Supporting Information

Dehydrogenative Formation of (η^4-Enone)ruthenium(0) Complex as a Key Intermediate in Catalytic Isomerization of Allyllic Alcohol to Ketone

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Table 1. Crystallographic and Physical data for **3**.

Formula	C21 H49 O P3 Ru
Formula weight	511.61
Crystal System	monoclinic
Space Group	$P2_1/n$ (*No. 14*)
Crystal Description	prismatic
Crystal Color	pale yellow
a (Å)	8.866(4)
b (Å)	18.635(4)
c (Å)	16.021(5)
β (deg)	100.57(3)
z	4
V (Å^3)	2601(1)
T (K)	200.2
size (mm x mm x mm)	0.47 x 0.42 x 0.34
D_{calcd} (g cm^{-3})	1.306
μ (mm^{-1})	0.796
Absorption Correction Type	psi-scan
Radiation	MoKα ($\lambda = 0.7107$ Å)
Measurement Device	Rigaku AFC7R
Measurement Method	$\omega-2\theta$
Number of Total Reflection Number	6376
R_{int}	0.027
θ_{max}	27.50
Number of Unique Reflections	5972
Number of Observations (I > 3.00 σ(I))	4094
Number of Variables	235
Reflection/Parameter ration	17.42
R, R_w	0.0343, 0.0479
S	1.228

Table 2. Atomic Coordinates and Displacement Parameters for **3**.

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Ru(1)  Ru  0.05989(3)   0.21242(2)   0.28354(2)   0.02771(7)
P(1)   P   -0.0670(1)   0.13571(5)   0.36290(6)   0.0303(2)
P(2)   P   0.0070(1)    0.14200(6)   0.16456(7)   0.0377(3)
P(3)   P   -0.1088(1)   0.30722(5)   0.24412(6)   0.0296(2 )
O(1)   O   0.1788(4)    0.2648(2)    0.4012(2)    0.0518(9)
C(1)   C   0.2645(5)    0.2118(3)    0.3828(3)    0.052(1)
C(2)   C   0.3111(5)    0.2115(3)    0.3047(3)    0.054(1)
C(3)   C   0.2530(5)    0.2691(3)    0.2475(3)    0.049(1)
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C(4)    C   -0.2773(5)   0.1245(2)    0.3401(3)    0.040(1)
C(5)    C   -0.3513(5)   0.0702(3)    0.3904(3)    0.052(1)
C(6)    C   -0.0338(5)   0.1547(3)    0.4776(3)    0.046(1)
C(7)    C   -0.1221(7)   0.2182(3)    0.5038(3)    0.065(2)
C(8)    C   -0.0077(5)   0.0395(2)    0.3677(3)    0.043(1)
C(9)    C    0.1647(6)   0.0271(3)    0.3971(4)    0.058(2)
C(10)   C    0.1253(9)   0.0588(3)    0.1636(4)    0.082(2)
C(11)   C    0.2848(9)   0.0688(5)    0.1532(5)    0.121(3)
C(12)   C    0.0382(6)   0.1824(3)    0.0646(3)    0.051(1)
C(13)   C    0.0126(8)   0.1366(3)   -0.0167(3)    0.071(2)
C(14)   C   -0.1805(7)   0.0958(3)    0.1317(3)    0.066(2)
C(15)   C   -0.3075(8)   0.1433(4)    0.1072(3)    0.078(2)
C(16)   C   -0.0349(5)   0.3913(2)    0.2994(3)    0.043(1)
C(17)   C   -0.0475(7)   0.3970(3)    0.3927(3)    0.059(2)
C(18)   C   -0.3075(5)   0.3060(2)    0.2658(3)    0.038(1)
C(19)   C   -0.4044(5)   0.3737(2)    0.2484(3)    0.051(1)
C(20)   C   -0.1445(5)   0.3424(2)    0.1337(2)    0.037(1)
C(21)   C   -0.0034(6)   0.3729(3)    0.1048(3)    0.049(1)
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Table 3. Anisotropic Parameters for **3**.

Ru(1)	0.0241(1)	0.0311(2)	0.0266(1)	-0.0021(1)	0.00132(10)	0.0025(1)
P(1)	0.0304(5)	0.0314(5)	0.0279(5)	0.0005(4)	0.0022(4)	0.0052(4)
P(2)	0.0404(6)	0.0399(6)	0.0344(5)	-0.0022(5)	0.0113(4)	-0.0031(4)
P(3)	0.0319(5)	0.0279(5)	0.0281(5)	-0.0028(4)	0.0030(4)	0.0027(4)
O(1)	0.049(2)	0.055(2)	0.045(2)	-0.012(2)	-0.007(1)	-0.010(2)
C(1)	0.035(2)	0.060(3)	0.054(3)	-0.007(2)	-0.008(2)	0.004(2)
C(2)	0.025(2)	0.062(3)	0.073(3)	-0.002(2)	0.006(2)	-0.001(3)
C(3)	0.037(2)	0.058(3)	0.053(3)	-0.016(2)	0.009(2)	0.003(2)
C(4)	0.038(2)	0.042(2)	0.039(2)	-0.002(2)	0.005(2)	0.010(2)
C(5)	0.043(2)	0.050(3)	0.063(3)	-0.005(2)	0.012(2)	0.017(2)
C(6)	0.050(3)	0.054(3)	0.031(2)	-0.003(2)	0.003(2)	0.008(2)
C(7)	0.082(4)	0.071(4)	0.046(3)	-0.003(3)	0.022(3)	-0.014(3)
C(8)	0.050(2)	0.030(2)	0.050(3)	0.004(2)	0.010(2)	0.008(2)
C(9)	0.056(3)	0.047(3)	0.074(4)	0.020(2)	0.015(3)	0.024(3)
C(10)	0.144(6)	0.052(3)	0.060(4)	0.032(4)	0.044(4)	0.007(3)
C(11)	0.103(6)	0.143(8)	0.116(6)	0.073(6)	0.020(5)	-0.032(6)
C(12)	0.071(3)	0.053(3)	0.031(2)	0.004(2)	0.015(2)	0.002(2)
C(13)	0.097(4)	0.079(4)	0.041(3)	0.021(3)	0.023(3)	-0.004(3)
C(14)	0.066(3)	0.083(4)	0.052(3)	-0.015(3)	0.016(3)	-0.019(3)
C(15)	0.084(4)	0.101(5)	0.045(3)	-0.006(4)	0.000(3)	0.002(3)
C(16)	0.047(2)	0.033(2)	0.046(2)	-0.007(2)	0.003(2)	-0.001(2)
C(17)	0.091(4)	0.042(3)	0.041(3)	-0.011(3)	0.006(3)	-0.009(2)
C(18)	0.038(2)	0.032(2)	0.047(2)	0.000(2)	0.010(2)	0.006(2)
C(19)	0.042(2)	0.043(3)	0.071(3)	0.008(2)	0.017(2)	0.011(2)
C(20)	0.046(2)	0.035(2)	0.030(2)	0.000(2)	0.004(2)	0.009(2)
C(21)	0.056(3)	0.053(3)	0.039(2)	-0.001(2)	0.013(2)	0.014(2)

Table 4. Bond distances for **3** (Å).

Ru(1)	P(1)	2.335(1)
Ru(1)	P(2)	2.291(1)
Ru(1)	P(3)	2.326(1)
Ru(1)	O(1)	2.211(3)
Ru(1)	C(1)	2.182(4)
Ru(1)	C(2)	2.191(4)
Ru(1)	C(3)	2.178(4)
P(1)	C(4)	1.845(4)
P(1)	C(6)	1.842(4)
P(1)	C(8)	1.865(4)
P(2)	C(10)	1.874(6)
P(2)	C(12)	1.836(5)
P(2)	C(14)	1.860(6)
P(3)	C(16)	1.859(4)
P(3)	C(18)	1.857(4)
P(3)	C(20)	1.858(4)
O(1)	C(1)	1.313(6)
C(1)	C(2)	1.389(7)
C(2)	C(3)	1.443(7)
C(4)	C(5)	1.516(6)
C(6)	C(7)	1.520(7)
C(8)	C(9)	1.532(6)
C(10)	C(11)	1.47(1)
C(12)	C(13)	1.539(7)
C(14)	C(15)	1.431(9)
C(16)	C(17)	1.523(7)
C(18)	C(19)	1.522(6)
C(20)	C(21)	1.522(6)

Table 5. Bond Angles for **3** (deg).

P(1)	Ru(1)	P(2)	93.26(4)
P(1)	Ru(1)	P(3)	105.24(4)
P(1)	Ru(1)	O(1)	90.47(9)
P(1)	Ru(1)	C(1)	91.1(1)
P(1)	Ru(1)	C(2)	119.3(1)
P(1)	Ru(1)	C(3)	157.2(1)
P(2)	Ru(1)	P(3)	100.71(4)
P(2)	Ru(1)	O(1)	162.79(10)
P(2)	Ru(1)	C(1)	128.3(1)
P(2)	Ru(1)	C(2)	99.8(1)
P(2)	Ru(1)	C(3)	96.2(1)
P(3)	Ru(1)	O(1)	94.48(10)
P(3)	Ru(1)	C(1)	127.5(1)
P(3)	Ru(1)	C(2)	129.3(1)
P(3)	Ru(1)	C(3)	93.3(1)
O(1)	Ru(1)	C(1)	34.8(2)
O(1)	Ru(1)	C(2)	63.9(2)
O(1)	Ru(1)	C(3)	74.7(2)
C(1)	Ru(1)	C(2)	37.0(2)
C(1)	Ru(1)	C(3)	66.8(2)
C(2)	Ru(1)	C(3)	38.6(2)
Ru(1)	P(1)	C(4)	122.1(1)
Ru(1)	P(1)	C(6)	114.9(2)
Ru(1)	P(1)	C(8)	116.8(1)
C(4)	P(1)	C(6)	101.0(2)
C(4)	P(1)	C(8)	99.6(2)
C(6)	P(1)	C(8)	98.7(2)
Ru(1)	P(2)	C(10)	116.8(2)
Ru(1)	P(2)	C(12)	116.8(2)
Ru(1)	P(2)	C(14)	122.4(2)

Table 5. Continued.

C(10)	P(2)	C(12)	99.1(2)
C(10)	P(2)	C(14)	95.0(3)
C(12)	P(2)	C(14)	102.3(2)
Ru(1)	P(3)	C(16)	111.0(1)
Ru(1)	P(3)	C(18)	121.7(1)
Ru(1)	P(3)	C(20)	121.0(1)
C(16)	P(3)	C(18)	100.6(2)
C(16)	P(3)	C(20)	98.0(2)
C(18)	P(3)	C(20)	100.4(2)
Ru(1)	O(1)	C(1)	71.4(2)
Ru(1)	C(1)	O(1)	73.8(2)
Ru(1)	C(1)	C(2)	71.8(3)
O(1)	C(1)	C(2)	119.0(5)
Ru(1)	C(2)	C(1)	71.2(2)

Ru(1)	C(2)	C(3)	70.2(2)
C(1)	C(2)	C(3)	116.0(4)
Ru(1)	C(3)	C(2)	71.2(2)
P(1)	C(4)	C(5)	119.4(3)
P(1)	C(6)	C(7)	115.4(3)
P(1)	C(8)	C(9)	114.6(3)
P(2)	C(10)	C(11)	116.7(5)
P(2)	C(12)	C(13)	119.2(4)
P(2)	C(14)	C(15)	114.1(5)
P(3)	C(16)	C(17)	116.3(3)
P(3)	C(18)	C(19)	118.6(3)
P(3)	C(20)	C(21)	114.6(3)

Table 6. Torsion angles for **3** (deg).

Ru(1)	P(1)	C(4)	C(5)	176.1(3)
Ru(1)	P(1)	C(6)	C(7)	77.1(4)
Ru(1)	P(1)	C(8)	C(9)	53.7(4)
Ru(1)	P(2)	C(10)	C(11)	-72.8(5)
Ru(1)	P(2)	C(12)	C(13)	176.9(4)
Ru(1)	P(2)	C(14)	C(15)	65.9(5)
Ru(1)	P(3)	C(16)	C(17)	-75.2(4)
Ru(1)	P(3)	C(18)	C(19)	172.4(3)
Ru(1)	P(3)	C(20)	C(21)	-61.4(4)
Ru(1)	O(1)	C(1)	C(2)	57.8(4)
Ru(1)	C(1)	C(2)	C(3)	55.7(4)
Ru(1)	C(2)	C(1)	O(1)	-58.8(4)
Ru(1)	C(3)	C(2)	C(1)	-56.2(4)
P(1)	Ru(1)	P(2)	C(10)	-76.9(2)
P(1)	Ru(1)	P(2)	C(12)	166.1(2)
P(1)	Ru(1)	P(2)	C(14)	39.0(3)
P(1)	Ru(1)	P(3)	C(16)	111.2(2)
P(1)	Ru(1)	P(3)	C(18)	-6.8(2)
P(1)	Ru(1)	P(3)	C(20)	-134.9(2)
P(1)	Ru(1)	O(1)	C(1)	91.2(3)
P(1)	Ru(1)	C(1)	O(1)	-89.3(2)
P(1)	Ru(1)	C(1)	C(2)	141.9(3)
P(1)	Ru(1)	C(2)	C(1)	-45.0(3)
P(1)	Ru(1)	C(2)	C(3)	-173.0(2)
P(1)	Ru(1)	C(3)	C(2)	16.0(5)
P(2)	Ru(1)	P(1)	C(4)	-68.8(2)
P(2)	Ru(1)	P(1)	C(6)	168.5(2)
P(2)	Ru(1)	P(1)	C(8)	53.6(2)
P(2)	Ru(1)	P(3)	C(16)	-152.4(2)
P(2)	Ru(1)	P(3)	C(18)	89.6(2)
P(2)	Ru(1)	P(3)	C(20)	-38.5(2)

Table 6. Continued.

P(2)	Ru(1)	O(1)	C(1)	-11.4(5)
P(2)	Ru(1)	C(1)	O(1)	175.7(2)
P(2)	Ru(1)	C(1)	C(2)	46.9(4)
P(2)	Ru(1)	C(2)	C(1)	-144.4(3)
P(2)	Ru(1)	C(2)	C(3)	87.6(3)
P(2)	Ru(1)	C(3)	C(2)	-98.0(3)
P(3)	Ru(1)	P(1)	C(4)	33.2(2)
P(3)	Ru(1)	P(1)	C(6)	-89.4(2)
P(3)	Ru(1)	P(1)	C(8)	155.7(2)
P(3)	Ru(1)	P(2)	C(10)	176.9(2)
P(3)	Ru(1)	P(2)	C(12)	59.9(2)
P(3)	Ru(1)	P(2)	C(14)	-67.2(3)
P(3)	Ru(1)	O(1)	C(1)	-163.5(3)
P(3)	Ru(1)	C(1)	O(1)	21.0(3)

P(3)	Ru(1)	C(1)	C(2)	-107.9(3)
P(3)	Ru(1)	C(2)	C(1)	102.9(3)
P(3)	Ru(1)	C(2)	C(3)	-25.1(4)
P(3)	Ru(1)	C(3)	C(2)	160.8(3)
0(1)	Ru(1)	P(1)	C(4)	128.0(2)
0(1)	Ru(1)	P(1)	C(6)	5.3(2)
0(1)	Ru(1)	P(1)	C(8)	-109.5(2)
0(1)	Ru(1)	P(2)	C(10)	25.3(4)
0(1)	Ru(1)	P(2)	C(12)	-91.6(4)
0(1)	Ru(1)	P(2)	C(14)	141.2(4)
0(1)	Ru(1)	P(3)	C(16)	19.5(2)
0(1)	Ru(1)	P(3)	C(18)	-98.5(2)
0(1)	Ru(1)	P(3)	C(20)	133.3(2)
0(1)	Ru(1)	C(1)	C(2)	-128.9(4)
0(1)	Ru(1)	C(2)	C(1)	29.6(3)
0(1)	Ru(1)	C(2)	C(3)	-98.3(3)
0(1)	Ru(1)	C(3)	C(2)	67.1(3)

Table 6. Continued.

0(1)	C(1)	Ru(1)	C(2)	128.9(4)
0(1)	C(1)	Ru(1)	C(3)	96.5(3)
0(1)	C(1)	C(2)	C(3)	-3.1(6)
C(1)	Ru(1)	P(1)	C(4)	162.8(2)
C(1)	Ru(1)	P(1)	C(6)	40.1(2)
C(1)	Ru(1)	P(1)	C(8)	-74.8(2)
C(1)	Ru(1)	P(2)	C(10)	17.0(3)
C(1)	Ru(1)	P(2)	C(12)	-99.9(3)
C(1)	Ru(1)	P(2)	C(14)	132.9(3)
C(1)	Ru(1)	P(3)	C(16)	7.7(2)
C(1)	Ru(1)	P(3)	C(18)	-110.3(2)
C(1)	Ru(1)	P(3)	C(20)	121.5(2)
C(1)	Ru(1)	C(2)	C(3)	-127.9(5)
C(1)	Ru(1)	C(3)	C(2)	31.1(3)
C(1)	0(1)	Ru(1)	C(2)	-31.5(3)
C(1)	0(1)	Ru(1)	C(3)	-71.3(3)
C(1)	C(2)	Ru(1)	C(3)	127.9(5)
C(2)	Ru(1)	P(1)	C(4)	-172.0(2)
C(2)	Ru(1)	P(1)	C(6)	65.3(2)
C(2)	Ru(1)	P(1)	C(8)	-49.5(2)
C(2)	Ru(1)	P(2)	C(10)	43.5(3)
C(2)	Ru(1)	P(2)	C(12)	-73.4(2)
C(2)	Ru(1)	P(2)	C(14)	159.4(3)
C(2)	Ru(1)	P(3)	C(16)	-40.1(2)
C(2)	Ru(1)	P(3)	C(18)	-158.1(2)
C(2)	Ru(1)	P(3)	C(20)	73.8(2)
C(2)	C(1)	Ru(1)	C(3)	-32.3(3)
C(3)	Ru(1)	P(1)	C(4)	176.6(4)
C(3)	Ru(1)	P(1)	C(6)	54.0(4)
C(3)	Ru(1)	P(1)	C(8)	-60.9(4)
C(3)	Ru(1)	P(2)	C(10)	82.3(3)

Table 6. Continued.

C(3)	Ru(1)	P(2)	C(12)	-34.6(2)
C(3)	Ru(1)	P(2)	C(14)	-161.8(3)
C(3)	Ru(1)	P(3)	C(16)	-55.4(2)
C(3)	Ru(1)	P(3)	C(18)	-173.4(2)
C(3)	Ru(1)	P(3)	C(20)	58.4(2)
C(4)	P(1)	C(6)	C(7)	-56.4(4)
C(4)	P(1)	C(8)	C(9)	-172.8(4)
C(5)	C(4)	P(1)	C(6)	-55.0(4)
C(5)	C(4)	P(1)	C(8)	45.9(4)
C(6)	P(1)	C(8)	C(9)	-70.0(4)
C(7)	C(6)	P(1)	C(8)	-158.0(4)
C(10)	P(2)	C(12)	C(13)	50.6(5)
C(10)	P(2)	C(14)	C(15)	-167.8(4)
C(11)	C(10)	P(2)	C(12)	53.5(6)
C(11)	C(10)	P(2)	C(14)	156.8(6)
C(12)	P(2)	C(14)	C(15)	-67.4(4)
C(13)	C(12)	P(2)	C(14)	-46.6(5)
C(16)	P(3)	C(18)	C(19)	49.4(4)
C(16)	P(3)	C(20)	C(21)	59.0(4)
C(17)	C(16)	P(3)	C(18)	54.9(4)
C(17)	C(16)	P(3)	C(20)	157.1(4)
C(18)	P(3)	C(20)	C(21)	161.4(3)
C(19)	C(18)	P(3)	C(20)	-50.8(4)