resolved into (+)- and (−)-fractions in the same manner as in Figure 2.

The results presented here clearly indicate that the loss of the optical rotation of PD2PyMA is not due to a helix-coil transition, since the chiral chromatography could not be expected to restore the helical conformation, but rather to a transition between helical states. Although experiments are underway to explore the precise conformational motions attending the helix reversal, the chiral chromatography experiment suggests that at equilibrium the sample is a mixture of diastereomeric helical chains.

Acknowledgment. We are deeply grateful to Professor Mark M. Green of the Polytechnic University for helpful discussions and review of the manuscript.

Ruthenium-Catalyzed Aldol and Michael Reactions of Activated Nitriles

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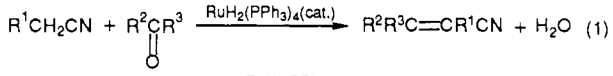
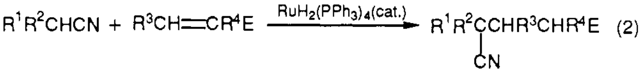
Transition-metal complex-catalyzed aldol and Michael reactions are one of the most attractive methods for selective carbon–carbon bond formation. However, the reported methods are limited to a few cases which involve rhodium-[1] and gold-[2] catalyzed aldol reactions. As part of programs aimed at the development of a method for activation of C–H bonds adjacent to hetero atoms with transition-metal complexes,[3] we have been investigating the activation of nitriles. We wish to report novel chemo- and stereoselective ruthenium-catalyzed aldol (eq 1) and Michael reactions (eq 2) of activated nitriles under mild and neutral conditions.



$$R^1CH_2CN + R^2C(=O)R^3 \xrightarrow{RuH_2(PPh_3)_4(cat.)} R^2R^3C{=}CR^1CN + H_2O \quad (1)$$



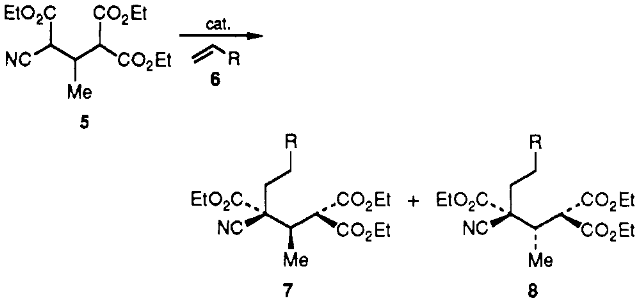
$$R^1R^2CHCN + R^3CH{=}CR^4E \xrightarrow{RuH_2(PPh_3)_4(cat.)} R^1R^2C(CN)CHR^3CHR^4E \quad (2)$$

$RuH_2(PPh_3)_4$ has proved to be the most effective catalyst for the carbon–carbon bond formations. Nitriles undergo condensation with various carbonyl compounds at room temperature to give α,β-unsaturated nitriles. Representative results of the condensation are shown in Table I. The stereochemistry of the product olefins was determined to be E (entries 1 and 2) by means of NMR spectral analyses.[4] The reactions of less reactive nitriles such as benzyl cyanide are enhanced remarkably by addition of a catalytic amount of bidentate phosphines such as 1,2-bis(diphenylphosphino)ethane (dppe) (entry 4), although addition of 1,3-bis(diphenylphosphino)propane (dppp) retards the reactions.[5]

Michael addition of nitriles to alkenes proceeds efficiently at room temperature under neutral conditions. Representative results are shown in Table I. The reaction of α,β-unsaturated carbonyl compounds gives Michael adducts without contamination by the corresponding aldol products (entries 5 and 6).

One important feature of the present reaction is the chemoselective reaction of nitriles with either carbonyl compounds or Michael acceptors in the presence of other active methylene compounds. Indeed, the $RuH_2(PPh_3)_4$-catalyzed reaction of benzaldehyde with an equimolar mixture of ethyl cyanoacetate (**3**, $pK_a > 9$) and acetylacetone, which has a similar pK_a value ($pK_a = 9.0$),[6] gave ethyl (*E*)-2-cyano-3-phenylpropanoate (**4**, 80%) exclusively. In contrast, the reaction of benzaldehyde with the same mixture in the presence of a conventional base such as KOH and $AcONH_4$ gave a mixture (3:1) of **4** and 3-benzylidene-2,4-pentanedione. Similarly, the treatment of crotononitrile with an equimolar mixture of **3** and nitroethane ($pK_a = 8.6$) gave ethyl 2,4-dicyano-3-methylbutanoate chemoselectively.

The utility of the present method has also been indicated by the high diastereoselectivity of the Michael additions. When cyano ester **5**, which can be readily obtained by the catalytic Michael addition of diethyl ethylidenemalonate to ethyl cyanoacetate (90% yield), was allowed to react with methyl vinyl ketone (**6a**) in the presence of $RuH_2(PPh_3)_4$ catalyst, adduct **7a** was obtained with high diastereoselectivity (**7a**/**8a** = 97/3) in 72% yield. These are quite rare examples of catalytic diastereoselective Michael reactions.[7] Similar reaction of **5** with acrylonitrile (**6b**) gave **7b** selectively (**7b**/**8b** = 90/10, 40%). In contrast, the same reaction of **5** with **6a** or **6b** in the presence of a base catalyst such as Triton B (*N*-benzyltrimethylammonium hydroxide) gave **7** and **8** nonselectively (**7a**/**8a** = 75/25, 82%; **7b**/**8b** = 44/56, 37%). It is noteworthy that **7a** was obtained conveniently by one-pot, ruthenium-catalyzed reaction of diethyl ethylidenemalonate with ethyl cyanoacetate and subsequently with **6a** (**7a**/**8a** = 97/3, 78% yield). The present reaction can be also applied to the stereoselective construction of cyclohexanes by Michael-aldol ring closure. Typically, the ruthenium-catalyzed reaction of **5** with acrolein gave **9** selectively (**9**/**10** = 95/5) in 54% yield.[8] In



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(1) Slough, G. A.; Bergman, R. G.; Heathcock, C. H. *J. Am. Chem. Soc.* **1989**, *111*, 938, and references cited therein.

(2) Ito, Y. Sawamura, M.; Hayashi, T. *J. Am. Chem. Soc.* **1986**, *108*, 6405.

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(4) The stereochemistry of these alkenes was determined by ^1H (270 MHz) and ^{13}C (67.9 MHz) NMR analysis. **1**: ^1H NMR ($CDCl_3$, δ) 7.66 (t, J = 7.8 Hz, 1 H, $CH{=}C(CN)CO_2Et$); ^{13}C NMR ($CDCl_3$, δ) 163.6 (C^3), 110.0 (C^2). **2**: ^1H NMR ($CDCl_3$, δ) 8.20 (s, 1 H, $CH{=}C(CN)CO_2Et$); ^{13}C NMR ($CDCl_3$, δ) 155.9 (C^3), 98.9 (C^2). See: Hayashi, T. *J. Org. Chem.* **1966**, *31*, 3253.

(5) Ruthenium-catalyzed Michael addition of crotononitrile to ethyl cyanoacetate (at 20 °C) to give 2,4-dicyano-2-methylbutanoate (conversion 29%, yield 89%) was enhanced by addition of 1,4-bis(diphenylphosphino)butane (dppb) (52%, 99%) and retarded by addition of dppe (9%, 99%).

(6) Pearson, R. G.; Dillon, R. L. *J. Am. Chem. Soc.* **1953**, *75*, 2439.

(7) Mukaiyama, T.; Tamura, M.; Kobayashi, S. *Chem. Lett.* **1986**, 1017, 1817, **1987**, 743. For a review of noncatalytic diastereoselective reactions, see: Tomioka, K.; Koga, K. In *Asymmetric Synthesis*; Morrision, J. D., Ed.; Academic Press: New York, 1983; Vol. 2, p 201.

(8) The stereochemistry of **9** and **10** was determined by NMR analysis: ^1H NMR signals were assigned through the use of ^1H–^1H COSY, ^1H–^{13}C COSY, and ^1H difference NOE experiments. The stereochemical assignments were determined based on ^1H difference NOE experiments and long-range deshielding by the cyano group (H^4(eq) signal of **9**; H^2(ax) and H^4(ax) signals of **10**). Typical spectral data are as follows. **9**: ^1H NMR ($CDCl_3$, 500 MHz) δ 1.93–2.00 (m, 2 H, H^4(ax), H^5(eq)), 2.16–2.30 (m, 1 H, H^5(ax)), 2.46 (ddd, J = 12.1, 5.5, 4.8 Hz, 1 H, H^4(eq)), 2.92 (br q, J = 7.1 Hz, 1 H, H^2(ax)), 4.11 (br, 1 H, H^6(ax)); ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 119.7 (CN), 73.0 (C^6OH(eq)), 41.7 (C^2CH_3(eq)). **10**: ^1H NMR ($CDCl_3$, 500 MHz) δ 1.82–1.99 (m, 1 H, H^5(eq)), 2.10–2.22 (m, 2 H, H^4(eq), H^5(ax)), 2.23–2.36 (m, 1 H, H^4(ax)), 3.20 (q, J = 7.3 Hz, 1 H, H^2(ax)), 4.41 (br, 1 H, H^6(ax)); ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 119.6 (CN), 68.1 (C^6OH(ax)), 37.0 (C^2CH_3(eq)).

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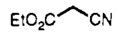
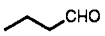
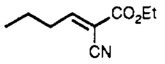
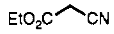
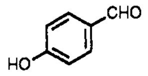
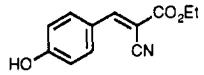
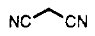
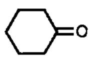
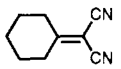
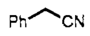
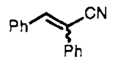
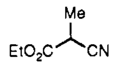
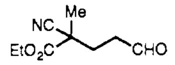
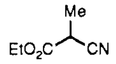
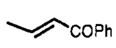
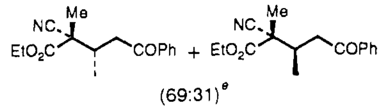
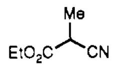
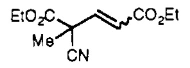
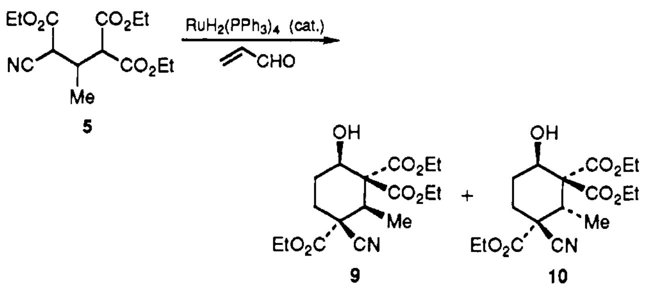
Table I. Ruthenium-Catalyzed Aldol and Michael Reaction of Nitriles[a]

entry	nitrile	electrophile	product	yield,[b] %
1			 1	83
2			 2	98
3				79
4		PhCHO	 (*E/Z* = 1/6)	87[c,d]
5				72
6			 (69:31)[e]	91
7		HC≡C—CO_2Et	 (*E/Z* = 65/35)	81

[a] A mixture of nitrile (2.0 mmol), carbonyl compounds or olefin (2.2 mmol), and $RuH_2(PPh_3)_4$ (0.06 mmol) in dry THF (0.5 mL) was stirred overnight at room temperature under argon. [b] Isolated yield based on the starting nitrile. [c] 1,2-Bis(diphenylphosphino)ethane (0.12 mmol) was added. [d] Reaction temperature; 60 °C. [e] Diastereomeric ratio was determined by 500 MHz ^1H NMR analysis.

contrast, the same reaction with Triton B gave **9** and **10** nonselectively (**9**/**10** = 72/28, 49% yield).



The present ruthenium-catalyzed reactions can be rationalized by assuming a mechanism which involves an oxidative addition of a low-valent ruthenium species into the C–H bond adjacent to the cyano groups.[9] The chemoselectivity toward nitriles clearly indicates the coordination of the cyano group to the low-valent ruthenium species.[10] The key step of this reaction is quite similar to those of palladium-catalyzed transalkylation[3a] and hydrolysis reactions[3b] of tertiary amines, where low-valent palladium inserts into the C–H bond adjacent to amino groups. Ittel et al. have succeeded in the isolation of the adduct of methyl cyanoacetate and low-valent $HFe(dmpe)_2$ (dmpe = $Me_2PCH_2CH_2PMe_2$).[9] Insertion of the ruthenium complexes into carbonyl compounds or alkenes and subsequent reductive elimination of ruthenium species would give aldol or Michael adducts. The coordination of the nitrile and carbonyl groups of **5** to ruthenium seems to play an important role in the diastereoselective formation of **7** and **9**.

Finally, the present reaction provides a versatile method for the addition of nitriles to acetylenic compounds (entry 7). Generally, such additions to acetylenic compounds is difficult,[11] because polycondensation[12] and nucleophilic reactions of the acetylide anion[13] proceed under the reaction conditions.

The ruthenium-catalyzed aldol and Michael reactions of nitriles disclosed above provide a potential method for chemo- and stereoselective C–C bond formation, and the origin of the high stereoselectivity arising from the coordination of ruthenium must wait further research.

Supplementary Material Available: Spectral data (^1H NMR, IR, and ^{13}C NMR) for **7**, **8**, **9** and **10** (3 pages). Ordering information is given on any current masthead page.

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(9) Ittel, S. D.; Tolman, C. A.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 7577.

(10) Coordination of ruthenium, see: Murahashi, S.-I.; Naota, T.; Saito, E. *J. Am. Chem. Soc.* **1986**, *108*, 7846.

(11) Successful examples, see: (a) Organocuprates: Marino, J. P.; Linderman, R. J. *J. Org. Chem.* **1983**, *48*, 4621 and the references cited therein. (b) Silyl enolates-$TiCl_4$: Quendo, A.; Rousseau, G. *Tetrahedron Lett.* **1988**, *29*, 6443.

(12) Woodward, R. B.; Singh, T. *J. Am. Chem. Soc.* **1950**, *72*, 494.

(13) House, H. O.; Roelofs, W. L.; Trost, B. M. *J. Org. Chem.* **1966**, *31*, 646. Grob, C. A.; Kaiser, A. *Helv. Chim. Acta* **1967**, *50*, 1599.

The Nitrogen Atom Transfer Reactivity of Nitridomanganese(V) Porphyrins with Chromium(III) Porphyrins

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The oxygen atom transfer reactivity of inorganic molecules has been avidly investigated during the past three decades.[1] Much of this work has utilized O═M complexes (where M may possess up to four d electrons) as the oxygen atom reagent and either phosphines, olefins, or paraffins as the oxygen atom acceptor. However, when metal complexes are utilized as the oxygen atom acceptor, binuclear, μ-oxo-bridged complexes are the usual product.[2] Complete intermetal oxygen atom transfer has been

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(1) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401-1449.

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