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Synthesis of Novel Rhenium(I) Enolate Complexes as Active Key Intermediates in the Catalytic Aldol Type Reaction

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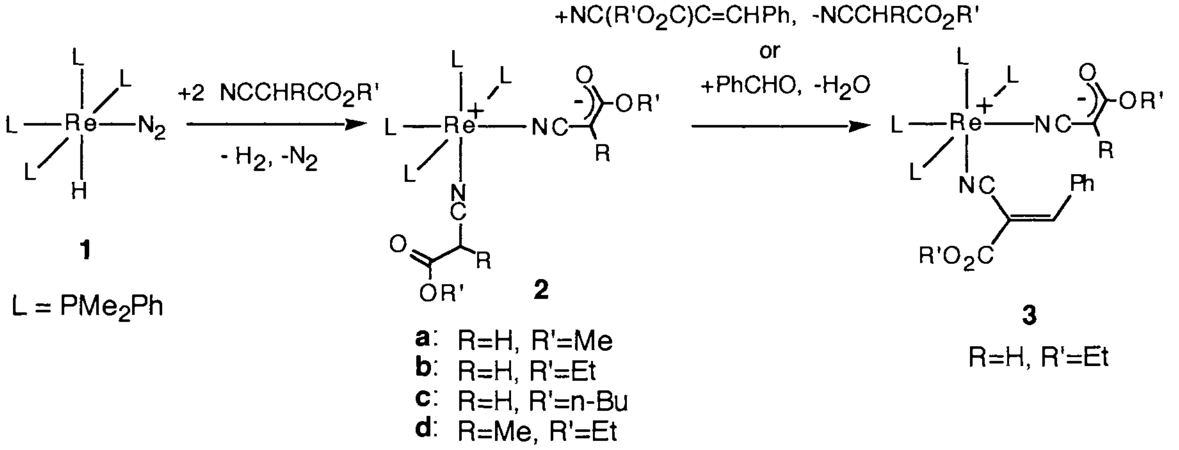
Rhenium(I) dinitrogen complex *cis*-$ReH(N_2)(PMe_2Ph)_4$ catalyzes an aldol type reaction of ethyl cyanoacetate with benzaldehyde under moderate conditions. Rhenium enolate complexes $Re(NCCRCO_2R')(NCCHRCO_2R')(PMe_2Ph)_4$ (R = H, R' = Me; R = H, R' = Et; R = H, R' = n-Bu; R = Me, R' = Et) and $Re(NCCHCO_2Et)$-$[NC(EtO_2C)C=CHPh](PMe_2Ph)_4$ as active intermediates of the aldol type reactions have been isolated.

Catalytic aldol type reaction under mild and neutral conditions is a fascinating and potentially useful reaction involving C-C bond formation. Recently, highly regio- and enantioselective transition metal catalyzed aldol reactions are reported.[1-5] They have stimulated the mechanistic studies of synthesis and isolation of transition metal enolate complexes. In the course of our investigation concerning the ruthenium catalyzed C-H bond activation, we have isolated ruthenium enolate complexes as active key intermediates of aldol and Michael type reactions.[6] On the other hand, the aldol type reaction catalyzed by *rhenium complex* is relatively unexplored so far. We recently found that the dinitrogen rhenium(I) complex $ReH(N_2)(PMe_2Ph)_4$ (**1**)[7] showed analogous catalytic activity toward the aldol type reactions. In this paper, we wish to report the synthesis of novel rhenium(I) enolate complexes $Re(NCCRCO_2R')(NCCHRCO_2R')(PMe_2Ph)_4$ (**2a**, R = H, R' = Me; **2b**, R = H,R' = Et; **2c**, R = H, R' = n-Bu; **2d**, R = Me, R' = Et) and $Re(NCCHCO_2Et)[NC(EtO_2C)C=CHPh]$-$(PMe_2Ph)_4$ (**3**) as active intermediates and describe their catalytic activity of the aldol type reaction.



Treatment of an Et_2O solution of rhenium(I) dinitrogen complex **1** with alkyl cyanoacetate or ethyl 2-cyanopropanoate at room temperature lead to formation of novel rhenium(I) enolate complexes **2a-2d** accompanied by evolution of quantitative amounts of dinitrogen and dihydrogen. The enolate complexes **2a** (69%), **2b** (74%), **2c** (52%) and **2d** (64%) were isolated as analytically pure crystals.[8)] Low molar electric conductivity of **2b** (0.035 S cm^2 mol^{-1}) in THF indicates nonionic character of **2b**. IR spectrum of **2b** shows two ν_{CN} bands at 2236 and 2169 cm^{-1} and two ν_{CO} bands at 1745 and 1629 cm^{-1} due to the ethyl cyanoacetate and enolato ligands, respectively. These data suggest that the enolato and the ethyl cyanoacetate ligands coordinate to the rhenium center by CN groups, creating a nucleophilic enolate anion.[6,9)] ^1H NMR spectrum of **2b** also supports the binding of the enolato ligand by CN group because the methine proton of the enolato ligand (δ 3.93, singlet) lacks any H-P coupling. Other enolate complexes **2a**, **2c** and **2d** also show similar spectroscopic data.

The reaction of **2b** with an equimolar amount of benzaldehyde gives a new enolato complex **3** (77%) which is coordinated with ethyl α-cyanocinnamate.[10)] Independently, **3** can be prepared by the reaction of **2b** with ethyl α-cyanocinnamate in 84% yield. IR spectrum of **3** shows two strong ν_{CN} bands at 2199 and 2153 cm^{-1} and two ν_{CO} bands at 1726 and 1617 cm^{-1} for the ethyl α-cyanocinnamate and enolate ligands, respectively.

Complexes **1**, **2b**, and **3** catalyzed the catalytic aldol type reaction of ethyl cyanoacetate with benzaldehyde to give corresponding ethyl (*E*)-α-cyanocinnamate derivatives under neutral conditions (Table 1). We believe that the stereoselective formation of the *E* isomer is ascribed to the steric repulsion between phenyl and ethyl ester groups in the transition state. While the reaction of **1** with ethyl 2-cyanopropanoate gives the corresponding enolate complex **2d**, the catalytic aldol type reaction of ethyl 2-cyanopropanoate with benzaldehyde in the

Table 1. Rhenium-catalyzed aldol reaction of benzaldehyde with active hydrogen compounds[a)]

Catalyst	Active Hydrogen Compound	Product	Yield[b)] / %
1	$NCCH_2CO_2Et$	$NC(EtO_2C)C=CHPh$	49
1	$NCCH_2CN$	$NC(NC)C=CHPh$	75
1	$NCCH(Me)CO_2Et$	no reaction	
1	$MeO_2CCH_2CO_2Me$	no reaction	
1	$MeCOCH_2COMe$	no reaction	
2b	$NCCH_2CO_2Et$	$NC(EtO_2C)C=CHPh$	29
3	$NCCH_2CO_2Et$	$NC(EtO_2C)C=CHPh$	26

a) A mixture of active hydrogen compound (0.75-1.6 mmol), benzaldehyde (0.75-1.6 mmol), and catalyst (1.0 mol%) in C_6D_6 was allowed to react at room temperature for 12-16 h. b) The yields were determined by ^1H NMR based on starting benzaldehyde.

presence of **1** did not proceed under the conditions. This may be due to the possible steric congestion among the enolato, ethyl 2-cyanopropanoate and four P ligands, since the related ruthenium complex $RuH(NCCMeCO_2Et)[NCCH(Me)CO_2Et](PPh_3)_3$ having three P ligands readily affords the aldol product.[1,11)]

Interestingly, neither acetylacetone nor dimethyl malonate afforded the aldol products at all in the rhenium-catalyzed aldol type reactions. This is very similar to the fact that the ruthenium-catalyzed aldol type reaction of benzaldehyde with a 1:1 mixture of ethyl cyanoacetate and acetylacetone gives only ethyl α-cyanocinnamate in spite of the coincidence of their pK_a values.[1,6)] In these reactions the unexpected enolate structure involving the coordination of the CN group plays an important role in the aldol type reactions: a zwitterionic structure of the enolate effectively increases of the nucleophilicity of the enolate to assist the C-C bond formation process in the aldol type reactions.

While **2b** shows a weak absorption band at 610 nm, complex **3** has an intensive blue color (λ_{max} = 610 nm, ε_{max} = 3500 M^{-1} cm^{-1} in THF), probably due to a charge transfer from ethyl α-cyanocinnamate. The absorption band at 610 nm of **2b** in benzene (1.89×10^{-7} M) increased immediately when 600-fold excess of benzaldehyde was added. On the other hand, the absorbance at 602 nm of **3** in THF (3.81×10^{-8} M) gradually reduced ($\tau_{1/2}$ = 7 min at r.t.) when 124-fold excess of ethyl cyanoacetate was added. The results suggest that the aldol product smoothly forms on the catalyst but is much more slowly replaced by ethyl cyanoacetate to reproduce the intermediate **2b** (Eq. 1). The most plausible mechanism of the rhenium-catalyzed aldol type reaction is demonstrated in Fig. 1.

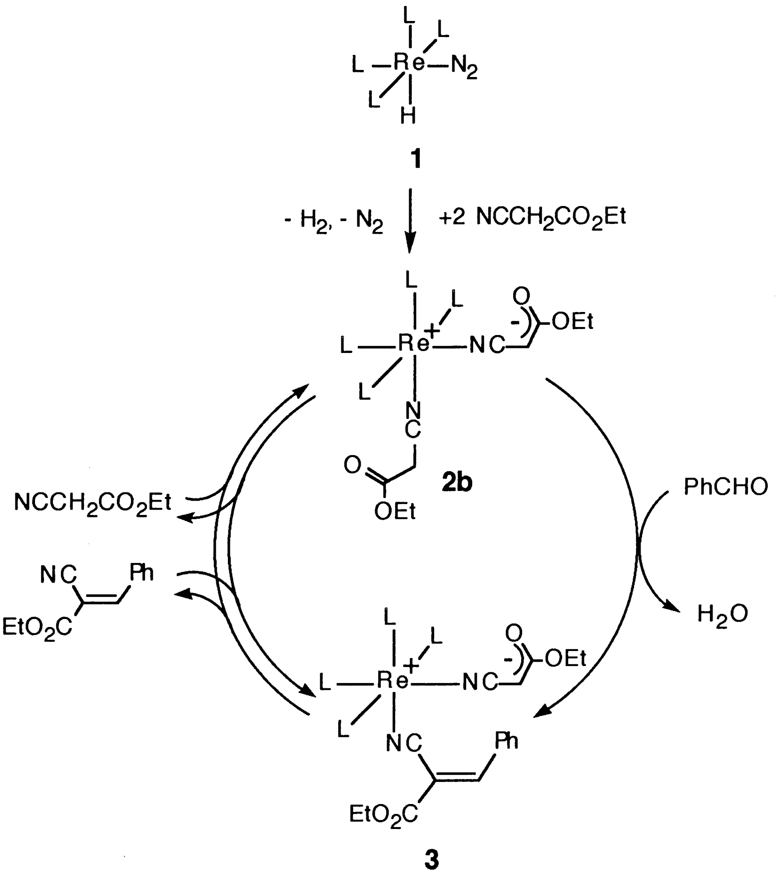
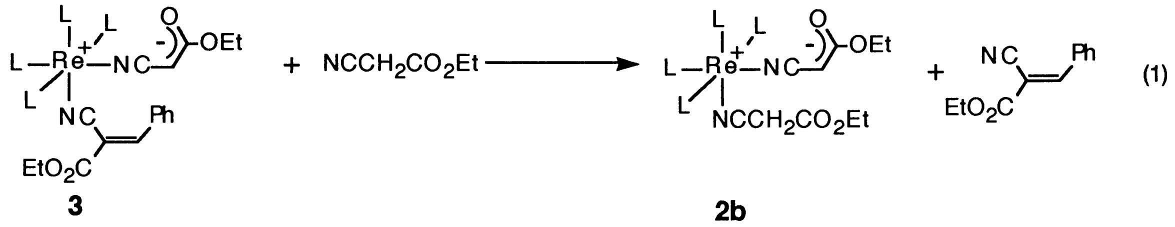


Fig. 1. A proposed mechanism for the rhenium-catalyzed aldol reaction (L = PMe_2Ph).



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8) Spectroscopic data for **2b** were typically given as follows: **2b**: ^{1}H NMR (200 MHz, C_6D_6): δ 0.87 (t, -$\mathrm{CH_2C}H_3$, J = 7.1 Hz, 3H), 0.93 (br, P-$\mathrm{C}H_3$, 6H), 1.35 (t, -$\mathrm{CH_2C}H_3$, J = 7.1 Hz, 3H), 1.80 (br, P-$\mathrm{C}H_3$, 6H), 1.80 (d, P-$\mathrm{C}H_3$, J = 7.1 Hz, 12H), 2.71 (s, NC-$\mathrm{C}H_2$-, 2H), 3.72 (q, -$\mathrm{C}H_2\mathrm{CH_3}$, J = 7.1 Hz, 2H), 3.93 (s, NC-C*H*-, 1H), 4.48 (q, -$\mathrm{C}H_2\mathrm{CH_3}$, J = 7.1 Hz, 2H), 6.9-7.6 (m, P-*Ph*, 20H); IR (KBr, cm^{-1}), 2236 (m, ν_{CN}), 2169 (m, ν_{CN}), 1745 (s, ν_{CO}), 1629 (vs, ν_{CO}). Anal. Found: C, 52.21; H, 6.65; N, 2.85%. Calcd for $C_{42}H_{57}N_2O_4P_4Re$: C, 52.33; H, 5.96; N, 2.91%.

9) A preliminary X-ray structure analysis for **2b** has been carried out, showing an octahedral geometry in which both enolato and ethyl α-cyanoacetate ligands bound to Re by the cyano groups in a *cis* fashion. Crystal data for **2b**: triclinic, space group $P\bar{1}$, R = 0.139, Rw = 0.156 for 4146 reflections ($3 < 2\theta < 40°$, $|F_o| > 5\sigma|F_o|$).

10) Spectroscopic data for **3**: ^{1}H NMR (200 MHz, C_6D_6): δ 0.88 (br, P-$\mathrm{C}H_3$, 6H), 1.15 (t, -$\mathrm{CH_2C}H_3$, J = 7.1 Hz, 3H), 1.36 (t, -$\mathrm{CH_2C}H_3$, J = 7.1 Hz, 3H), 1.74 (br, P-$\mathrm{C}H_3$, 6H), 1.80 (d, P-$\mathrm{C}H_3$, J = 6.6 Hz, 12 H), 3.95 (s, NC-C*H*-, 1H), 4.0 (q, -$\mathrm{C}H_2\mathrm{CH_3}$, J = 7.3 Hz, 2H), 4.52 (q, -$\mathrm{C}H_2\mathrm{CH_3}$, J = 7.1 Hz, 2H), 7.8-6.7 (m, P-*Ph*, =CH*Ph*, =C*H*Ph, 26H); IR (KBr, cm^{-1}): 2199 (m, ν_{CN}), 2153 (m, ν_{CN}), 1726 (m, ν_{CO}), 1617 (s, ν_{CO}). Anal. Found: C, 55. 62; H, 6.14; N, 2.76%. Calcd for $C_{49}H_{61}N_2O_2P_4Re$: C, 55.94; H, 5.84; N, 2.66%.

11) S. Komiya, Y. Mizuho, and A. Fukuoka, unpublished result.

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