. It should be noted that detail analysis of ^{1}H and ^{31}P{^{1}H}-NMR at low temperature indicates the presence of the other isomer (ca. 15%) for **2b** (see Section 3). This may be caused by *E* and *Z* isomerism around the enolate linkage (C(2)–C(3) bond) as shown in Scheme 1. The major isomer in solution probably have the same (*E*) structure as observed in the crystal structure, while the minor isomer would have (*Z*) configuration. Similarly, two isomers were observed for **2d** (4:3) by the NMR



Scheme 1.

spectrum, whereas no distinguishable isomers were detected for **2a** and **2c**.

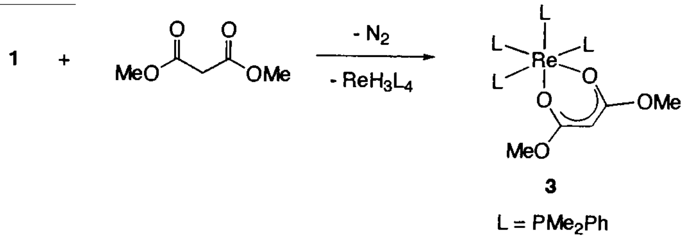
When ethyl cyanoacetate was added into a benzene-d_6 solution of **2b** at room temperature, the peaks due to the coordinated ester and enolato ligands became much broader without significant change of their chemical shifts. Line broadening of signals caused by an additive generally suggests the occurrence of some facile associative exchange process. However, in this case increasing the coordination number in **2b** is less likely, since it would produce an unfavorable 20e species. One possible interpretation for the broadening induced by the addition of ester involves deprotonation of the incoming ester by the enolate ligand giving a new enolato and ester. At the same time, the originally coordinated ester could be liberated with concomitant coordination of the newly formed enolate (Eq. (2)).



(2)

On the other hand, upon addition of ten equivalent amounts of PMe_2Ph, significant broadening of the signals due to **2b** was also observed, although the resonance of added PMe_2Ph (-43.8 ppm) remained sharp in the $^{31}P\{^1H\}$-NMR spectrum. In this case, basic phosphine may encourage the intramolecular proton transfer from the coordinated ester to the enolate. Such processes would cause the line broadening of the signals, as if there is an associative ligand exchange process.

Complex **1** also reacted with a diester such as dimethyl malonate. Treatment of **1** with dimethylmalonate gave a chelated rhenium(I) complex, $Re[OC(OMe)CHCOOMe](PMe_2Ph)_4$ (**3**) in 50% yield. In contrast to the reaction with cyanoalkyl carboxylate, the reaction yielded $ReH_3(PMe_2Ph)_4$ without evolution of molecular hydrogen (Eq. (3)). Hydrogen produced may be trapped by **1** during the slow reaction of **1** with dimethyl malonate.

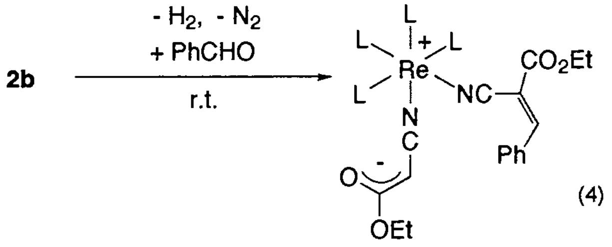


(3)

IR spectrum of **3** shows a single intensive peak at 1625 cm^{-1} due to the ν_{CO} band. The ^1H-NMR spectrum shows two singlets at 2.94 and 4.90 ppm, which are assignable to the two magnetically equivalent methoxy groups in the enolate and the methine proton of the enolato ligand having no H–P coupling. The methyl groups of two *trans*-PMe_2Ph ligands appear as a virtual triplet at 1.23 ppm, whereas those of two *cis*-PMe_2Ph ligands are observed as a doublet at 1.81 ppm. $^{31}P\{^1H\}$-NMR spectrum of **3** shows two singlets at -20.7 and -4.9 ppm with equal intensities. Absence of $J_{P\text{-}P}$ coupling may arise from the perpendicular P–Re–P angle between *cis* and *trans* P nuclei. From these spectroscopic data, the chelate structure of the enolate was proposed for **3** (Eq. (3)). It should be noted that the reaction of **3** with benzaldehyde gave no Knoevenagel products at room temperature. Analogous little reactivity of such chelated enolate ligand was observed in the enolatorhenium complexes [9].

2.2. Chemical reactivity of 2b

Enolatorhenium(I) complex **2b** reacted with 5-fold excess amount of methyl iodide at room temperature giving ethyl 2-cyanopropionate and ethyl cyanoacetate in ca. 1:1 ratio. This fact suggests that the enolato ligand in **2b** is nucleophilic enough to react with methyl iodide, but the coordinated ester remained unreacted. Accordingly, the reaction of **2b** with an equimolar amount of benzaldehyde as an electrophile in Et_2O at room temperature led to drastic color change of the solution from yellow to green and finally to deep blue. From this solution an air sensitive enolatorhenium(I) complex having an ethyl 2-cyano-3-phenylpropenoate ligand, $Re(NCCHCO_2Et)[NC(EtO_2C)C{=}CHPh](PMe_2Ph)_4$ (**4**) gradually precipitated as an analytically pure yellow powder (Eq. (4)). The enolato ligand is considered to react with benzaldehyde to give an aldolato ligand which further deprotonates the coordinated ester giving the aldol type product and enolato ligands. The resulted aldol product may finally be dehydrated to give **4**.



(4)

4

L = PMe₂Ph

IR spectrum of **4** shows two strong peaks at 2199 and 2153 cm^{-1} due to ν_{CN} bands, and 1726 and 1617 cm^{-1} due to ν_{CO} bands, of which each lower band may arise from the enolato ligand and the higher one corresponds to the signals due to ethyl 2-cyano-3-phenylpropenoate ligand. In the ^1H-NMR spectrum, a singlet at 3.95 ppm assignable to the methine proton of the *N*-bonded enolato ligand is observed. A triplet at 1.05 ppm and a quartet at 4.00 ppm are assigned to the ethyl group of the enolato ligand. Signals due to the ethyl group of the ethyl 2-cyano-3-phenylpropenoate ligand appear as a triplet at 1.36 ppm and a quartet at 4.52 ppm. The vinyl and aromatic protons are observed in the range 6.8–7.8 ppm. In the $^{31}P\{^1H\}$-NMR spectrum of **4**, three broad peaks are observed at -29.6, -26.2 and -21.0 ppm in 1:2:1 ratio at room temperature, suggesting a similar configuration of four PMe_2Ph ligands as observed in **2b**. Thus the enolato and ethyl 2-cyano-3-phenylpropenoate ligands are considered to occupy mutually *cis* in an octahedral geometry. The enolato ligand may coordinate to Re by the cyano group by analogy of the coordination mode in **2b**. Coordination mode of the ethyl 2-cyano-3-phenylpropenoate ligand is not clear at present, but it probably binds to the Re atom by the cyano group to reduce steric congestion around the Re center. Complex **4** was also obtained by the reactions of **1** with a mixture of ethyl cyanoacetate and ethyl 2-cyano-3-phenylpropenoate, as well as by the reaction of **2b** with ethyl 2-cyano-3-phenylpropenoate.

Reactions of **2b** with various substituted aromatic aldehydes such as *o*-chlorobenzaldehyde, *o*- and *p*-tolaldehydes, and *p*-methoxybenzaldehyde also gave deep blue compounds, $Re(NCCHCO_2Et)[NC(EtO_2C)C{=}CH\text{-}Ar](PMe_2Ph)_4$. Wavelengths of these strong absorption bands were insensitive to the substituents of the aryl ring (ca. $\lambda = 610$ nm, $\varepsilon = 3500$ cm^{-1} M^{-1} in benzene), being consistent with the coordination by the cyano group of ethyl 3-aryl-2-cyanopropenoate, where the coordination site is remote from the aromatic ring. The origin of this intensive color is not clear at present, but the large molar absorption extinction coefficient suggests a charge transfer between metal and ethyl 3-aryl-2-cyanopropenoate ligands. By monitoring the increase in the UV spectra at ca. 610 nm, time-course of the reactions were briefly followed. The rate of the reaction with *o*-chlorobenzaldehyde was found to be the fastest among the aldehydes employed (half life = 1 min, others = 4–10 min). The results suggest the involvement of nucleophilic addition of the enolate to the aldehyde, as previously proposed in the Ru-catalyzed aldol type reactions [9]. It is notable that the color of **4** was yellow when it was isolated from a Et_2O solution [15]. When the yellow precipitate of **4** were redissolved in THF, strong blue color appeared. The strong blue color can be kept if the excess ethyl 2-cyano-3-phenylpropenoate is present. However addition of either PMe_2Ph or ethyl cyanoacetate bleached the deep blue THF solution of **4** within 3 h at room temperature. When 124-fold excess of ethyl cyanoacetate was added to the THF solution of **4**, the half life of the bleaching reaction becomes approximately 7 min at room temperature. These results suggest that the extensive liberation of ethyl 2-cyano-3-phenylpropenoate takes place by the ligand exchange reactions with ethyl cyanoacetate showing the reversibility of this process. Addition of benzonitrile and succinonitrile into a benzene solution of **2b** at 50°C also enhanced the liberation of ethyl 2-cyano-3-phenylpropenoate with formation of uncharacterized Re compounds.

2.3. Catalytic Knoevenagel and Michael reactions by rhenium complexes

As we described above, the enolate complex **2b** was isolated from the stoichiometric reaction of **1** with ethyl cyanoacetate, where the enolato ligand can further react with benzaldehyde to give ethyl 2-cyano-3-phenylpropenoate. Since the ethyl 2-cyano-3-phenylpropenoate ligand can be replaced by ethyl cyanoacetate, the reaction of ethyl cyanoacetate with benzaldehyde would be catalytic in the presence of **1**. Thus, Re catalyzed Knoevenagel and Michael reactions were carried out under neutral and mild conditions [16–18]. Representative results are summarized in Table 3. In the presence

Table 3
Rhenium catalyzed Knoevenagel and Michael reactions[a]

Entry	Cat.	Electrophile	Active hydrogen compound	Product	Yield[b] (%)
1	**1**	PhCHO	$NCCH_2CO_2Et$	$PhCH{=}C(CN)CO_2Et$	49
2	**1**	PhCHO	$NCCH(Me)CO_2Et$	No reaction	
3	**1**	PhCHO	$NCCH_2CN$	$PhCH{=}C(CN)_2$	75
4[c]	**1**	PhCHO	$MeO_2CCH_2CO_2Me$	No reaction	
5[c]	**1**	PhCHO	$MeOCCH_2COMe$	No reaction	
6	**1**	p-MeC_6H_4CHO	$NCCH_2CO_2Et$	p-$MeC_6H_4CH{=}C(CN)CO_2Et$	45
7[d]	**1**	o-ClC_6H_4CHO	$NCCH_2CO_2Et$	o-$ClC_6H_4CH{=}C(CN)CO_2Et$	69
8	**1**	p-$MeOC_6H_4CHO$	$NCCH_2CO_2Et$	p-$MeOC_6H_4CH{=}C(CN)CO_2Et$	79
9[e]	**1**	Me_2CHCHO	$NCCH_2CO_2Et$	$Me_2CHCH{=}C(CN)CO_2Et$	61
10	**2b**	PhCHO	$NCCH_2CO_2Et$	$PhCH{=}C(CN)CO_2Et$	29
11	**2b**	p-MeC_6H_4CHO	$NCCH_2CO_2Et$	p-$MeC_6H_4CH{=}C(CN)CO_2Et$	68
12	**2b**	o-ClC_6H_4CHO	$NCCH_2CO_2Et$	o-$ClC_6H_4CH{=}C(CN)CO_2Et$	72
13	**2b**	p-$MeOC_6H_4CHO$	$NCCH_2CO_2Et$	p-$MeOC_6H_4CH{=}C(CN)CO_2Et$	43
14	**2b**	Me_2CHCHO	$NCCH_2CO_2Et$	$Me_2CHCH{=}C(CN)CO_2Et$	20
15	**4**	PhCHO	$NCCH_2CO_2Et$	$PhCH{=}C(CN)CO_2Et$	26
16	**4**	p-MeC6H4CHO	$NCCH_2CO_2Et$	p-$MeC_6H_4CH{=}C(CN)CO_2Et$	65
17	**4**	o-ClC_6H_4CHO	$NCCH_2CO_2Et$	o-$ClC_6H_4CH{=}C(CN)CO_2Et$	82
18	**4**	p-$MeOC_6H_4CHO$	$NCCH_2CO_2Et$	p-$MeOC_6H_4CH{=}C(CN)CO_2Et$	58
19	**1**	$CH_2{=}CHCN$	$NCCH_2CO_2Et$	$(NCCH_2CH_2)_2C(CN)CO_2Et$	77
20	**1**	$CH_2{=}CHCO_2Me$	$NCCH_2CO_2Et$	$(MeO_2CCH_2CH_2)_2C(CN)CO_2Et$	70
21	**1**	$CH_2{=}CHCOMe$	$NCCH_2CO_2Et$	$MeOCCH_2CH_2CH(CN)CO_2Et$	45

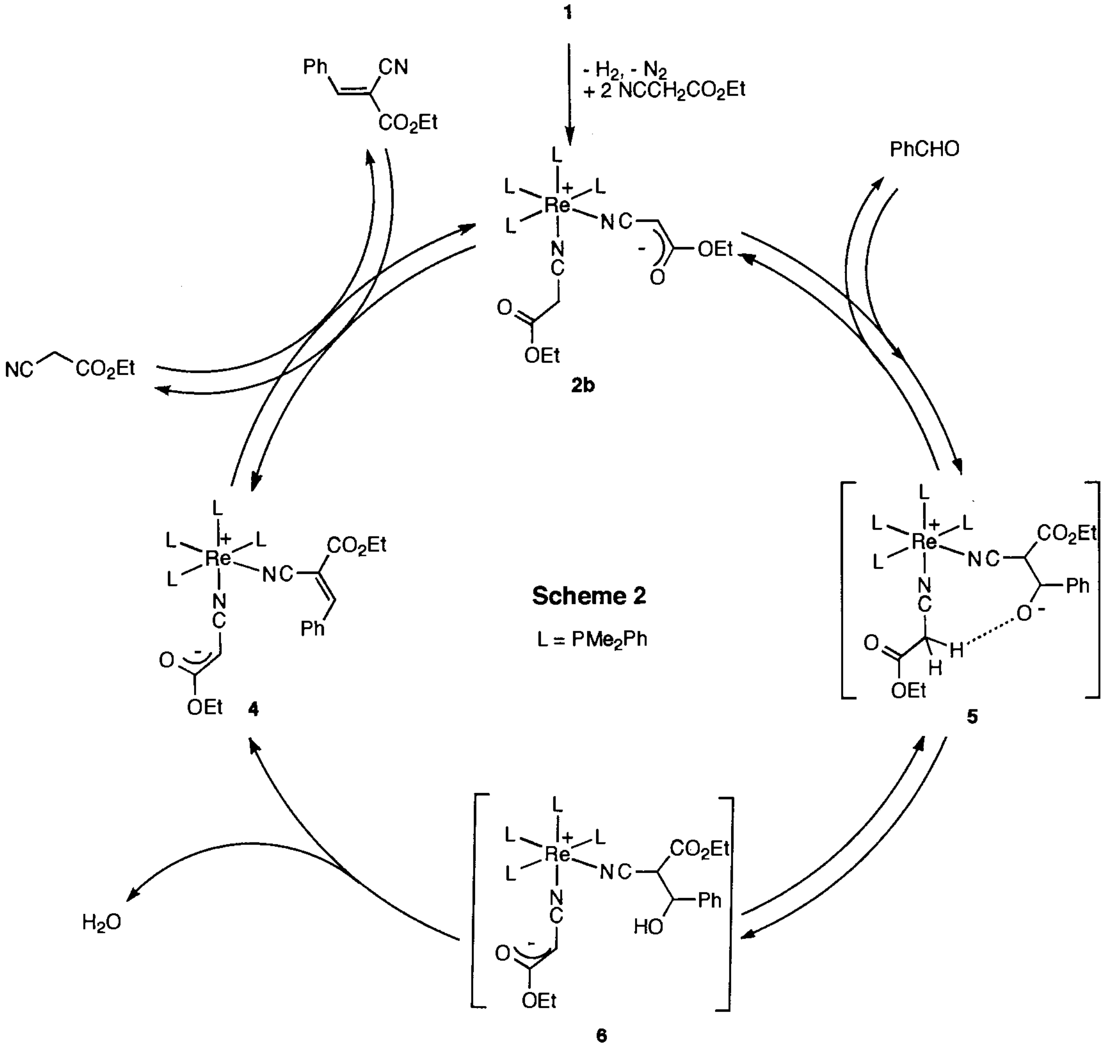
[a] A typical catalysis was carried out in a mixture of electrophile (0.79 mmol), active hydrogen compound (0.79 mmol) and catalyst (1.0 mol.%) in benzene (1.0 ml) for 14 h at r.t. under nitrogen.
[b] Isolated yield.
[c] Reaction time 72 h.
[d] Reaction time 18 h.
[e] Cat. = 7.0 mol.%.

of catalytic amount of **1**, ethyl cyanoacetate smoothly reacted with benzaldehyde to give ethyl 2-cyano-3-phenylpropenoate in benzene at room temperature (entry 1). However, no reaction took place for ethyl 2-cyanopropionate (entry 2). While reaction of benzaldehyde with malononitrile ($pK_a = 11$) smoothly proceeded (entry 3), no reaction was observed with dimethyl malonate ($pK_a = 13$) nor 2,4-pentanedione ($pK_a = 9$) (entries 4 and 5). Such significant difference in the catalytic activity is similar to the analogous reactions catalyzed by Ru complexes, where the nucleophilicity of the enolate is increased by the zwitterionic character [8,9]. In fact the enolate **2b** derived from cyanoester smoothly reacted with benzaldehyde to give the product, but the enolate **3** derived from dimethyl malonate showed no reactivity toward benzaldehyde (see Section 3). Knoevenagel reactions of substituted aryl and alkyl aldehydes with nitrile were also successfully catalyzed by **1** (entries 6–9). Both of the isolated enolatorhenium complexes **2b** and **4** also catalyzed the Knoevenagel reactions, indicating that **2b** and **4** are active intermediates in the catalysis (entries 10–18).

Another representative nucleophilic reactions catalyzed by the enolatorhenium complex were also performed. Thus, Michael additions of ethyl cyanoacetate to acrylonitrile, methyl acrylate and methyl vinyl ketone catalyzed by **1** smoothly took place at room temperature (run 19–21).

On the basis of these results, a plausible mechanism for the catalytic Knoevenagel reaction of ethyl cyanoacetate with benzaldehyde by rhenium enolate is proposed as outlined in Scheme 2. The first step involves the formation of enolatorhenium complex **2b** by the reaction of **1** with ethyl cyanoacetate with evolution of molecular hydrogen and nitrogen. The enolato ligand in **2b** would be nucleophilic enough to abstract a proton from the coordinated ester as discussed above. Then, direct attack of the enolato ligand toward benzaldehyde probably takes place to give intermediate **5**. After migration of the methylene proton of the coordinated ester to the aldolato ligand (intermediate **6**), (enolato)(ethyl 2-cyano-3-phenylpropenoate)rhenium(I) complex **4** is formed with dehydration process. The dehydration process undergoes rapidly and irreversibly, though the mechanism is still unclear. The coordinated ethyl 2-cyano-3-phenylpropenoate is replaced by ethyl cyanoacetate to complete the catalytic cycle. It is worthwhile to note that only (enolato)(ethyl cyanoacetate)ruthenium complex was observable during the catalysis for the ruthenium analogue. The final ligand displacement step giving ethyl 2-cyano-3-phenylpropenoate and **2b** should be reversible, since independent experiment of **2b** with ethyl 2-cyano-3-phenylpropenoate gave **4**.

In summary, N-bonded enolatorhenium(I) complex **2** was derived by the treatment of hydrido(dinitro-



Scheme 2.

gen)rhenium(I) complex **1** with cyanocarboxylates. These complexes are highly nucleophilic to catalyze Knoevenagel and Michael reactions due to its zwitterionic character.

3. Experimental section

3.1. General

All manipulations were performed under nitrogen or argon using standard Schlenk and vacuum-line techniques. Benzene, toluene, hexane and Et_2O dried over calcium chloride, and THF dried over calcium hydride were distilled from potassium benzophenone ketyl under nitrogen prior to use. Acetone was dried over Drierite and distilled from fresh Drierite under nitrogen atmosphere. Ethanol was distilled from magnesium ethoxide under nitrogen. Methyl-, ethyl- and *n*-butyl cyanoacetate, ethyl 2-cyanopropionate and benzaldehyde (Tokyo Kasei) were dried over calcium chloride and distilled under reduced pressure and then kept under nitrogen atmosphere. Ethyl (*E*)-2-cyano-3-phenylpropenoate (Kasei, Tokyo) and potassium perrhenate (Strem) were used as received. PMe_2Ph was prepared by the reaction of dichlorophenylphosphine with a Grignard reagent. *cis*-$ReH(N_2)(PMe_2Ph)_4$ (**1**) was synthesized according to the procedure published in our previous paper [12]. ^1H-NMR spectra were recorded on a JEOL FX-200 or a LA-300 spectrometer and chemical shifts were reported in ppm from tetramethylsilane. $^{31}P\{^1H\}$-NMR spectra were recorded on a JEOL LA-300 spectrometer at 121.55 MHz and chemical shifts were given relative to external 85% H_3PO_4 in D_2O. IR spectra were recorded on a JASCO A-302 or a FT/IR-5M spectrometer. UV-Vis spectra were recorded on Shimadzu UV-120-02 under nitrogen [19]. Mass spectra were recorded on a Shimadzu GC-MS spectrometer (QP-2000A) with a TC-wax glass capillary column (0.25∅ × 30 m). GLC analyses were performed with Shimadzu GC-8APF, GC-3BT or GC-14B gas liquid phase chromatographs using glass packed Porapack-Q and Unicarbon A-400, stainless packed molecular sieves, active carbon, and capillary TC-wax and HR-1 columns. The volume of generated gases was measured by Toepler pump. Melting points were measured under nitrogen with Yazawa capillary melting apparatus and the values were uncorrected. Elemental analyses were performed with Yanaco MT-2 CHN auto corder or Perkin Elmer 2400 series II CHN analyzer.

3.2. Preparation of $Re(NCCHCO_2R)(NCCH_2CO_2R)(PMe_2Ph)_4$ (**2**)

Methyl cyanoacetate (50.0 µl, 0.570 mmol) was added to a Et_2O (5 ml) solution of *cis*-$ReH(N_2)(PMe_2Ph)_4$ (**1**) (145.1 mg, 0.189 mmol) and the solution was stirred for 6 h at room temperature. The solution color slowly changed from yellow to greenish yellow. During the reaction, nitrogen and hydrogen gases were generated in 68 and 55%, respectively. Evaporation of the solvent followed by recrystallization from Et_2O/hexane gave air sensitive yellow crystals of $Re(NCCHCO_2Me)(NCCH_2CO_2Me)(PMe_2Ph)_4$ (**2a**) (123.0 mg, 0.131 mmol, 69%). ^1H-NMR (200 MHz, C_6D_6, r.t.): δ 0.92 (br. s, 6H, P–CH_3), 1.69 (br. s, 6H, P–CH_3), 1.69 (d, $J = 7$ Hz, 12H, P–CH_3), 2.65 (s, 2H, NCCH_2–), 3.17 (s, 3H, –OCH_3), 3.89 (s, 3H, –OCH_3), 3.93 (s, 1H, NCCH–), 6.9–7.6 (m, 20H, P–*Ph*). IR (KBr, cm^{-1}): 2236 (s, ν_{CN}), 2166 (s, ν_{CN}), 1751 (s, ν_{CO}), 1627 (s, ν_{CO}). M.p.(dec.): 150–152°C. Anal. Found: C, 50.57; H, 6.33; N, 3.22%. Calc. for $C_{40}H_{53}N_2O_4P_4Re$: C, 51.33; H, 5.71; N, 2.99%.

$Re(NCCHCO_2Et)(NCCH_2CO_2Et)(PMe_2Ph)_4$ (**2b**), $Re(NCCHCO_2Bu)(NCCH_2CO_2Bu)(PMe_2Ph)_4$ (**2c**) and $Re(NCCMeCO_2Et)(NCCHMeCO_2Et)(PMe_2Ph)_4$ (**2d**) were prepared analogously and their yields, m.p., analytical and spectroscopic data are listed below.

2b: From **1** (269.7 mg, 0.351 mmol) and ethyl cyanoacetate (120 µl, 1.12 mmol), hydrogen and nitrogen gases were evolved in 98% and 96%, respectively. Yield, 203.6 mg, 74%. Complex **2b** is found to have two isomers, which are likely to be due to (*E*)- and (*Z*)-isomers of the enolato ligand. The population of these isomers is approximately 85/15. No significant change of the population was observed within VT NMR temperature range (27– −40°C). Major isomer: ^1H-NMR (300 MHz, $C_6D_5CD_3$, 27°C): δ 0.91 (t, $J = 7$ Hz, 3H, –OCH$_2$–CH_3 of the ester), 0.93 (virtual triplet, $J = 4$ Hz, 6H, mutually *trans*-P–CH_3), 1.33 (t, $J = 7$ Hz, 3H, –OCH$_2$–CH_3 of the enolate), 1.64 (virtual triplet, $J = 3$ Hz, 6H, mutually *trans*-P–CH_3), 1.68 (d, $J = 5$ Hz, 6H, P–CH_3 *trans* to the enolate or the ester), 1.72 (d, $J = 5$ Hz, 6H, P–CH_3 *trans* to the ester or the enolate), 2.69 (br, 2H, NCCH_2–), 3.71 (q, $J = 7$ Hz, 2H, –OCH_2–CH$_3$ of the ester), 3.75 (s, 1H, NCCH–), 4.39 (q, $J = 7$ Hz, 2H, –OCH_2–CH$_3$ of the enolate), 6.9–7.6 (m, 20H, P–*Ph*). $^{31}P\{^1H\}$-NMR (121.6 MHz, $C_6D_5CD_3$, 27°C): δ −26.9 (br, 1P), −22.6 (br, 3P); (0°C): δ −26.6 (br. s, 1P), −22.4 (br. s, 2P), −20.6 (br. s, 1P); (−10°C): δ −26.6 (br. s, 1P), −22.3 (br. s, 2P), −20.6 (br. s, 1P); (−20°C): δ −26.4 (br. s, 1P), −22.2 (br. s, 2P), −20.3 (br. s, 1P); (−30°C): δ −26.3 (br. s, 1P), −22.2 (br. s, 2P), −19.2 (br. s, 1P); (−40°C): δ −26.2 (br. s, 1P), −22.0 (br. s, 2P), −20.1 (br. s, 1P). Minor isomer: Overlapping of signals due to the minor isomer with the major ones prevented complete characterization and only several peaks are assigned. ^1H-NMR ($C_6D_5CD_3$, 27°C): δ 4.49 (q, $J = 7$ Hz, 2H, –OCH_2–CH$_3$ of the enolate); (10°C): δ 3.74 (q, $J = 7$ Hz, 2H, –OCH_2–CH$_3$ of the ester), 4.48 (q, $J = 7$ Hz, 2H, –OCH_2–CH$_3$ of the enolate); (0°C): δ 0.95 (t, $J = 7$ Hz, 3H, –OCH$_2$–CH_3 of the ester), 3.74 (q, $J = 7$ Hz, 2H, –OCH_2–CH$_3$ of the ester), 4.49 (q, $J = 7$ Hz, 2H, –OCH_2–CH$_3$ of the enolate); (−10°C): δ 0.93 (t, $J = 7$ Hz, 3H, –OCH$_2$–CH_3 of the ester), 3.73 (q, $J = 7$Hz, 2H, –OCH_2–CH$_3$ of the ester), 4.52 (q, $J = 7$ Hz, 2H, –OCH_2–CH$_3$ of the enolate); (−20°C): δ 0.89 (t, $J = 7$ Hz, 3H, –OCH$_2$–CH_3 of the ester), 3.70 (q, $J = 7$ Hz, –OCH_2–CH$_3$ of the ester), 4.53 (q, $J = 7$Hz, –OCH_2–CH$_3$ of the enolate); (−30°C): δ 0.90 (t, $J = 7$ Hz, 3H, –OCH$_2$–CH_3 of the ester), 3.63 (br., 1H, NCCH–), 3.68 (q, $J = 7$ Hz, –OCH_2–CH$_3$ of the ester), 4.51 (q, $J = 7$Hz, –OCH_2–CH$_3$ of the enolate); (−40°C): δ 0.90 (t, $J = 7$ Hz, 3H, –OCH$_2$–CH_3 of the ester), 2.91 (br. s., 2H, NCCH_2–), 3.63 (q, $J = 7$ Hz, 2H, –OCH_2–CH$_3$ of the ester), 3.67 (s, 1H, NCCH–), 4.52 (q, $J = 7$ Hz, 2H, –OCH_2–CH$_3$ of the enolate). $^{31}P\{^1H\}$-NMR (121.6 MHz, $C_6D_5CD_3$, 0°C): δ −26.6 (br. s, overlapped with a peak of the major species), −21.6 (br. s, 2P), −20.0 (br. s, 1P); (−10°C): δ −26.6 (br. s, overlapped with a peak of the major species), −21.5 (br. s, 2P), −19.4 (br. s, 1P); (−20°C): δ −26.4 (br. s, overlapped with a peak of the major species), −21.4 (br. s, 2P), −19.3 (br. s, 1P); (−30°C): δ −26.3 (br. s, 1P overlapped with a peak of the major species), −21.3 (br. s, 2P), −19.2 (br. s, 1P); (−40°C): δ −26.2 (br. s, 1P, overlapped with a peak of the major species), −21.2 (br. s, 2P), −19.0 (br. s, 1P). IR (KBr, cm^{-1}): 2236 (s, ν_{CN}), 2169 (s, ν_{CN}), 1745 (s, ν_{CO}), 1629 (s, ν_{CO}). UV-Vis (C_6H_6, r.t.): $\lambda_{max} = 610$ nm, $\varepsilon = 3500$ M^{-1} cm^{-1}. Molar electric conductivity: 0.035 S cm^2 mol^{-1} (THF, 25°C). M.p.(dec.): 94–95°C. Anal. Found: C, 52.21; H, 6.05; N, 2.85%. Calc. for $C_{42}H_{57}N_2O_4P_4Re$: C, 52.33; H, 5.96; N, 2.91%.

2c: From **1** (92.6 mg, 0.121 mmol) and n-butyl cyanoacetate (36.0 µl, 0.253 mmol). Yield, 64.3 mg, 52%. ^1H-NMR (200 MHz, C_6D_6, r.t.): δ 0.79 (br, 3H, –OC$_3$H$_6$–CH_3), 0.91 (br. s, 6H, P–CH_3), 1.07 (br, 3H, –OC$_3$H$_6$–CH_3), 1.0–1.6 (br, 8H, –OCH$_2$–C$_2H_4$–), 1.69 (br. s, 6H, P–CH_3), 1.69 (br, 12H, P–CH_3), 2.74 (s, 2H, NCC*H*$_2$–), 3.76 (br, 2H, –OC*H*$_2$–), 3.96 (s, 1H, NCC*H*–), 4.44 (br, 2H, –OC*H*$_2$–), 6.9–7.8 (m, 20H, P–*Ph*). IR (KBr, cm^{-1}): 2226 (s, ν_{CN}), 2165 (s, ν_{CN}), 1744 (s, ν_{CO}), 1622 (s, ν_{CO}). M.p.(dec.): 113–114°C. Anal. Found: C, 53.62; H, 6.61; N, 3.04%. Calc. for $C_{46}H_{65}N_2O_4P_4Re$: C, 54.17; H, 6.42; N, 2.75%.

2d: From **1** (88.1 mg, 0.115 mmol) and ethyl 2-cyanopropionate (30.0 μl, 0.238 mmol) hydrogen and nitrogen gases were evolved in 92 and 100%, respectively. Yield, 76.0 mg, 64%. Two stereoisomers arisen from the (*E*)- and (*Z*)-enolato ligands were observed in ca. 4:3 ratio. ^{1}H-NMR (200 MHz, C_6D_6, r.t.): δ 0.90 (br. s, 12H, P–C*H*$_3$), 0.90–0.97 (m, 12H, –OCH$_2$–C*H*$_3$), 1.38 (br. s, 12H, P–C*H*$_3$), 2.48 (s, 3H, NC-C(C*H*$_3$)– of minor isomer), 2.5 (br, 1H, NCC*H*(CH$_3$)–), 2.53 (s, 3H, NCC(C*H*$_3$)– of major isomer), 3.8 (m, 4H, –OC*H*$_2$–), 4.6 (m, 4H, –OC*H*$_2$–), 6.9–7.8 (m, 20H, P-*Ph*). IR (KBr, cm^{-1}): 2221 (s, ν_{CN}), 2152 (s, ν_{CN}), 1742 (s, ν_{CO}), 1615 (s, ν_{CO}). M.p.(dec.): 64–66°C. Anal. Found: C, 52.41; H, 6.61; N, 3.44%. Calc. for $C_{44}H_{61}N_2O_4P_4Re$: C, 53.27; H, 6.20; N, 2.82%.

*3.3. Reaction of **2b** with methyl iodide*

Methyl iodide (11.9 μl, 0.191 mmol) was added into a benzene solution (2 ml) of **2b** (36.7 mg, 0.0382 mmol) and the reaction mixture was stirred for 36 h at room temperature. The color of the solution turned from yellow to reddish brown during the reaction. GLC analysis of the solution showed evolution of ethyl cyanoacetate (0.0199 mmol, 52%) and ethyl 2-cyanopropionate (0.0169 mmol, 44%).

*3.4. Reaction of **2b** with ethyl cyanoacetate in benzene-d$_6$*

Ethyl cyanoacetate was added to an oxygen free benzene-d$_6$ solution (300 μl) of **2b** (11.7 mg, 0.0121 mmol) in 5 mm diameter NMR tube with an Aldrich rubber septum in a stepwise manner by using hypodermic syringe. NMR spectra of the reaction mixture were measured at room temperature at the following ratios of added ethyl cyanoacetate to Re: 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.2, 2.6, 3.0, 3.5, 4.0, 5.0, 8.0, and 10.0.

*3.5. Reaction of **2b** with dimethylphenylphosphine in benzene-d$_6$*

By the similar way described above, one and then nine equivalent amounts of dimethylphenylphosphine were added into the benzene-d$_6$ solution (600 μl) of **2b** (8.8 mg, 0.0091 mmol) and ^{1}H- and ^{31}P{^{1}H}-NMR spectra were measured at room temperature.

*3.6. Preparation of Re[OC(OMe)CHCOOMe](PMe$_2$Ph)$_4$ (**3**)*

Dimethyl malonate (15.0 μl, 0.131 mmol) was added to a benzene solution (2 ml) of **1** (99.3 mg, 0.129 mmol) and the reaction mixture was stirred for 5 h at room temperature. After removal of benzene, fractional recrystallization of the resulted solid from Et$_2$O gave orange crystals of **3** (55.7 mg, 0.0640 mmol, 50%) and ReH$_3$–(PMe$_2$Ph)$_4$ as a yellow powder (24.4 mg, 0.0329 mmol, 25%). ^{1}H-NMR (300 MHz, C_6D_6): δ 1.23 (virtual triplet, $J = 3$ Hz, P*Me*$_2$Ph, 12H), 1.81 (d, $J = 7$ Hz, P*Me*$_2$Ph, 12H), 2.94 (s, O*Me*, 6H), 4.90 (s, =C*H*–, 1H), 6.97–7.60 (m, PMe$_2$*Ph*, 20H). ^{31}P{^{1}H}-NMR (121.6 MHz, C_6D_6): δ −20.7 (s, 2P), −4.9 (s, 2P). IR (KBr, cm^{-1}): 1625 (s, ν_{CO}).

*3.7. Reaction of Re[OC(OMe)CHCOOMe](PMe$_2$Ph)$_4$ (**3**) with benzaldehyde*

Benzaldehyde (10 μl, 0.094 mmol) was added to a C_6D_6 solution (600 μl) of **3** (17.8 mg, 0.0204 mmol) with 1,4-dioxane (0.4 μl) as an internal standard and the reaction mixture was stirred at room temperature for 3 days. Although **3** partially decomposed to give unidentified products, 91% of benzaldehyde remained unreacted.

*3.8. Preparation of Re(NCCHCO$_2$Et)[NC(EtO$_2$C)C=CHPh](PMe$_2$Ph)$_4$ (**4**)*

Method A: Benzaldehyde (44.0 μl, 0.435 mmol) was added to an Et$_2$O solution (5 ml) of **2b** (211.7 mg, 0.220 mmol). The color of the solution changed from yellow to deep green and finally to dark blue. A yellow powder was formed within a few hours. After 1 day at room temperature, the deep blue solution was removed by filtration and the resulting yellow precipitate was washed with cold pentane to give **4** (156.8 mg, 68%). Complex **4** can also be synthesized in benzene (89%). ^{1}H-NMR (200 MHz, C_6D_6): δ 0.88 (s, 6H, P–C*H*$_3$), 1.05 (t, $J = 7.1$ Hz, 3H, –OCH$_2$–C*H*$_3$), 1.36 (t, $J = 7.1$ Hz, 3H, –CH$_2$C*H*$_3$), 1.74 (s, 6H, P–C*H*$_3$), 1.80 (d, $J = 6.6$ Hz, 12H, P–C*H*$_3$), 3.95 (s, 1H, NCC*H*–), 4.00 (q, $J = 7.3$ Hz, 2H, –OC*H*$_2$–), 4.52 (q, $J = 7.1$ Hz, 2H, –OC*H*$_2$–), 6.7–7.8 (m, 26H, P–*Ph*, C=CH–*Ph*, C=C–*H*). ^{31}P{^{1}H}-NMR (C_6D_6): δ −29.6 (br), −26.2 (br), −21.0 (br). IR (KBr, cm^{-1}): 2199 (s, ν_{CN}), 2153 (s, ν_{CN}), 1726 (s, ν_{CO}), 1617 (s, ν_{CO}). Anal. Found: C, 55.62; H, 6.14; N, 2.76%. Calc. for $C_{49}H_{61}N_2O_4P_4Re$: C, 55.94; H, 5.84; N, 2.66%.

Method B: Ethyl (*E*)-2-cyano-3-phenylpropenoate (13.6 mg, 0.0677 mmol) and ethyl cyanoacetate (8.0 μl, 0.075 mmol) were added to a toluene solution (2 ml) of **1** (43.5 mg, 0.0566 mmol). During the reaction at room temperature, the solution color changed from yellow to green and then dark blue in 12 h. Hydrogen and nitrogen gases were generated in 100 and 76%, respectively. After evaporation of toluene under reduced pressure, the resulting blue powder was washed by cold hexane repeatedly, and dried in vacuo to give **4** as a blue powder (20.0 mg, 0.0190 mmol, 36%).

Method C: Ethyl (*E*)-2-cyano-3-phenyl-propenoate (19 mg, 0.095 mmol) was added to a benzene solution (2 ml) of **2b** (30.4 mg, 0.0315 mmol), and then the color of the solution changed from yellow to deep green and finally to dark blue. After 1 day at room temperature, the solvent was removed by evaporation and the resulting dark blue powder was washed with cold hexane to give **4** (27.8 mg, 0.0264 mmol, 84%).

Similar reactions of **2b** with various substituted benzaldehydes also gave [alkyl (*E*)-2-cyano-3-arylpropenoate](enolato)rhenium(I) complexes. Following are the yields, IR data and elemental analysis.

Re(NCCHCO$_2$Me)[NC(MeO$_2$C)C=CH(C$_6$H$_4$Me-4)]–(PMe$_2$Ph)$_4$; 60%; IR (KBr, cm^{-1}): 2135 (s, ν_{CN}), 1743 (s, ν_{CO}), 1617 (s, ν_{CO}); UV-Vis (C$_6$H$_6$, r.t.): $\lambda_{max} = 594$ nm. Anal. Found: C, 54.47; H, 6.12; N, 2.55%. Calc.: C, 55.54, H, 5.79, N, 2.69%.

Re–(NCCHCO$_2$Et)[NC(EtO$_2$C)C=CH(C$_6$H$_4$Cl-2)] (PMe$_2$Ph)$_4$; 36%, IR (KBr, cm^{-1}): 2199 (s, ν_{CN}), 2152 (s, ν_{CN}), 1732 (s, ν_{CO}), 1608 (s, ν_{CO}), UV-Vis (C$_6$H$_6$, r.t.): $\lambda_{max} = 610$ nm. Anal. Found: C, 53.29; H, 5.60; N, 2.84%. Calc.: C, 54.16; H, 5.57; N, 2.58%.

The following complexes were characterized only by spectroscopic methods.

Re(NCCHCO$_2$Me)[NC(MeO$_2$C)C=CH(C$_6$H$_4$Cl-2)] (PMe$_2$Ph)$_4$; 46%, IR (KBr, cm^{-1}): 2228 (s, ν_{CN}), 2168 (s, ν_{CN}), 1743 (s, ν_{CO}), 1616 (s, ν_{CO}). Re(NCCHCO$_2$Me)[NC(MeO$_2$C)C=CH(C$_6$H$_4$OMe-4)](PMe$_2$Ph)$_4$; 46%, IR (KBr, cm^{-1}): 2155 (s, ν_{CN}), 1732 (s, ν_{CO}), 1608 (s, ν_{CO}). Re(NCCHCO$_2$Et)[NC–(EtO$_2$C)C=CH-(C$_6$H$_4$Me-4)](PMe$_2$Ph)$_4$; 73%; IR (KBr, cm^{-1}): 2220 (s, ν_{CN}), 2116 (s, ν_{CN}), 1715 (s, ν_{CO}), 1614 (s, ν_{CO}), UV-Vis (C$_6$H$_6$, r.t.): $\lambda_{max} = 592$ nm. Re–(NCCHCO$_2$Et) [NC(EtO$_2$C)C=CH(C$_6$H$_4$Me-2)](PMe$_2$Ph)$_4$; 41%, IR (KBr, cm^{-1}): 2192 (s, ν_{CN}), 2163 (s, ν_{CN}), 1728 (s, ν_{CO}), 1618 (s, ν_{CO}), UV-Vis (C$_6$H$_6$, r.t.): $\lambda_{max} = 600$ nm. Re(NCCHCO$_2$Et)[NC(EtO$_2$C)C=CH(C$_6$H$_4$OMe-4)] (PMe$_2$Ph)$_4$; 54%, IR (KBr, cm^{-1}): 2140 (s, ν_{CN}), 1713 (s, ν_{CO}), 1614 (s, ν_{CO}), UV-Vis (C$_6$H$_6$, r.t.): $\lambda_{max} = 598$ nm.

3.9. Catalytic Knoevenagel reaction of benzaldehyde with ethyl cyanoacetate by 1

Ethyl cyanoacetate (80 µl, 0.75 mmol) and benzaldehyde (72 µl, 0.75 mmol) were added to a benzene solution (1 ml) of **1** (11.5 mg, 0.0150 mmol). The reaction mixture was stirred at room temperature for 12 h, during which the solution color changed from yellow to deep blue. After evaporation of benzene, the resulting powder was dissolved in benzene-d$_6$ with internal standard (dioxane, 10 µl). Formation of ethyl (*E*)-2-cyano-3-phenylpropenoate (0.37 mmol, 49%) was confirmed by the ^{1}H-NMR spectrum. ^{1}H-NMR (200 MHz, C$_6$D$_6$): δ 1.00 (t, $J = 7.1$ Hz, 3H, –CH$_2$CH_3), 4.00 (q, $J = 7.1$ Hz, 2 H, –CH_2CH$_3$), 7.02 (m, 3H, –*Ph*), 7.70 (m, 2H, –*Ph*), 8.04 (s, 1H, C=C–*H*).

Catalytic Knoevenagel reactions of ethyl cyanoacetate with other substituted benzaldehydes promoted by **1** and **2b** were performed analogously and the results are summarized in Table 2. ^{1}H-NMR data for substituted ethyl cyanopropenoate in C$_6$D$_6$ were listed below: ethyl 2-cyano-3-(*p*-tolyl)propenoate: δ 1.00 (t, $J = 7.1$ Hz, 3H, –CH$_2$CH_3), 1.93 (s, 3H, C$_6$H$_4$–CH_3), 4.00 (q, $J = 7.1$ Hz, 2 H, –CH_2CH$_3$), 7.02 (m, 3H, –C$_6$H$_4$–), 7.70 (m, 2H, –C$_6$H$_4$–), 8.04 (s, 1H, C=C–*H*(tol)); ethyl 2-cyano-3-(*p*-anisyl)propenoate: δ 1.00 (t, $J = 8$ Hz, 3H, –CH$_2$CH_3), 3.2 (s, 3H, –OCH_3), 4.00 (q, $J = 8$ Hz, 2H, –CH_2CH$_3$), 6.5 (d, $J = 8$ Hz, 2H, –C$_6H_4$–), 7.7 (d, $J = 8$ Hz, 2H, –C$_6H_4$–), 8.0 (s, 1H, C=C(anisyl)–*H*); ethyl 2-cyano-3-(*o*-chlorophenyl)propenoate: δ 0.9 (t, $J = 8$ Hz, 3H, –CH$_2$CH_3), 4.0 (q, $J = 8$ Hz, 2 H, –CH_2CH$_3$), 6.9 (m, 2H, –C$_6H_4$–Cl), 8.1 (m, 2H, –C$_6$H$_4$–Cl), 8.6 (s, 1H, C=C–*H*(C$_6$H$_4$Cl)); ethyl 2-cyano-4-methyl-2-pentenoate: δ 0.62 (d, $J = 6.9$ Hz, 6H, –CH$_2$(CH_3)$_2$), 0.92 (t, $J = 7.4$ Hz, 3H, –CH_2CH$_3$), 2.6–2.8 (m, 1H, –C*H*(CH$_3$)$_2$), 3.92 (q, $J = 7.4$ Hz, 2 H, –CH_2CH$_3$), 7.20 (d, $J = 10.2$ Hz, 1H, =C*H*–CH(CH$_3$)$_2$).

3.10. Catalytic Michael reaction of acrylonitrile with ethyl cyanoacetate by 1

Ethyl cyanoacetate (130 µl, 1.22 mmol) and acrylonitrile (80 µl, 1.2 mmol) were added to a benzene solution (1 ml) of **1** (13.4 mg, 0.0175 mmol). The reaction mixture was stirred at room temperature for 12 h, during which the solution color changed from yellow to light brown. After removal of benzene in vacuo, the resulting powder was dissolved in benzene-d$_6$ with an internal standard (dioxane). 1,3,5-Tricyano-3-ethoxycarbonylpentane (0.94 mmol, 77%) was detected by ^{1}H-NMR. ^{1}H-NMR (200 MHz, C$_6$D$_6$): δ 1.00 (t, $J = 6.8$ Hz, 3H, –CH$_2$CH_3), 1.29 (dt, $J = 14.1$, 2.2 Hz, 2H, NCCH$_2$CH_2), 1.60 (dt, $J = 14.1$, 2.2 Hz, 2H,NCCH$_2$CH_2), 1.83 (t, $J = 7.4$ Hz, 4H, NCCH_2-), 4.00 (q, $J = 6.8$ Hz, 2H, –CH_2CH$_3$).

Michael additions of ethyl cyanoacetate to methyl acrylate and methyl vinyl ketone were performed similarly and the results are summarized in Table 3. ^{1}H-NMR assignment for the products in C$_6$D$_6$ are shown below: dimethyl 4-cyano-4-ethoxycarbonyl-pimelate: δ 0.85 (t, $J = 7.3$ Hz, 3H, –CH$_2$CH_3), 1.88–2.61 (m, 8H, –CH_2CH_2CO$_2$CH$_3$), 3.33 (s, 6H, –CO$_2$CH_3), 3.82 (q,

Table 4
Atomic coordinates for **2b**

	x	y	z	U_{eq}
Re1	0.10670(2)	0.23637(2)	0.92583(6)	0.03222(15)
P1	0.11176(14)	0.16132(15)	0.9628(5)	0.0426(11)
P2	0.17340(14)	0.2393(2)	0.8177(5)	0.0416(11)
P3	0.12707(14)	0.2516(2)	1.1541(4)	0.0411(10)
P4	0.09059(14)	0.30700(15)	0.8439(5)	0.0396(10)
N1	0.0760(5)	0.2171(4)	0.7384(17)	0.048(4)
N2	0.0453(4)	0.2306(4)	0.9949(14)	0.033(3)
O1	−0.0335(4)	0.1929(6)	0.7024(16)	0.076(5)
O2	−0.0384(5)	0.1648(6)	0.4868(17)	0.097(6)
O3	−0.0938(5)	0.2366(7)	1.1665(27)	0.121(9)
O4	−0.0295(5)	0.2558(6)	1.2454(20)	0.097(6)
C1	0.0531(5)	0.2029(5)	0.6473(19)	0.041(4)
C2	0.0263(6)	0.1869(6)	0.5594(19)	0.063(6)
C3	−0.0167(6)	0.1816(6)	0.5930(21)	0.055(5)
C4	−0.0799(9)	0.1551(13)	0.5191(30)	0.122(13)
C5	−0.0803(11)	0.1051(14)	0.5244(38)	0.161(17)
C6	0.0095(6)	0.2238(6)	1.0214(20)	0.049(4)
C7	−0.0335(5)	0.2123(7)	1.0378(22)	0.060(6)
C8	−0.0562(7)	0.2364(7)	1.1590(32)	0.080(8)
C9	−0.0491(11)	0.2703(11)	1.3737(28)	0.130(13)
C10	−0.0262(11)	0.3074(12)	1.4040(45)	0.164(18)
C11	0.1256(7)	0.1290(7)	0.8110(29)	0.080(7)
C12	0.1471(5)	0.1341(6)	1.0825(25)	0.062(6)
C13	0.0613(5)	0.1328(5)	1.0052(22)	0.045(5)
C14	0.0511(8)	0.1230(9)	1.1381(30)	0.093(9)
C15	0.0140(9)	0.1021(9)	1.1622(36)	0.102(10)
C16	−0.0141(7)	0.0918(8)	1.0502(38)	0.092(9)
C17	−0.0048(7)	0.1047(7)	0.9300(29)	0.080(8)
C18	0.0327(6)	0.1240(7)	0.8978(23)	0.063(6)
C19	0.1735(6)	0.2229(6)	0.6363(21)	0.057(5)
C20	0.2175(5)	0.2061(6)	0.8801(21)	0.057(6)
C21	0.2025(5)	0.2899(5)	0.8076(16)	0.038(4)
C22	0.2079(6)	0.3122(6)	0.6827(20)	0.049(4)
C23	0.2309(7)	0.3507(7)	0.6744(31)	0.074(7)
C24	0.2482(6)	0.3656(6)	0.8005(29)	0.065(6)
C25	0.2438(5)	0.3448(6)	0.9230(26)	0.053(4)
C26	0.2202(5)	0.3060(5)	0.9271(24)	0.050(4)
C27	0.1783(6)	0.2377(6)	1.2263(21)	0.051(5)
C28	0.0925(6)	0.2273(7)	1.2935(19)	0.060(6)
C29	0.1221(5)	0.3062(5)	1.2236(18)	0.038(4)
C30	0.0820(7)	0.3218(6)	1.2336(21)	0.060(6)
C31	0.0767(8)	0.3626(7)	1.2731(26)	0.074(6)
C32	0.1104(10)	0.3850(8)	1.3203(28)	0.092(9)
C33	0.1505(10)	0.3678(8)	1.3271(23)	0.091(9)
C34	0.1541(8)	0.3308(9)	1.2689(24)	0.084(8)
C35	0.0940(7)	0.3146(7)	0.6576(19)	0.061(6)
C36	0.1195(6)	0.3543(5)	0.8968(25)	0.059(6)
C37	0.0369(6)	0.3237(7)	0.8674(22)	0.057(5)
C38	0.0027(6)	0.3006(6)	0.8021(22)	0.056(5)
C39	−0.0395(8)	0.3111(10)	0.8086(33)	0.097(9)
C40	−0.0497(6)	0.3458(8)	0.8802(25)	0.076(8)
C41	−0.0182(9)	0.3719(9)	0.9463(38)	0.106(9)
C42	0.0251(7)	0.3591(8)	0.9404(26)	0.082(8)

$U_{eq} = 1/3[\Sigma_{ij} U a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j]$.

$J = 7.3$ Hz, 2H, $-CH_2CH_3$); ethyl 2-cyano-5-oxohexanoate: δ 0.94 (t, $J = 7.3$ Hz, 3H, $-CH_2CH_3$), 1.65 (s, 3H, $-COCH_3$), 1.90–2.69 (m, 5 H, $-CH_2CH_2COCH_3$, $-CH-$), 3.93 (q, $J = 7.3$ Hz, 2H, $-CH_2CH_3$).

3.11. Crystallography of ***2b***

Yellow single crystals of **2b** suitable for X-ray analysis were obtained from a Et_2O solution by diffusing vapor of hexane at −30°C. After removing the solution layer, residual crystals were carefully washed with cold dry pentane, repeatedly, and dried under vacuum. A selected single crystal was sealed in a thin glass capillary (GLAS, ∅0.7 mm) under argon. The diffraction experiment was performed on a Rigaku AFC-5S diffractometer equipped with graphite-monochromated Mo–K_α radiation ($\lambda = 0.71069$ Å). Crystal data are summarized in Table 1 and positions and thermal parameters are listed in Table 4. The structure was solved by direct methods [20,21] and refined by a full matrix least-squares techniques on the basis of F^2 using SHELXL93 program [22]. The non-hydrogen atoms except N(2), C(1), C(6), C(19), C(25), C(26), C(27), C(29), C(31), C(38) and C(41) were refined anisotropically. All hydrogen atoms were located on the calculated positions and their parameters were unrefined. A restraint was adopted for the bond length between C(9) and C(10). The function minimized was $wR_2 = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{0.5}$ with $w = [\Sigma^2 F_o^2 + (aP)^2 + bP]^{-1}$ and $P = 0.33F_o^2 + 0.67F_c^2$. Additionally, a residual R_1 was calculated which could be compared with refinements carried out on F more conveniently. Due to statistical factors, the residuals for refinement on F^2 are normally about twice to three times larger than those for the same refinement carried out on F. The final R_1 factor is 0.066 for 4085 reflections ($|F_o| > 4\sigma|Fo|$) and wR_2 on F^2 for all reflections is 0.151.

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[16] We had observed that a reaction of **4** (23.4 mg, 0.0206 mmol) with tetracyanethylene (TCNE) (11.8 mg, 0.092 mmol) in THF solution (2 ml) resulted in the formation of ethyl (*E*)-2-cyano-3-phenylpropenoate (0.011 mmol, 52%), benzalomalononitrile (0.0012 mmol, 12%) and ethyl 2,3,3-tricyano-propenoate (0.0021 mmol, 10%). Although formation of 1,1-dicyano-2-phenylethylene and ethyl 2,3,3-tricyanopropenoate can be regarded as a formal olefin metathesis of TCNE with ethyl (*E*)-2-cyano-3-phenylpropenoate [17], this reaction actually proceeded in the absence of Re complexes. It is known that hydrolysis of TCNE gives malononitrile and dicyanoketone. Michael reaction of the generated malononitrile with ethyl (*E*)-2-cyano-3-phenylpropenoate followed by the elimination of ethyl cyanoacetate gives 1,1-dicyano-2-phenylethylene. The resulting ethyl cyanoacetate successively reacts with TCNE to yield ethyl 2,3,3-tricyanopropenoate and malononitrile [18]. All these reactions were independently determined.

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