

Supporting Information Available

CryptoCope Rearrangement of 1,3-Dicyano-5-phenyl-4,4- d_2 -hexa-2,5-diene. Chameleonic or Centauric?

W. von E. Doering* and Yonghui Wang

Contribution of the Department of Chemistry and Chemical Biology, Harvard University, Cambridge, MA 02138-2902

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<i>t</i> , s	Prod. ^{a,b}	Rec. ^{a,c}	(<i>k</i> ₁ + <i>k</i> ₋₁) ^d	<i>t</i> , s	Prod. ^{a,b}	Rec. ^{a,c}	(<i>k</i> ₁ + <i>k</i> ₋₁) ^d
165.2 ± 0.3 °C (mesitylene)				176.9 ± 0.1 °C (4-methylanisole)			
0	6.76	100.0		0	6.65	100.0	
65280	13.34	93.3	2.7763	33300	15.65	94.4	7.5639
177900	23.03	92.0	2.9131	90900	27.68	96.0	8.0508
353700	32.97	86.5	2.9622	174000	36.35	92.4	7.5786
697089	41.29	83.5	2.7621	346800	43.76	88.1	7.1090
1375620	44.60	75.4	1.9950	687600	44.88	82.3	4.1563
185.4 ± 0.1 °C (diethyl oxalate)				194.1 ± 0.1 °C (2-(2-methoxyethoxy)ethanol)			
0	6.25	100.0		0	6.83	100.0	
17400	15.88	92.9	14.896	10800	17.07	89.7	27.585
49200	27.40	94.1	14.585	25680	27.73	93.4	28.597
101100	37.82	93.5	14.482	45180	35.64	91.2	27.786
161100	43.24	89.7	14.432	73260	41.67	87.8	27.188
356820	45.48	83.4	8.844	147960	45.89	72.7	23.156

^aRelative concentrations in %. ^bArea of hydrons C4 [3.05 (*E*), 2.97 (*Z*)] relative to hydrons C2 [6.15 (*E*), 6.29 (*Z*)]. ^cArea of hydrons C2 relative the residual methyl hydron in the solvent, perdeuterioisopropyl alcohol. ^dCalculated from the expression for a reversible first-order reaction, (*k*₁ + *k*₋₁) = ln[(*x*_e - *x*₀)/(*x*_e - *x*_{*t*})]/*t*, in which *x*_e = 47.21%, and *x*₀ = 6.61%, the mean of the four values at *t* = 0 (all the same standard solution). Values of (*k*₁ + *k*₋₁) in units of 10⁻⁶ sec⁻¹. The values used for the calculation of the activation parameters are by linear regression to zero time of the first four points.

Table S2. Kinetic Data for the Interconversion of 4,4-D₂- and 6,6-D₂-1,3-dicyano-5-phenylhexa-1,4-diene in Isopropyl Alcohol-*d*₈ (90%) and Pyridine-*d*₅ (10%).

<i>t</i> , s	Educt ^{a,b}	Product ^c	Recov. ^d	Norm. prod.	(<i>k</i> ₁ + <i>k</i> ₋₁) ^d
164.9 ± 0.2 °C (mesitylene)					
0	95.36	4.73	100.0	4.73	
21180	88.24	12.29	100.8	12.2	9.1652
54960	80.90	21.15	96.7	20.73	8.5964
108360	69.46	30.91	94.6	30.80	8.7754
216060	57.77	40.57	86.7	41.22	9.0936
387540	52.22	43.08	80.8	45.20	
644340	50.67	43.64	70.1	46.27	
176.7 ± 0.2 °C (4-methylanisole)					
0	96.42	4.93	100.0	4.86	
10500	85.26	13.96	99.1	14.07	23.646
28500	75.50	25.38	95.8	25.16	23.006
58320	63.86	35.32	94.0	35.61	22.260
115560	54.19	42.60	85.6	44.01	22.385
218160	49.50	43.63	60.7	46.85	21.849
411300	47.08	42.47	52.0	47.43	
185.2 ± 0.2 °C (diethyl oxalate)					
0	96.46	4.59	100.0	4.54	
5340	87.27	13.20	104.6	13.14	41.304
16140	73.70	26.20	97.7	26.23	43.698

33960	62.30	37.07	92.1	37.31	42.874
62520	53.98	43.83	89.2	44.81	
121320	50.06	45.35	72.9	47.53	
213540	48.06	42.69	62.7	47.04	

t, s	Educt ^{a,b}	Product ^c	Recov. ^d	Norm. prod.	$(k_1 + k_{-1})^d$
194.4 ± 0.3 °C (2-(2-methoxyethoxy)ethanol)					
0	96.23	4.85	100.0	4.80	
2580	88.76	12.63	100.0	12.46	77.815
8400	74.43	26.28	92.6	26.09	83.219
16560	63.35	36.10	97.3	36.30	82.085
32280	54.95	42.78	83.8	43.77	77.900
57900	51.08	45.22	80.2	46.96	
114900	46.29	43.14	56.4	48.24	

^a Relative concentrations in %. ^a Hydrons C4 [3.24 (*E*), 3.20 (*Z*)] relative to hydron C2 [6.13 (*E*), 6.12 (*Z*)]. ^c Hydrons C6 [4.92 (*E*) and (*Z*)] relative to hydron C2. ^d Recovery is measured relative to the residual methyl hydron in the solvent, perdeuterioisopropyl alcohol. ^d Calculated from the expression for a reversible first-order reaction, $(k_1 + k_{-1}) = \ln[(x_e - x_0)/(x_e - x_t)]/t$, in which $x_e = 47.21\%$, and $x_0 = 6.61\%$, the mean of the four values at $t = 0$ (all the same standard solution). Values of $(k_1 + k_{-1})$ in units of 10^{-6} sec^{-1} . The values used for the calculation of the activation parameters are by linear regression to zero time of the first four points.

Table S3. Concentration Data (%) and Specific Rate Constants for the Reversible Rearrangement of (*E*)- and (*Z*)-3-Cyanocyclohex-2-enylidene (**3**) in Benzene-*d*₆

154.0 ± 0.2 °C (anisole)				
time × 10 ⁻⁵ s	(<i>E</i>)- 3	(<i>Z</i>)- 3	(<i>E</i>)- 3	(<i>Z</i>)- 3
0.000	100.00	0.0	0.0	100.00
0.326	95.99	4.01	7.13	92.87
0.950	89.51	10.49	16.55	83.45
1.958	80.91	19.09	28.27	71.73
3.323	73.47	26.53	38.95	61.05
5.121	67.34	32.66	47.71	52.29
9.469	61.74	38.26	56.65	43.35
15.204	60.12	39.88	59.25	40.75
20.412	59.96	40.04	59.58	40.42

(*E*)-**3**: ($k_1 + k_{-1}$) = $(3.26 \pm 0.1 \times 10^{-6} \text{ s}^{-1})$; $K = 0.673 = (\text{Z})\text{-3}/(\text{E})\text{-3} = k_1/k_{-1}$

(*Z*)-**3**: ($k_1 + k_{-1}$) = $(3.10 \pm 0.03 \times 10^{-6} \text{ s}^{-1})$; $K = 0.673 = (\text{Z})\text{-3}/(\text{E})\text{-3} = k_1/k_{-1}$

165.2 ± 0.1 °C (mesitylene)				
time, × 10 ⁻⁵ s	(<i>E</i>)- 3	(<i>Z</i>)- 3	(<i>E</i>)- 3	(<i>Z</i>)- 3
0	100.00	0	0	100
0.150	94.58	5.42	8.01	91.99
0.438	85.75	14.25	20.94	79.06
0.876	76.98	23.02	33.79	66.21
1.512	68.89	31.11	45.83	54.17
2.385	63.42	36.58	53.50	46.50
5.019	59.97	40.03	59.12	40.88
8.358	59.84	40.16	59.74	40.26
10.871	59.74	40.26	59.71	40.29

(E)-3: ($k_1 + k_{-1}$) = $(9.98 \pm 0.08 \times 10^{-6} \text{ s}^{-1})$; $K = 0.674 = (\text{Z})\text{-3}/(\text{E})\text{-3} = k_1/k_{-1}$

(Z)-3: ($k_1 + k_{-1}$) = $(9.49 \pm 0.06 \times 10^{-6} \text{ s}^{-1})$; $K = 0.674 = (\text{Z})\text{-3}/(\text{E})\text{-3} = k_1/k_{-1}$

186.1 \pm 0.1 °C (diethyl oxalate)				
time, $\times 10^{-5}$ s	(E)-3	(Z)-3	(E)-3	(Z)-3
0	100	0	0	100
0.0360	90.71	9.29	13.41	86.59
0.0960	79.80	20.20	29.06	70.94
0.1704	71.49	28.51	41.28	58.72
0.2730	65.39	34.61	50.26	49.74
0.9090	59.54	40.46	59.17	40.83
1.7892	59.47	40.53	59.42	40.58

(E)-3: ($k_1 + k_{-1}$) = $(70.4 \pm 0.4 \times 10^{-6} \text{ s}^{-1})$; $K = 0.682 = (\text{Z})\text{-3}/(\text{E})\text{-3} = k_1/k_{-1}$

(Z)-3: ($k_1 + k_{-1}$) = $(68.4 \pm 0.5 \times 10^{-6} \text{ s}^{-1})$; $K = 0.682 = (\text{Z})\text{-3}/(\text{E})\text{-3} = k_1/k_{-1}$

193.9 \pm 0.1 °C (2-(2-methoxyethoxy)ethanol)				
time, $\times 10^{-5}$ s	(E)-3	(Z)-3	(E)-3	(Z)-3
0	100	0	0	100
0.0150	92.13	7.87	11.46	88.54
0.0576	77.28	22.72	32.56	67.44
0.0990	69.67	30.33	44.30	55.70
0.1548	64.20	35.80	52.40	47.60
0.7578	59.51	40.49	59.36	40.64
2.5458	59.43	40.57	59.35	40.65

(E)-3: ($k_1 + k_{-1}$) = $(137.7 \pm 0.9 \times 10^{-6} \text{ s}^{-1})$; $K = 0.684 = (\text{Z})\text{-3}/(\text{E})\text{-3} = k_1/k_{-1}$

(Z)-3: ($k_1 + k_{-1}$) = $(138.0 \pm 0.3 \times 10^{-6} \text{ s}^{-1})$; $K = 0.684 = (\text{Z})\text{-3}/(\text{E})\text{-3} = k_1/k_{-1}$

Table S4. Temperature-dependent Equilibrium Concentrations (%) Among Four Pentenenitriles (Series 1 of Scheme 5) by NMR (Chemical Shift of Methyl Signals).

$T, ^\circ\text{C}$	$1\Delta^1(E)$ (0.40)	$1\Delta^2(E)$ (1.28)	$1\Delta^1(Z)$ (0.54)	$1\Delta^2(Z)$ (1.08)
154.0 ^a	40.48	19.23	34.81	5.49
136.3 ^a	41.06	18.77	34.96	5.21
111.0 ^a	42.23	18.23	35.05	4.49
97.3 ^a	43.37	17.61	34.89	4.12
80.5 ^a	44.00	17.36	34.78	3.87
61.1 ^a	44.71	16.84	35.14	3.31
154.0 ^b	40.20	19.47	35.56	4.76
121.0 ^b	40.57	18.34	36.27	4.82
92.1 ^a	42.63	17.60	35.99	3.76
61.1 ^b	42.03	17.06	37.87	3.04
154.0 ^c	39.46	19.88	35.18	5.48
121.0 ^c	41.03	18.23	35.79	4.94
92.1 ^c	42.77	17.70	35.84	3.70
61.1 ^c	43.05	16.54	36.99	3.42
Linear Regression: $1/T(K)$ versus $\ln(\text{conc}, \%)$				
	$1\Delta^1(E)$	$1\Delta^2(E)$	$1\Delta^1(Z)$	$1\Delta^2(Z)$
slope	129.50	223.55	51.39	770.88
st. error	23.48	14.81	26.01	66.99
intercept	3.393	3.485	3.437	3.489
st. error	0.063	0.039	0.069	0.178
$-R(\text{slope})/1000$	-0.257 ± 0.05	0.444 ± 0.03	-0.102 ± 0.05	$+1.532 \pm 0.13$
$R(\text{intercept})$	6.743 ± 0.12	6.926 ± 0.08	6.831 ± 0.14	6.934 ± 0.35

$\Delta\Delta_f H$	-0.70 ± 0.08	0.00 ± 0.00	-0.54 ± 0.08	$+1.09 \pm 0.16$
$\Delta\Delta_f S$	-0.18 ± 0.20	0.00 ± 0.00	-0.10 ± 0.22	$+0.01 \pm 0.43$

^a In order to have the four methyl signals well separated in the NMR (relaxation delay (RD): 20s), the solvent used was benzene-*d*₆:pyridine-*d*₅ (2.5:1). ^b Run in benzene-*d*₆; methyl signals, 500 MHz (RD 175 s) ^a Run in benzene-*d*₆; vinyl hydrons, 500 MHz (RD 175 s).

Table S5. Temperature-dependent Equilibrium Concentrations (%) Among Four 2-Methylpentenenitriles (Series 2 of Scheme 5 by NMR (Chemical Shift Vinyl Hydron).

$T, ^\circ\text{C}$	$2\Delta^2(E)$ (5.73)	$2\Delta^3(E)$ (5.43)	$2\Delta^2(Z)$ (5.35)	$2\Delta^1$ (5.19)
191	29.10	4.06	64.41	2.42
191	29.47	4.06	64.05	2.41
163	28.85	3.51	65.68	1.96
163	27.84	3.44	66.74	1.98
151	27.77	3.02	67.51	1.71
151	27.31	2.97	67.99	1.73
136	26.82	2.71	68.89	1.58
136	26.49	2.72	69.23	1.57
121	26.16	2.32	70.22	1.29
121	25.76	2.31	70.63	1.29
101	25.03	1.87	72.03	1.08
101	24.04	1.84	73.01	1.11
Linear Regression: 1/T(K) versus ln(conc,%)				
	$2\Delta^2(E)$	$2\Delta^3(E)$	$2\Delta^2(Z)$	$2\Delta^1$
slope	345.65	1529.80	-236.66	1552.06
st. error	25.56	39.51	10.62	40.12

intercept	4.129	4.720	3.654	4.224
st. error	0.062	0.095	0.026	0.097
$-R(\text{slope})/1000$	0.687 ± 0.05	3.040 ± 0.08	-0.470 ± 0.02	$+3.084 \pm 0.08$
$R(\text{intercept})$	8.205 ± 0.12	9.380 ± 0.19	7.261 ± 0.05	8.394 ± 0.19
$\Delta\Delta_f H$	-2.35 ± 0.13	0.00 ± 0.00	-3.51 ± 0.10	$+0.04 \pm 0.16$
$\Delta\Delta_f S$	-1.18 ± 0.31	0.00 ± 0.00	-2.12 ± 0.24	-0.99 ± 0.38

Table S6. Temperature-dependent Equilibrium Concentrations (%) Among Four 2,4-Dimethylpentenenitriles (Series 3 of Scheme 5) by NMR (Chemical Shifts).

$T, ^\circ\text{C}$	$3\Delta^2(E)$ (5.64)	$3\Delta^3$ (4.73)	$3\Delta^2(Z)$ (5.25)	$3\Delta^4$ (4.62)
160	21.11	19.44	55.87	3.57
160	22.01	19.97	56.09	1.94
160	21.35	19.64	56.67	2.36
160	21.24	19.81	56.81	2.15
137	21.00	18.00	58.15	2.85
137	21.43	18.95	58.14	1.48
121	21.34	17.20	59.08	2.38
121	21.42	17.67	59.72	1.21
121	21.01	17.68	59.72	1.59
121	20.98	17.68	59.88	1.48
101	20.96	16.57	61.39	1.29
101	20.50	16.22	61.88	1.41
98	20.84	15.56	61.70	1.90
98	20.53	16.03	62.14	1.30
82	20.70	14.70	63.21	1.39

82	20.56	15.09	63.51	0.84
80	20.44	14.61	63.81	1.12
80	20.15	14.88	63.75	1.23
61	19.93	13.70	64.73	1.65
61	20.29	13.57	65.21	0.93
61	20.57	13.56	64.89	1.00
61	19.67	13.51	65.76	1.09
40	20.12	11.99	67.15	0.74
40	19.60	12.04	67.77	0.60
Linear Regression: 1/T(K) versus ln(conc,%)				
	$3\Delta^2(E)$	$3\Delta^3$	$3\Delta^2(Z)$	$3\Delta^4$
slope	92.93	558.57	-206.79	1280.63
st. error	10.32	11.06	6.13	185.37
intercept	3.282	4.276	3.561	3.807
st. error	0.028	0.030	0.017	0.502
-R(slope)/1000	0.185 ± 0.02	1.110 ± 0.02	-0.411 ± 0.01	$+2.545 \pm 0.37$
R(intercept)	6.522 ± 0.05	8.498 ± 0.06	7.077 ± 0.03	7.567 ± 0.99
$\Delta\Delta_f H$	-0.93 ± 0.08	0.00 ± 0.00	-1.52 ± 0.03	$+1.43 \pm 0.39$
$\Delta\Delta_f S$	-1.98 ± 0.12	0.00 ± 0.00	-1.42 ± 0.09	-0.93 ± 1.06

Experimental Section Supplement.

General Procedures. Solvents are redistilled before use: THF from sodium/benzophenone, benzene from P_2O_5 . In many of the nitrile preparations, a *standard work-up* consists in quenching with saturated aqueous NH_4Cl , extraction first with diethyl ether, then with CH_2Cl_2 , drying the combined organic layers over anhydrous $MgSO_4$, filtration, and concentration to an oil.

2,4-Dimethyl-2-pentenitriles [$3\Delta^2(E)$ and $3\Delta^2(Z)$]. Following published procedures,^{50,51} a flame-dried, 1-L, three-necked flask equipped with a pressure-equalizing funnel and magnetic stirring bar was flushed with N_2 and charged with diisopropylamine (56 mL, 0.4 mol) in 160 mL of THF. To the solution cooled to $-76^\circ C$ by a dry-ice/isopropyl alcohol bath, butyllithium (0.4 mol, 160 mL of 2.5 M in hexane) was added dropwise. After 1 h, a solution of propanenitrile (0.2 mol, 14.2 mL) in 40 mL of THF was added dropwise, followed after 30 min by the dropwise addition of diethylchlorophosphate (29.8 mL, 0.2 mol) in 60 mL of THF. After 1 hour's stirring, freshly distilled 2-methylpropanal (18.2 mL, 0.2 mol) in 60 mL of THF was added. Over 1 h with stirring but without cooling, the reaction temperature rose to ambient. After 2 hour's additional stirring, the reaction mixture was quenched with 20% aqueous NH_4Cl , extracted with diethyl ether/ H_2O , and dried over anhydrous $MgSO_4$. Concentration and vacuum distillation gave a mixture of (*E*) and (*Z*) isomers (13.1 g, 61%), which was separated by preparative GC ($100^\circ C$): (*Z*)-2,4-dimethyl-2-pentenitrile, 1H NMR 5.25 (d, $J = 9.9$, 1H), 2.71 (m, 1H), 1.31 (s, 3H), 0.69 (d, $J = 6.7$, 6H); (*E*)-2,4-dimethyl-2-pentenitrile, 1H NMR 5.64 (d, $J = 9.7$, 1H), 1.96 (m, 1H), 1.23 (s, 3H), 0.52 (d, $J = 6.7$, 6H).

2,4-Dimethyl-3-pentenitrile ($3\Delta^3$). From the reaction mixtures recovered from the *tert*-BuOK-catalyzed equilibration of 2,4-dimethyl-2-pentenitriles, 2,4-dimethyl-3-pentenitrile was separated by preparative GC ($100^\circ C$): 1H NMR 4.73 (d, $J = 8.7$, 1H), 2.77 (m, 1H), 1.34 (s, 3H), 1.18 (s, 3H), 0.81 (d, $J = 7.0$, 3H).

2,4-Dimethyl-4-pentenitrile ($3\Delta^4$). Propanenitrile (7.1 mL, 0.1 mol) was added dropwise to a freshly prepared solution of lithium dimethylamide (LDA, 0.1 mol, *vide supra*) in THF. After 1 hour's stirring, this solution was slowly transferred into a solution of 3-chloro-2-

methylpropene (10.4 mL, 0.1 mol) in THF, and stirred for 30 min. The usual work-up—quenching with aqueous NH_4Cl , extraction with ether, drying over anhydrous MgSO_4 , concentration, vacuum distillation followed by preparative GC (110 °C)—yielded pure 2,4-dimethylpent-4-enenitrile: ^1H NMR (300 MHz) 4.72 (s, 1H), 4.62 (s, 1H), 1.99 (m, 1H), 1.83 (dd, $J = 7.4, 5.6$, 1H), 1.57 (dd, $J = 6.8, 7.3$, 1H), 1.37 (s, 3H), 0.69 (d, $J = 7.0$, 3H).

2-Cyano-4-methylpent-1-ene ($3\Delta^1$).^{52,53} To a 100-mL, three-necked flask, 10.2 g (12.7 mL, 0.1 mol) of 4-methylpentan-2-one, 4.0 g (0.08 mol) of sodium cyanide, and 10 mL of water were added. The solution was kept in an ice- H_2O bath (<15 °C) and stirred vigorously. From a dropping funnel, 40% H_2SO_4 (17 mL, 5.75 mL of 98% H_2SO_4 diluted with 11.25 mL H_2O) was added dropwise with vigorous stirring, which was continued overnight. The organic layer was separated from the aqueous layer, which was extracted with diethyl ether. Combined organic layer and ether extract was dried over anhydrous MgSO_4 , and concentrated. Vacuum distillation yielded 7.5 g of starting material, and 2.1 g of 2,4-dimethyl-2-hydroxypentanenitrile (79 % based on 31 % conversion): ^1H NMR (300Hz) 1.91 (m, 2H), 1.65 (q, 2H), 1.58 (s, 3H), 1.01 (d, 6H).

In a three-necked flask fitted with reflux condenser and stirrer were placed 2.0 g (0.0158 mol) of 2,4-dimethyl-2-hydroxypentanenitrile, 6.0 mL (0.063 mol) of acetic anhydride and 0.9 mL (0.0158 mol) of glacial acetic acid. The reaction mixture was heated under reflux overnight. Vacuum distillation afforded 1.02 g (38%) of 2-acetoxy-2,4-dimethylpentanenitrile: ^1H NMR (300 Hz) 2.08 (s, 3H), 1.95 (m, 1H), 1.85 (m, 2H), 1.74 (s, 3H), 1.01 (dd, 6H).

2-Acetoxy-2,4-dimethylpentanenitrile, 0.89 g (0.00474 mol), was injected dropwise into a 15-in quartz tube heated to 375 °C, through which a stream of argon was passed into a receiving flask cooled with dry-ice/isopropyl alcohol. The product (26%) consisted of a mixture of (*E*)- and (*Z*)-2-cyano-4-methylpent-2-ene [$3\Delta^2(E)$ and $3\Delta^2(Z)$], and 2-cyano-4-methylpent-1-ene ($3\Delta^1$) in a ratio 1:1.75:1.96 as determined by GC. Pure $3\Delta^1$ was separated by two-stage preparative GC: first, at 90 °C for 13 min, and then at 110 °C, which provided a mixture of $3\Delta^2(Z)$ and $3\Delta^1$; and,

second, by repassing at 60 °C: ^1H NMR (300 Hz) 5.17 (s, 1H), 4.81 (s, 1H), 1.62 (m, 1H), 1.52 (d, $J = 7.3$ Hz, 1H), 0.61 (d, $J = 6.4$ Hz, 6H).

Hydridonitrosyltris(triphenylphosphine)ruthenium ($\text{RuH}(\text{NO})(\text{PPh}_3)_3$). A two-step preparation of Ru complex is modified from the literature procedures.⁵⁴ Nitric oxide is freshly prepared by dropwise addition of 50% H_2SO_4 (40 mL) to 34.5 g of NaNO_2 (0.65 mol). The brown gas is passed through a 50% aqueous solution of KOH (10 mL) into which air is being bled at approximately the same rate. The mixture of NO and air is then passed through a 3% aqueous solution (15 mL) of 0.5 g of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (0.002 mol) at reflux temperature over a period of 2 h. Heating is continued for an additional 15 min after all NaNO_2 is consumed. The reaction mixture is cooled to room temperature, and treated with 5 mL of concentrated HCl. Removal of solvent by evaporation under reduced pressure affords a black, oily residue, which is treated with 15 mL of ethanol, and filtered through a bed of celite. Removal of ethanol leaves $\text{Ru}(\text{NO})\text{Cl}_3$ as a purple oil.

In a 100-mL, three-necked flask equipped with a dropping funnel, a solution of 5.0 g of KOH (0.009 mol) and 3.0 g of PPh_3 (0.011 mol) in absolute ethanol (40 mL) is purged with a stream of argon for 30 min, then heated for an additional hour at reflux under argon. A solution of $\text{Ru}(\text{NO})\text{Cl}_3$ in absolute ethanol (15 mL) is added over a period of 15 min. The initially dark brown precipitate turns rust-colored when the addition is complete. The mixture is heated for an additional hour at reflux temperature, and cooled to room temperature. The precipitate is collected, washed three times with hot absolute ethanol (10 mL), water (10 mL), finally with cold ethanol (10 mL), dried under vacuum overnight, and stored in desiccator under argon. The yield of $\text{RuH}(\text{NO})(\text{PPh}_3)_3$ is 1.5 g (91%): mp 146–150 °C; IR (CDCl_3) 1973, 1657; ^1H NMR 4.72 (q, $J = 30$, 1H, RuH).

(E)- and (Z)-2-Methyl-2-pentenitrile [$2\Delta^2(\text{E})$ and $2\Delta^2(\text{Z})$]. Preparation on a 0.1-mol scale follows the procedure for 2,4-dimethyl-2-pentenitrile above except propanal is substituted for 2-methylpropanal. Solvent is removed by fractional distillation; product is isolated by vacuum distillation: 5.9 g (62%) of a mixture of $2\Delta^2(\text{Z})$ and $2\Delta^2(\text{E})$ (ratio, 1.46:1.00),

which is separated by preparative GC (100 °C). $2\Delta^2(Z)$: ^1H NMR 5.35 (t, $J = 7.5$, 1H), 2.00 (p, $J = 7.5$, 2H), 1.34 (s, 3H), 0.64 (t, $J = 7.5$, 3H); $2\Delta^2(E)$ 5.73 (t, $J = 7.5$, 1H), 1.43 (p, $J = 7.5$, 2H), 1.20 (s, 3H), 0.48 (t, $J = 7.6$, 3H).

(E)- and (Z)-2-Methyl-3-pentenitrile [$2\Delta^3(E)$ and $2\Delta^3(Z)$]. A tube containing 100 mg of 2-methyl-4-pentenitrile, 20 mg of Ru complex, and 1.5 mL of benzene- d_6 is degassed, sealed under vacuum, and placed in a vapor bath at 101 °C for 20 h. The reaction mixture is distilled (trap to trap), and yields a mixture of $2\Delta^2(E)$ and $2\Delta^2(Z)$ in a ratio of 1: 3 after preparative GC at 80 °C. Resolution of the ^1H NMR spectrum is easily achieved: $2\Delta^2(Z)$ 5.22 (m, 1H), 4.97 (m, 1H); 2.84 (p, $J = 7.4$, 1H), 1.18 (dd, $J = 7.0$ Hz, $J = 1.75$, 3H), 0.80 (d, $J = 7.0$, 3H); $2\Delta^2(E)$: 5.43 (m, 1H), 4.85 (m, 1H), 2.49 (p, $J = 6.1$, 1H), 1.31 (dt, $J = 6.6$, $J = 1.36$, 3H), 0.78 (d, $J = 7.3$, 3H).

2-Methyl-4-pentenitrile ($2\Delta^4$). Preparation on a 0.1-mol scale followed the procedure for 2,4-dimethyl-4-pentenitrile above except 3-chloropropene is used in place of 2-methyl-3-chloropropene. The desired product, along with dimer 2-methyl-2-(2-propenyl)-4-pentenitrile, was produced (the ratio of monomer to dimer is about 3: 1). Vacuum distillation followed by preparative GC (120 °C) gave the pure 2-methyl-4-pentenitrile: ^1H NMR 5.44 (m, 1H), 4.89 (dd, $J = 10.4$, $J = 15.5$, 2H), 1.82 (m, $J = 7.0$, 1H), 1.70 (m, 2H), 0.68 (d, $J = 6.9$, 3H).

2-Cyanopent-1-ene ($2\Delta^1$). Method 1: Pentan-2-one replaced 4-methylpentan-2-one in the preparation of 2-cyano-4-methylpentene above: 2-hydroxy-2-methylpentenenitrile (44%): ^1H NMR 2.77 (s, 3H), 1.31 (m, 4H), 1.13 (s, 3H), 0.70 (t, 3H); 2-acetoxy-2-methylpentenenitrile (64%): ^1H NMR 1.50-1.20 (m, 4H), 1.46 (s, 3H), 1.29 (s, 3H), 0.65 (t, 3H); 2-cyanopent-1-ene (21%): ^1H NMR 5.19 (s, 1H), 4.85 (s, 1H), 1.63 (t, $J = 7.0$, 2H), 1.23 (m, $J = 7.5$, 2H), 0.63 (t, $J = 7.4$, 3H). Method 2: To a solution of 21.3 g of cyanoacetic acid (0.25 mol) and 30 mL of acetonitrile in a 250-mL flask, 17.4 g of propanal (0.30 mol), 0.25 g of 10% Pd on charcoal, and, with cooling, 0.5 mL of piperidine were added. Hydrogenation was effected by attaching a hydrogen balloon. The slow progress of the hydrogenation was monitored by ^1H NMR. After three days, hydrogenation was stopped. The solution was filtered into a 500-mL, round-bottomed

flask, to which 20.4 g of dimethylamine hydrochloride (0.25 mol) and 9 g of paraformaldehyde (0.3 mol) were added. The mixture was heated slowly to 90–95 °C in an oil bath. Above 70 °C, evolution of CO₂ commenced. After 3 h at reflux, the solution was cooled and concentrated by fractional distillation. Addition of 30 mL water, steam-distillation, extraction with pentane, and fractional distillation followed by preparative GC (90 °C) yielded pure **2Δ¹**.

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