Arabian Journal of Chemical and Environmental Researches

Vol. 01 Issue 1 (2014) 76–99

www.mocedes.org/ajcer

Hydroformylation reaction of styrene using new rhodium pyrazole complex

R. Touzani [1,2*]

[1]*LCAE, COSTE, Faculté des Sciences, Université Mohammed Premier, BP524, 60000 Oujda, Morocco.*

[2]*Faculté Pluridisciplinaire de Nador, Université Mohammed Premier, BP300, Selouane 62700, Nador, Morocco*

Received 18 Dec 2014, Revised 26 Jan 2015, Accepted 28 Jan 2015

Abstract

The synthesis of new rhodium complex based on pyrazole was reported and examined for its hydroformylation reaction of styrene at different conditions. The studies of the X-ray spectrum show that we have selective coordination with the rhodium COD just the *head-to-tail* was observed no *head-to-head.* We found that reaction rate depends on different parameters: temperature, and the nature of solvent. We found very interesting results; the selectivity for the branched aldehyde is increasing with the decreases of temperature.

Keywords: pyrazol, catechol, multidentate, transition metal; oxidation reaction.

*Corresponding author. Tel: + 212 677 968 240
E-mail address: touzanir@yahoo.fr

1. Introduction

The hydroformylation reaction is one of the largest industrial catalytic processes producing millions of tons of aldehydes from alkenes annually. Branched aryl aldehydes are useful intermediates in the pharmaceutical industry while straight chain linear aldehydes have been produced on megaton scales annually [1-11]. Mononuclear rhodium phosphines (Rh/Par_3) catalysts dominate the hydroformylation industry predominantly for C3 through C6 1-alkenes, where regioselectivity towards straight chain aldehyde products is still a problem [12]. Moreover, the use of binuclear rhodium complexes bearing bridge ligands as catalysts precursors for the hydroformylation of olefins has been less exploited considering that their catalytic activity is known for several years. As example ofit, Stanley et al., reported an elegant work for the synthesis of the Rh complex

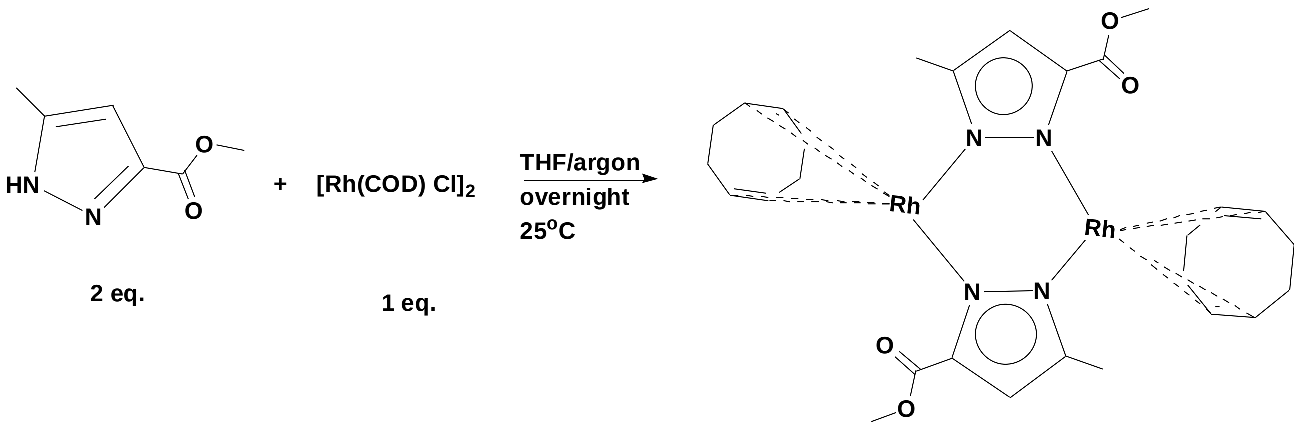
ISSN : 2458-6544

[$Rh_2(NBD)_2$P-P] with P-P: different diphos-phines. They proposed the first mechanism for bimetallic hydroformylation with a cooperative effect of both metal [13-14]. Otherwise, pyrazole presents a huge importance in coordination chemistry and catalysis as nitrogen rich ligand [15-25]. Herein, we report the synthesis of new pyrazolate Rh and its catalytic activity via the hydroformylation of styrene.

2. Results and Discussion

2.1 Synthesis of the Rhodium complex with the 5-Methyl-1H-pyrazole-3-carboxylic acid ester.

The structure of *Head-to-tail* PzRh(1**)** is presented below in Scheme 1.



Scheme 1: Structure of *Head-to-tail* PzRh(1**)**

2.2 Characterisation of the Complex PzRh(1):The structure was confirmed by using proton, carbon NMR and X-ray (Figure 1)

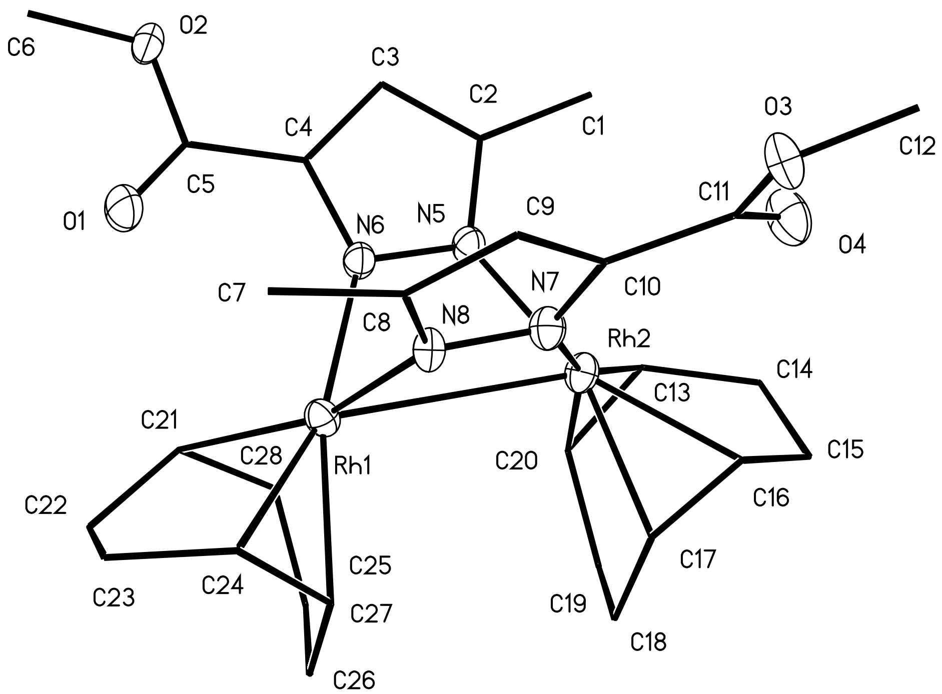


Figure 1: Structure RX of PzRh(I)

Table 1. Crystal data and structure refinement for PzRh(I).

Identification code	PzRh(I)
Empirical formula	C56 H76 N8 O8 Rh4
Formula weight	1400.89
Temperature	208(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 11.797(19) A alpha = 81.48(11) deg. b = 15.503(19) A beta = 71.56(17) deg. c = 16.440(16) A gamma = 79.11(9) deg.
Volume	2788(6) A^3
Z, Calculated density	2, 1.668 Mg/m^3
Absorption coefficient	1.224 mm^-1
F(000)	1424
Crystal size	0.25 x 0.20 x 0.15 mm
Theta range for data collection	1.31 to 23.30 deg.
Limiting indices	-7<=h<=13, -17<=k<=17, -18<=l<=15
Reflections collected / unique	11247 / 7512 [R(int) = 0.0270]
Completeness to theta = 23.30	93.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8377 and 0.7495
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7512 / 0 / 693
Goodness-of-fit on F^2	1.085
Final R indices [I>2sigma(I)]	R1 = 0.0419, wR2 = 0.0945
R indices (all data)	R1 = 0.0553, wR2 = 0.0997
Largest diff. peak and hole	0.695 and -0.800 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for ha1. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(14)	-1647(7)	2928(5)	7747(5)	70(2)
Rh(1)	1526(1)	2620(1)	10020(1)	31(1)
Rh(2)	-593(1)	2992(1)	9157(1)	33(1)
N(6)	415(4)	1644(3)	10313(3)	31(1)
O(4)	-3468(4)	3893(3)	10193(3)	52(1)
O(3)	-3987(3)	4596(2)	11394(3)	42(1)
N(5)	-476(4)	1795(3)	9918(3)	32(1)
N(7)	-1005(4)	3544(3)	10331(3)	32(1)
C(10)	-2006(5)	3913(3)	10919(3)	30(1)
C(11)	-3206(5)	4122(4)	10761(4)	36(1)
O(2)	590(4)	-55(3)	12026(3)	45(1)
C(5)	889(5)	695(4)	11538(4)	36(1)
O(1)	1623(4)	1086(3)	11637(3)	54(1)
C(7)	256(5)	3462(4)	12089(4)	39(1)
C(4)	174(5)	963(4)	10940(4)	33(1)
C(9)	-1731(5)	3973(3)	11670(3)	32(1)
C(2)	-1252(5)	1213(4)	10306(4)	35(1)
N(8)	-82(4)	3386(3)	10691(3)	29(1)
C(20)	447(5)	2485(4)	7954(4)	41(2)
C(27)	3497(6)	2558(4)	8297(4)	53(2)
C(8)	-519(5)	3630(3)	11504(3)	30(1)
C(3)	-866(5)	673(4)	10930(4)	40(2)
C(28)	2903(5)	1935(4)	9026(4)	40(2)
C(17)	-161(6)	4211(4)	8429(4)	45(2)
C(21)	3198(5)	1705(4)	9781(4)	45(2)
C(19)	1008(6)	3190(4)	7284(4)	52(2)
C(24)	2620(5)	3476(4)	10190(4)	47(2)
C(25)	2500(5)	3697(4)	9369(4)	41(2)
C(18)	907(6)	4046(4)	7648(4)	55(2)
C(22)	4175(6)	2074(5)	9968(5)	67(2)
C(16)	-1337(6)	4145(4)	8489(4)	48(2)
C(13)	-755(6)	2359(4)	8144(4)	46(2)
C(26)	3495(6)	3449(4)	8559(4)	52(2)
C(6)	1200(6)	-364(4)	12674(4)	57(2)
C(23)	3731(6)	2929(5)	10391(5)	67(2)
C(15)	-1700(7)	3912(5)	7752(5)	74(2)
C(1)	-2397(5)	1236(5)	10049(4)	57(2)
Rh(3)	6285(1)	1988(1)	5009(1)	30(1)
Rh(4)	4032(1)	2450(1)	4320(1)	31(1)
O(6)	4660(3)	357(2)	7875(2)	41(1)
O(7)	1854(3)	5250(2)	5620(3)	40(1)
C(42)	2347(7)	2285(5)	3347(5)	67(2)
O(8)	1712(4)	4050(3)	5055(3)	50(1)
N(1)	3787(4)	1622(3)	5473(3)	32(1)
N(3)	4181(4)	3384(3)	5064(3)	29(1)
O(5)	6148(4)	1066(3)	7002(3)	46(1)
N(4)	5186(4)	3200(3)	5346(3)	31(1)
C(33)	5177(5)	828(3)	7144(4)	34(1)
C(30)	2823(5)	1336(3)	6077(3)	30(1)
C(36)	5091(5)	3801(3)	5900(3)	29(1)
C(32)	4392(5)	1039(3)	6590(3)	28(1)
C(38)	3487(5)	4111(3)	5435(3)	30(1)

C(53)	7641(5)	2514(4)	3924(4)	42(2)
N(2)	4757(4)	1443(3)	5791(3)	31(1)
C(45)	4859(5)	3168(4)	3130(3)	35(1)
C(41)	3162(6)	1673(4)	3800(4)	47(2)
C(49)	7505(5)	783(4)	5080(4)	45(2)
C(39)	2281(5)	4438(4)	5334(4)	36(1)
C(56)	7073(5)	803(4)	4380(4)	43(2)
C(31)	3157(5)	960(3)	6793(4)	34(1)
C(54)	8326(5)	1832(4)	3287(4)	47(2)
C(48)	4400(6)	1430(4)	3469(4)	44(2)
C(55)	7771(6)	992(4)	3456(4)	51(2)
C(43)	2808(6)	3150(5)	2935(4)	58(2)
C(40)	650(5)	5619(4)	5583(4)	51(2)
C(46)	5592(6)	2564(4)	2447(4)	52(2)
C(52)	7898(5)	2561(4)	4692(4)	44(2)
C(37)	4037(5)	4393(3)	5954(4)	35(1)
C(35)	6005(5)	3743(4)	6372(4)	46(2)
C(47)	5103(6)	1709(4)	2543(4)	55(2)
C(44)	3633(5)	3435(4)	3349(4)	41(2)
C(34)	5352(6)	131(4)	8486(4)	54(2)
C(29)	1587(5)	1481(4)	5947(4)	39(2)
C(51)	8805(6)	1930(5)	5026(5)	61(2)
C(50)	8761(6)	964(5)	4977(5)	62(2)
C(12)	-5201(5)	4845(4)	11330(4)	54(2)

Table 3. Bond lengths [A] and angles [deg] for ha1.

C(14)-C(13)	1.492(9)
C(14)-C(15)	1.516(10)
Rh(1)-N(6)	2.091(5)
Rh(1)-N(8)	2.107(6)
Rh(1)-C(24)	2.120(6)
Rh(1)-C(28)	2.148(7)
Rh(1)-C(25)	2.161(6)
Rh(1)-C(21)	2.162(6)
Rh(1)-Rh(2)	3.170(5)
Rh(2)-N(5)	2.086(5)
Rh(2)-N(7)	2.106(5)
Rh(2)-C(13)	2.128(6)
Rh(2)-C(17)	2.138(7)
Rh(2)-C(20)	2.143(7)
Rh(2)-C(16)	2.147(7)
N(6)-C(4)	1.364(7)
N(6)-N(5)	1.369(6)
O(4)-C(11)	1.190(7)
O(3)-C(11)	1.355(7)
O(3)-C(12)	1.443(7)
N(5)-C(2)	1.353(7)
N(7)-C(10)	1.358(7)
N(7)-N(8)	1.364(6)
C(10)-C(9)	1.391(8)
C(10)-C(11)	1.488(8)
O(2)-C(5)	1.349(7)
O(2)-C(6)	1.445(7)
C(5)-O(1)	1.209(7)
C(5)-C(4)	1.458(8)
C(7)-C(8)	1.489(8)

C(4)-C(3)	1.389(8)
C(9)-C(8)	1.382(8)
C(2)-C(3)	1.362(8)
C(2)-C(1)	1.531(8)
N(8)-C(8)	1.356(7)
C(20)-C(13)	1.397(9)
C(20)-C(19)	1.517(9)
C(27)-C(28)	1.497(9)
C(27)-C(26)	1.505(8)
C(28)-C(21)	1.373(9)
C(17)-C(16)	1.382(9)
C(17)-C(18)	1.502(9)
C(21)-C(22)	1.508(9)
C(19)-C(18)	1.505(9)
C(24)-C(25)	1.388(9)
C(24)-C(23)	1.523(9)
C(25)-C(26)	1.513(9)
C(22)-C(23)	1.515(10)
C(16)-C(15)	1.516(10)
Rh(3)-N(2)	2.098(6)
Rh(3)-N(4)	2.110(5)
Rh(3)-C(52)	2.134(6)
Rh(3)-C(49)	2.144(6)
Rh(3)-C(56)	2.149(6)
Rh(3)-C(53)	2.159(7)
Rh(3)-Rh(4)	3.132(5)
Rh(4)-N(3)	2.092(5)
Rh(4)-N(1)	2.097(5)
Rh(4)-C(41)	2.136(6)
Rh(4)-C(45)	2.139(6)
Rh(4)-C(44)	2.141(6)
Rh(4)-C(48)	2.158(6)
O(6)-C(33)	1.340(7)
O(6)-C(34)	1.449(7)
O(7)-C(39)	1.358(7)
O(7)-C(40)	1.444(7)
C(42)-C(41)	1.508(9)
C(42)-C(43)	1.525(10)
O(8)-C(39)	1.205(7)
N(1)-C(30)	1.351(7)
N(1)-N(2)	1.370(6)
N(3)-C(38)	1.362(7)
N(3)-N(4)	1.372(6)
O(5)-C(33)	1.211(7)
N(4)-C(36)	1.362(7)
C(33)-C(32)	1.458(8)
C(30)-C(31)	1.372(8)
C(30)-C(29)	1.510(8)
C(36)-C(37)	1.385(7)
C(36)-C(35)	1.500(8)
C(32)-N(2)	1.343(7)
C(32)-C(31)	1.413(8)
C(38)-C(37)	1.382(8)
C(38)-C(39)	1.470(8)
C(53)-C(52)	1.403(9)
C(53)-C(54)	1.529(8)
C(45)-C(44)	1.372(8)
C(45)-C(46)	1.508(8)
C(41)-C(48)	1.386(9)
C(49)-C(56)	1.391(9)
C(49)-C(50)	1.513(9)

C(56)-C(55)	1.497(9)
C(54)-C(55)	1.516(9)
C(48)-C(47)	1.528(9)
C(43)-C(44)	1.509(8)
C(46)-C(47)	1.512(9)
C(52)-C(51)	1.490(9)
C(51)-C(50)	1.522(9)
C(13)-C(14)-C(15)	115.0(6)
N(6)-Rh(1)-N(8)	82.7(2)
N(6)-Rh(1)-C(24)	159.5(2)
N(8)-Rh(1)-C(24)	92.6(2)
N(6)-Rh(1)-C(28)	93.8(2)
N(8)-Rh(1)-C(28)	162.3(2)
C(24)-Rh(1)-C(28)	96.4(3)
N(6)-Rh(1)-C(25)	162.6(2)
N(8)-Rh(1)-C(25)	97.4(2)
C(24)-Rh(1)-C(25)	37.8(2)
C(28)-Rh(1)-C(25)	80.8(3)
N(6)-Rh(1)-C(21)	95.0(2)
N(8)-Rh(1)-C(21)	160.2(2)
C(24)-Rh(1)-C(21)	82.7(3)
C(28)-Rh(1)-C(21)	37.1(2)
C(25)-Rh(1)-C(21)	90.6(3)
N(6)-Rh(1)-Rh(2)	64.47(16)
N(8)-Rh(1)-Rh(2)	64.11(15)
C(24)-Rh(1)-Rh(2)	130.9(2)
C(28)-Rh(1)-Rh(2)	98.7(2)
C(25)-Rh(1)-Rh(2)	99.8(2)
C(21)-Rh(1)-Rh(2)	132.35(19)
N(5)-Rh(2)-N(7)	83.80(19)
N(5)-Rh(2)-C(13)	91.6(2)
N(7)-Rh(2)-C(13)	161.7(2)
N(5)-Rh(2)-C(17)	161.7(2)
N(7)-Rh(2)-C(17)	91.8(2)
C(13)-Rh(2)-C(17)	97.8(3)
N(5)-Rh(2)-C(20)	96.5(2)
N(7)-Rh(2)-C(20)	159.9(2)
C(13)-Rh(2)-C(20)	38.2(2)
C(17)-Rh(2)-C(20)	81.6(3)
N(5)-Rh(2)-C(16)	160.4(2)
N(7)-Rh(2)-C(16)	95.9(2)
C(13)-Rh(2)-C(16)	82.6(3)
C(17)-Rh(2)-C(16)	37.6(2)
C(20)-Rh(2)-C(16)	90.5(3)
N(5)-Rh(2)-Rh(1)	64.44(15)
N(7)-Rh(2)-Rh(1)	65.10(17)
C(13)-Rh(2)-Rh(1)	128.3(2)
C(17)-Rh(2)-Rh(1)	97.6(2)
C(20)-Rh(2)-Rh(1)	96.8(2)
C(16)-Rh(2)-Rh(1)	132.9(2)
C(4)-N(6)-N(5)	107.7(4)
C(4)-N(6)-Rh(1)	135.4(4)
N(5)-N(6)-Rh(1)	115.3(3)
C(11)-O(3)-C(12)	115.3(5)
C(2)-N(5)-N(6)	107.6(4)
C(2)-N(5)-Rh(2)	134.2(4)
N(6)-N(5)-Rh(2)	115.7(3)
C(10)-N(7)-N(8)	107.4(4)
C(10)-N(7)-Rh(2)	137.4(4)
N(8)-N(7)-Rh(2)	114.3(3)

N(7)-C(10)-C(9)	109.7(5)
N(7)-C(10)-C(11)	121.9(5)
C(9)-C(10)-C(11)	128.1(5)
O(4)-C(11)-O(3)	124.6(6)
O(4)-C(11)-C(10)	126.5(5)
O(3)-C(11)-C(10)	108.9(5)
C(5)-O(2)-C(6)	116.0(5)
O(1)-C(5)-O(2)	122.1(6)
O(1)-C(5)-C(4)	126.9(5)
O(2)-C(5)-C(4)	110.9(5)
N(6)-C(4)-C(3)	108.8(5)
N(6)-C(4)-C(5)	121.4(5)
C(3)-C(4)-C(5)	129.6(6)
C(8)-C(9)-C(10)	105.1(5)
N(5)-C(2)-C(3)	110.3(5)
N(5)-C(2)-C(1)	121.1(5)
C(3)-C(2)-C(1)	128.6(5)
C(8)-N(8)-N(7)	108.5(4)
C(8)-N(8)-Rh(1)	133.5(4)
N(7)-N(8)-Rh(1)	116.5(3)
C(13)-C(20)-C(19)	123.6(6)
C(13)-C(20)-Rh(2)	70.3(4)
C(19)-C(20)-Rh(2)	112.7(4)
C(28)-C(27)-C(26)	113.8(5)
N(8)-C(8)-C(9)	109.3(5)
N(8)-C(8)-C(7)	121.0(5)
C(9)-C(8)-C(7)	129.6(5)
C(2)-C(3)-C(4)	105.6(5)
C(21)-C(28)-C(27)	125.3(6)
C(21)-C(28)-Rh(1)	72.0(3)
C(27)-C(28)-Rh(1)	112.0(4)
C(16)-C(17)-C(18)	124.8(6)
C(16)-C(17)-Rh(2)	71.5(4)
C(18)-C(17)-Rh(2)	110.4(4)
C(28)-C(21)-C(22)	122.5(6)
C(28)-C(21)-Rh(1)	70.9(4)
C(22)-C(21)-Rh(1)	111.5(4)
C(18)-C(19)-C(20)	113.2(5)
C(25)-C(24)-C(23)	124.8(6)
C(25)-C(24)-Rh(1)	72.7(4)
C(23)-C(24)-Rh(1)	109.2(4)
C(24)-C(25)-C(26)	123.3(6)
C(24)-C(25)-Rh(1)	69.5(3)
C(26)-C(25)-Rh(1)	112.8(4)
C(17)-C(18)-C(19)	114.2(6)
C(21)-C(22)-C(23)	113.8(6)
C(17)-C(16)-C(15)	123.2(6)
C(17)-C(16)-Rh(2)	70.8(4)
C(15)-C(16)-Rh(2)	111.6(5)
C(20)-C(13)-C(14)	124.0(6)
C(20)-C(13)-Rh(2)	71.5(4)
C(14)-C(13)-Rh(2)	109.4(4)
C(27)-C(26)-C(25)	114.3(5)
C(22)-C(23)-C(24)	114.5(6)
C(14)-C(15)-C(16)	113.2(6)
N(2)-Rh(3)-N(4)	83.9(2)
N(2)-Rh(3)-C(52)	158.0(2)
N(4)-Rh(3)-C(52)	92.0(2)
N(2)-Rh(3)-C(49)	94.0(2)
N(4)-Rh(3)-C(49)	160.3(2)
C(52)-Rh(3)-C(49)	82.7(3)

N(2)-Rh(3)-C(56)	92.9(2)
N(4)-Rh(3)-C(56)	161.6(2)
C(52)-Rh(3)-C(56)	97.5(3)
C(49)-Rh(3)-C(56)	37.8(2)
N(2)-Rh(3)-C(53)	163.9(2)
N(4)-Rh(3)-C(53)	97.3(2)
C(52)-Rh(3)-C(53)	38.1(2)
C(49)-Rh(3)-C(53)	90.2(3)
C(56)-Rh(3)-C(53)	80.9(3)
N(2)-Rh(3)-Rh(4)	65.23(16)
N(4)-Rh(3)-Rh(4)	65.03(15)
C(52)-Rh(3)-Rh(4)	131.9(2)
C(49)-Rh(3)-Rh(4)	131.49(19)
C(56)-Rh(3)-Rh(4)	97.1(2)
C(53)-Rh(3)-Rh(4)	100.6(2)
N(3)-Rh(4)-N(1)	84.06(19)
N(3)-Rh(4)-C(41)	157.8(2)
N(1)-Rh(4)-C(41)	92.2(2)
N(3)-Rh(4)-C(45)	93.3(2)
N(1)-Rh(4)-C(45)	162.1(2)
C(41)-Rh(4)-C(45)	96.6(2)
N(3)-Rh(4)-C(44)	93.1(2)
N(1)-Rh(4)-C(44)	160.2(2)
C(41)-Rh(4)-C(44)	83.0(3)
C(45)-Rh(4)-C(44)	37.4(2)
N(3)-Rh(4)-C(48)	164.6(2)
N(1)-Rh(4)-C(48)	97.0(2)
C(41)-Rh(4)-C(48)	37.7(2)
C(45)-Rh(4)-C(48)	80.9(2)
C(44)-Rh(4)-C(48)	90.9(3)
N(3)-Rh(4)-Rh(3)	65.44(15)
N(1)-Rh(4)-Rh(3)	65.07(18)
C(41)-Rh(4)-Rh(3)	132.2(2)
C(45)-Rh(4)-Rh(3)	97.7(2)
C(44)-Rh(4)-Rh(3)	131.13(19)
C(48)-Rh(4)-Rh(3)	101.0(2)
C(33)-O(6)-C(34)	115.5(5)
C(39)-O(7)-C(40)	115.4(4)
C(41)-C(42)-C(43)	114.2(6)
C(30)-N(1)-N(2)	108.9(4)
C(30)-N(1)-Rh(4)	134.8(4)
N(2)-N(1)-Rh(4)	115.0(3)
C(38)-N(3)-N(4)	107.2(4)
C(38)-N(3)-Rh(4)	137.5(4)
N(4)-N(3)-Rh(4)	115.0(3)
C(36)-N(4)-N(3)	108.4(4)
C(36)-N(4)-Rh(3)	136.0(4)
N(3)-N(4)-Rh(3)	114.5(3)
O(5)-C(33)-O(6)	122.7(6)
O(5)-C(33)-C(32)	126.2(6)
O(6)-C(33)-C(32)	110.9(5)
N(1)-C(30)-C(31)	109.2(5)
N(1)-C(30)-C(29)	122.2(5)
C(31)-C(30)-C(29)	128.6(5)
N(4)-C(36)-C(37)	109.0(5)
N(4)-C(36)-C(35)	121.7(5)
C(37)-C(36)-C(35)	129.3(5)
N(2)-C(32)-C(31)	109.1(5)
N(2)-C(32)-C(33)	121.8(5)
C(31)-C(32)-C(33)	128.9(5)
N(3)-C(38)-C(37)	109.8(5)

N(3)-C(38)-C(39)	121.4(5)
C(37)-C(38)-C(39)	128.5(5)
C(52)-C(53)-C(54)	123.7(6)
C(52)-C(53)-Rh(3)	70.0(3)
C(54)-C(53)-Rh(3)	112.7(4)
C(32)-N(2)-N(1)	107.6(4)
C(32)-N(2)-Rh(3)	137.2(4)
N(1)-N(2)-Rh(3)	114.6(3)
C(44)-C(45)-C(46)	126.4(6)
C(44)-C(45)-Rh(4)	71.4(4)
C(46)-C(45)-Rh(4)	112.1(4)
C(48)-C(41)-C(42)	126.4(6)
C(48)-C(41)-Rh(4)	72.0(3)
C(42)-C(41)-Rh(4)	108.6(4)
C(56)-C(49)-C(50)	122.5(6)
C(56)-C(49)-Rh(3)	71.3(3)
C(50)-C(49)-Rh(3)	111.2(4)
O(8)-C(39)-O(7)	123.0(5)
O(8)-C(39)-C(38)	126.2(5)
O(7)-C(39)-C(38)	110.8(5)
C(49)-C(56)-C(55)	125.2(6)
C(49)-C(56)-Rh(3)	70.9(3)
C(55)-C(56)-Rh(3)	112.2(4)
C(30)-C(31)-C(32)	105.3(5)
C(55)-C(54)-C(53)	113.7(5)
C(41)-C(48)-C(47)	122.6(6)
C(41)-C(48)-Rh(4)	70.3(3)
C(47)-C(48)-Rh(4)	112.9(4)
C(56)-C(55)-C(54)	113.1(5)
C(44)-C(43)-C(42)	114.4(5)
C(45)-C(46)-C(47)	113.1(5)
C(53)-C(52)-C(51)	125.3(6)
C(53)-C(52)-Rh(3)	71.9(4)
C(49)-C(50)-C(51)	113.1(5)

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for ha1. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(14)	80(6)	101(6)	44(5)	-7(4)	-42(4)	-11(5)
Rh(1)	29(1)	30(1)	36(1)	-6(1)	-12(1)	-5(1)
Rh(2)	38(1)	34(1)	28(1)	-5(1)	-15(1)	-1(1)
N(6)	32(3)	29(2)	35(3)	0(2)	-16(2)	-5(2)
O(4)	43(3)	79(3)	43(3)	-17(2)	-23(2)	-4(2)
O(3)	27(2)	47(2)	53(3)	-15(2)	-16(2)	6(2)
N(5)	35(3)	34(3)	33(3)	-3(2)	-17(2)	-6(2)
N(7)	33(3)	34(3)	31(3)	-7(2)	-13(2)	0(2)
C(10)	32(3)	27(3)	32(3)	0(3)	-11(3)	-4(2)
C(11)	37(3)	33(3)	35(4)	1(3)	-10(3)	-4(3)
O(2)	47(3)	48(2)	46(3)	15(2)	-28(2)	-13(2)
C(5)	38(4)	34(3)	33(4)	1(3)	-9(3)	-3(3)

O(1)	57(3)	59(3)	63(3)	13(2)	-39(2)	-24(2)
C(7)	46(4)	42(3)	36(4)	-1(3)	-20(3)	-10(3)
C(4)	31(3)	37(3)	32(3)	-5(3)	-13(3)	-4(3)
C(9)	39(4)	31(3)	27(3)	-7(3)	-11(3)	-2(3)
C(2)	34(3)	40(3)	35(4)	-3(3)	-14(3)	-10(3)
N(8)	30(3)	30(2)	31(3)	-7(2)	-15(2)	2(2)
C(20)	50(4)	45(4)	35(4)	-15(3)	-23(3)	6(3)
C(27)	46(4)	49(4)	56(4)	-11(3)	-1(3)	-5(3)
C(8)	34(3)	29(3)	29(3)	-4(2)	-9(3)	-5(2)
C(3)	40(4)	42(3)	38(4)	3(3)	-11(3)	-17(3)
C(28)	28(3)	40(3)	48(4)	-13(3)	-6(3)	1(3)
C(17)	59(4)	42(4)	31(4)	5(3)	-18(3)	-2(3)
C(21)	29(3)	44(4)	57(5)	-8(3)	-6(3)	-4(3)
C(19)	55(4)	64(4)	34(4)	-10(3)	-10(3)	-4(3)
C(24)	38(4)	49(4)	56(5)	-12(3)	-2(3)	-26(3)
C(25)	44(4)	37(3)	45(4)	3(3)	-15(3)	-16(3)
C(18)	59(4)	47(4)	47(4)	3(3)	-10(3)	2(3)
C(22)	50(4)	83(5)	80(6)	-6(5)	-38(4)	-5(4)
C(16)	52(4)	47(4)	33(4)	4(3)	-8(3)	7(3)
C(13)	58(4)	62(4)	24(3)	-10(3)	-17(3)	-9(3)
C(26)	64(4)	50(4)	38(4)	-2(3)	-5(3)	-22(3)
C(6)	55(4)	66(4)	52(4)	22(4)	-31(4)	-12(4)
C(23)	59(5)	92(6)	63(5)	-12(4)	-27(4)	-26(4)
C(15)	61(5)	93(6)	66(5)	-8(5)	-35(4)	21(4)
C(1)	40(4)	86(5)	57(5)	1(4)	-23(3)	-28(4)
Rh(3)	24(1)	28(1)	36(1)	-2(1)	-9(1)	-1(1)
Rh(4)	34(1)	31(1)	31(1)	-3(1)	-15(1)	-6(1)
O(6)	42(2)	47(2)	34(2)	8(2)	-17(2)	-6(2)
O(7)	30(2)	37(2)	55(3)	-10(2)	-19(2)	7(2)
C(42)	64(5)	83(5)	71(5)	-6(4)	-42(4)	-18(4)
O(8)	41(3)	59(3)	66(3)	-24(2)	-34(2)	4(2)
N(1)	31(3)	32(2)	32(3)	-2(2)	-10(2)	-6(2)
N(3)	28(3)	30(2)	35(3)	-2(2)	-19(2)	-1(2)
O(5)	36(2)	64(3)	42(3)	6(2)	-20(2)	-9(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for ha1.

	x	y	z	U(eq)
H(14A)	-2452	2773	8055	84
H(14B)	-1451	2794	7150	84
H(7A)	805	2914	11973	59
H(7B)	-250	3420	12682	59
H(7C)	717	3944	11991	59
H(9)	-2256	4197	12180	39
H(20)	934	2114	8258	50
H(27A)	3081	2638	7855	64
H(27B)	4335	2292	8039	64
H(3)	-1228	203	11280	48
H(28)	2277	1681	8962	48
H(17)	-19	4371	8914	54
H(21)	2775	1302	10198	54
H(19A)	1864	2970	7020	62
H(19B)	611	3300	6829	62
H(24)	1969	3679	10655	56
H(25)	1763	4016	9313	49

H(18A)	1646	4048	7799	66
H(18B)	854	4532	7201	66
H(22A)	4810	2175	9426	81
H(22B)	4535	1635	10344	81
H(16)	-1941	4250	9012	57
H(13)	-1017	1886	8547	55
H(26A)	3413	3897	8086	62
H(26B)	4276	3456	8648	62
H(6A)	2043	-581	12397	85
H(6B)	820	-837	13055	85
H(6C)	1148	118	13005	85
H(23A)	4387	3286	10207	80
H(23B)	3543	2791	11017	80
H(15A)	-2525	4206	7791	89
H(15B)	-1163	4138	7206	89
H(1A)	-2670	1835	9847	86
H(1B)	-3024	1032	10545	86
H(1C)	-2222	854	9594	86
H(42A)	1549	2419	3764	80
H(42B)	2249	1978	2899	80
H(53)	7012	2925	3795	51
H(45)	5283	3382	3435	42
H(41)	2794	1434	4361	56
H(49)	6997	652	5637	54
H(56)	6280	688	4498	51
H(31)	2669	704	7308	41
H(54A)	8353	2098	2703	57
H(54B)	9160	1680	3311	57
H(48)	4823	1080	3829	52
H(55A)	7231	1042	3099	61
H(55B)	8416	495	3283	61
H(43A)	3242	3088	2325	69
H(43B)	2111	3616	2962	69
H(40A)	654	5739	4986	77
H(40B)	388	6164	5859	77
H(40C)	100	5202	5878	77
H(46A)	6426	2430	2474	62
H(46B)	5608	2872	1879	62
H(52)	7463	3028	5023	53
H(37)	3756	4883	6277	41
H(35A)	6299	3128	6511	69
H(35B)	5632	4029	6900	69
H(35C)	6676	4035	6012	69
H(47A)	5779	1241	2337	65
H(47B)	4572	1773	2178	65
H(44)	3285	3820	3783	50
H(34A)	6056	-298	8260	81
H(34B)	4853	-117	9028	81
H(34C)	5609	658	8578	81
H(29A)	1484	2030	5590	59
H(29B)	972	1512	6502	59
H(29C)	1512	996	5667	59
H(51A)	8673	2023	5628	73
H(51B)	9615	2060	4697	73
H(50A)	9301	785	4420	74
H(50B)	9063	603	5429	74
H(12A)	-5185	5226	10803	81
H(12B)	-5702	5156	11821	81
H(12C)	-5530	4319	11321	81

Table 6. Torsion angles [deg] for ha1.

N(6)-Rh(1)-Rh(2)-N(5)	-1.25(18)
N(8)-Rh(1)-Rh(2)-N(5)	-95.6(2)
C(24)-Rh(1)-Rh(2)-N(5)	-164.8(3)
C(28)-Rh(1)-Rh(2)-N(5)	88.8(2)
C(25)-Rh(1)-Rh(2)-N(5)	170.9(2)
C(21)-Rh(1)-Rh(2)-N(5)	71.0(3)
N(6)-Rh(1)-Rh(2)-N(7)	93.9(2)
N(8)-Rh(1)-Rh(2)-N(7)	-0.40(18)
C(24)-Rh(1)-Rh(2)-N(7)	-69.6(3)
C(28)-Rh(1)-Rh(2)-N(7)	-176.0(2)
C(25)-Rh(1)-Rh(2)-N(7)	-94.0(2)
C(21)-Rh(1)-Rh(2)-N(7)	166.1(3)
N(6)-Rh(1)-Rh(2)-C(13)	-71.4(3)
N(8)-Rh(1)-Rh(2)-C(13)	-165.7(3)
C(24)-Rh(1)-Rh(2)-C(13)	125.0(3)
C(28)-Rh(1)-Rh(2)-C(13)	18.7(3)
C(25)-Rh(1)-Rh(2)-C(13)	100.7(3)
C(21)-Rh(1)-Rh(2)-C(13)	0.8(3)
N(6)-Rh(1)-Rh(2)-C(17)	-177.6(2)
N(8)-Rh(1)-Rh(2)-C(17)	88.1(2)
C(24)-Rh(1)-Rh(2)-C(17)	18.9(3)
C(28)-Rh(1)-Rh(2)-C(17)	-87.5(3)
C(25)-Rh(1)-Rh(2)-C(17)	-5.5(2)
C(21)-Rh(1)-Rh(2)-C(17)	-105.4(3)
N(6)-Rh(1)-Rh(2)-C(20)	-95.2(3)
N(8)-Rh(1)-Rh(2)-C(20)	170.5(2)
C(24)-Rh(1)-Rh(2)-C(20)	101.3(3)
C(28)-Rh(1)-Rh(2)-C(20)	-5.1(2)
C(25)-Rh(1)-Rh(2)-C(20)	76.9(3)
C(21)-Rh(1)-Rh(2)-C(20)	-23.0(3)
N(6)-Rh(1)-Rh(2)-C(16)	167.8(3)
N(8)-Rh(1)-Rh(2)-C(16)	73.5(3)
C(24)-Rh(1)-Rh(2)-C(16)	4.2(3)
C(28)-Rh(1)-Rh(2)-C(16)	-102.1(3)
C(25)-Rh(1)-Rh(2)-C(16)	-20.1(3)
C(21)-Rh(1)-Rh(2)-C(16)	-120.0(3)
N(8)-Rh(1)-N(6)-C(4)	-96.7(5)
C(24)-Rh(1)-N(6)-C(4)	-19.0(9)
C(28)-Rh(1)-N(6)-C(4)	100.8(5)
C(25)-Rh(1)-N(6)-C(4)	171.8(6)
C(21)-Rh(1)-N(6)-C(4)	63.5(5)
Rh(2)-Rh(1)-N(6)-C(4)	-161.4(5)
N(8)-Rh(1)-N(6)-N(5)	66.6(4)
C(24)-Rh(1)-N(6)-N(5)	144.3(6)
C(28)-Rh(1)-N(6)-N(5)	-95.9(4)
C(25)-Rh(1)-N(6)-N(5)	-24.9(8)
C(21)-Rh(1)-N(6)-N(5)	-133.2(4)
Rh(2)-Rh(1)-N(6)-N(5)	1.9(3)
C(4)-N(6)-N(5)-C(2)	0.3(5)
Rh(1)-N(6)-N(5)-C(2)	-167.5(3)
C(4)-N(6)-N(5)-Rh(2)	164.9(3)
Rh(1)-N(6)-N(5)-Rh(2)	-2.9(4)
N(7)-Rh(2)-N(5)-C(2)	95.9(5)
C(13)-Rh(2)-N(5)-C(2)	-66.3(5)
C(17)-Rh(2)-N(5)-C(2)	172.9(6)
C(20)-Rh(2)-N(5)-C(2)	-104.3(5)
C(16)-Rh(2)-N(5)-C(2)	5.8(9)

Rh(1)-Rh(2)-N(5)-C(2)	161.3(5)
N(7)-Rh(2)-N(5)-N(6)	-63.4(4)
C(13)-Rh(2)-N(5)-N(6)	134.3(4)
C(17)-Rh(2)-N(5)-N(6)	13.6(8)
C(20)-Rh(2)-N(5)-N(6)	96.3(4)
C(16)-Rh(2)-N(5)-N(6)	-153.5(6)
Rh(1)-Rh(2)-N(5)-N(6)	1.9(3)
N(5)-Rh(2)-N(7)-C(10)	-101.9(5)
C(13)-Rh(2)-N(7)-C(10)	-25.9(10)
C(17)-Rh(2)-N(7)-C(10)	95.9(6)
C(20)-Rh(2)-N(7)-C(10)	166.2(6)
C(16)-Rh(2)-N(7)-C(10)	58.4(6)
Rh(1)-Rh(2)-N(7)-C(10)	-166.6(6)
N(5)-Rh(2)-N(7)-N(8)	65.3(4)
C(13)-Rh(2)-N(7)-N(8)	141.3(7)
C(17)-Rh(2)-N(7)-N(8)	-96.9(4)
C(20)-Rh(2)-N(7)-N(8)	-26.6(8)
C(16)-Rh(2)-N(7)-N(8)	-134.4(4)
Rh(1)-Rh(2)-N(7)-N(8)	0.6(3)
N(8)-N(7)-C(10)-C(9)	-1.5(6)
Rh(2)-N(7)-C(10)-C(9)	166.3(4)
N(8)-N(7)-C(10)-C(11)	-176.2(4)
Rh(2)-N(7)-C(10)-C(11)	-8.4(8)
C(12)-O(3)-C(11)-O(4)	-1.8(8)
C(12)-O(3)-C(11)-C(10)	-179.6(5)
N(7)-C(10)-C(11)-O(4)	11.0(9)
C(9)-C(10)-C(11)-O(4)	-162.6(6)
N(7)-C(10)-C(11)-O(3)	-171.2(5)
C(9)-C(10)-C(11)-O(3)	15.2(7)
C(6)-O(2)-C(5)-O(1)	-0.1(8)
C(6)-O(2)-C(5)-C(4)	-177.2(5)
N(5)-N(6)-C(4)-C(3)	1.0(6)
Rh(1)-N(6)-C(4)-C(3)	165.2(4)
N(5)-N(6)-C(4)-C(5)	-173.9(4)
Rh(1)-N(6)-C(4)-C(5)	-9.7(8)
O(1)-C(5)-C(4)-N(6)	10.9(9)
O(2)-C(5)-C(4)-N(6)	-172.2(5)
O(1)-C(5)-C(4)-C(3)	-162.8(6)
O(2)-C(5)-C(4)-C(3)	14.1(8)
N(7)-C(10)-C(9)-C(8)	0.5(6)
C(11)-C(10)-C(9)-C(8)	174.7(5)
N(6)-N(5)-C(2)-C(3)	-1.5(6)
Rh(2)-N(5)-C(2)-C(3)	-162.1(4)
N(6)-N(5)-C(2)-C(1)	176.7(5)
Rh(2)-N(5)-C(2)-C(1)	16.2(8)
C(10)-N(7)-N(8)-C(8)	1.9(5)
Rh(2)-N(7)-N(8)-C(8)	-169.0(3)
C(10)-N(7)-N(8)-Rh(1)	170.0(3)
Rh(2)-N(7)-N(8)-Rh(1)	-0.9(4)
N(6)-Rh(1)-N(8)-C(8)	99.9(5)
C(24)-Rh(1)-N(8)-C(8)	-60.0(5)
C(28)-Rh(1)-N(8)-C(8)	179.4(6)
C(25)-Rh(1)-N(8)-C(8)	-97.7(5)
C(21)-Rh(1)-N(8)-C(8)	15.5(9)
Rh(2)-Rh(1)-N(8)-C(8)	165.0(5)
N(6)-Rh(1)-N(8)-N(7)	-64.5(4)
C(24)-Rh(1)-N(8)-N(7)	135.6(4)
C(28)-Rh(1)-N(8)-N(7)	15.1(8)
C(25)-Rh(1)-N(8)-N(7)	97.9(4)
C(21)-Rh(1)-N(8)-N(7)	-148.9(5)
Rh(2)-Rh(1)-N(8)-N(7)	0.6(3)

N(5)-Rh(2)-C(20)-C(13)	84.3(4)
N(7)-Rh(2)-C(20)-C(13)	173.9(5)
C(17)-Rh(2)-C(20)-C(13)	-114.1(4)
C(16)-Rh(2)-C(20)-C(13)	-77.4(4)
Rh(1)-Rh(2)-C(20)-C(13)	149.2(4)
N(5)-Rh(2)-C(20)-C(19)	-156.6(4)
N(7)-Rh(2)-C(20)-C(19)	-67.0(8)
C(13)-Rh(2)-C(20)-C(19)	119.1(6)
C(17)-Rh(2)-C(20)-C(19)	5.0(4)
C(16)-Rh(2)-C(20)-C(19)	41.7(5)
Rh(1)-Rh(2)-C(20)-C(19)	-91.7(4)
N(7)-N(8)-C(8)-C(9)	-1.6(6)
Rh(1)-N(8)-C(8)-C(9)	-166.9(4)
N(7)-N(8)-C(8)-C(7)	174.6(5)
Rh(1)-N(8)-C(8)-C(7)	9.3(8)
C(10)-C(9)-C(8)-N(8)	0.7(6)
C(10)-C(9)-C(8)-C(7)	-175.1(5)
N(5)-C(2)-C(3)-C(4)	2.1(6)
C(1)-C(2)-C(3)-C(4)	-176.0(6)
N(6)-C(4)-C(3)-C(2)	-1.9(6)
C(5)-C(4)-C(3)-C(2)	172.4(5)
C(26)-C(27)-C(28)-C(21)	-54.7(8)
C(26)-C(27)-C(28)-Rh(1)	28.2(7)
N(6)-Rh(1)-C(28)-C(21)	-93.2(4)
N(8)-Rh(1)-C(28)-C(21)	-171.1(5)
C(24)-Rh(1)-C(28)-C(21)	68.9(4)
C(25)-Rh(1)-C(28)-C(21)	103.5(4)
Rh(2)-Rh(1)-C(28)-C(21)	-158.0(3)
N(6)-Rh(1)-C(28)-C(27)	145.2(5)
N(8)-Rh(1)-C(28)-C(27)	67.3(8)
C(24)-Rh(1)-C(28)-C(27)	-52.7(5)
C(25)-Rh(1)-C(28)-C(27)	-18.2(5)
C(21)-Rh(1)-C(28)-C(27)	-121.6(6)
Rh(2)-Rh(1)-C(28)-C(27)	80.4(5)
N(5)-Rh(2)-C(17)-C(16)	-173.0(5)
N(7)-Rh(2)-C(17)-C(16)	-97.3(4)
C(13)-Rh(2)-C(17)-C(16)	67.1(4)
C(20)-Rh(2)-C(17)-C(16)	101.8(4)
Rh(1)-Rh(2)-C(17)-C(16)	-162.4(3)
N(5)-Rh(2)-C(17)-C(18)	65.8(9)
N(7)-Rh(2)-C(17)-C(18)	141.5(5)
C(13)-Rh(2)-C(17)-C(18)	-54.1(5)
C(20)-Rh(2)-C(17)-C(18)	-19.4(5)
C(16)-Rh(2)-C(17)-C(18)	-121.2(7)
Rh(1)-Rh(2)-C(17)-C(18)	76.4(5)
C(27)-C(28)-C(21)-C(22)	0.7(9)
Rh(1)-C(28)-C(21)-C(22)	-103.9(6)
C(27)-C(28)-C(21)-Rh(1)	104.6(5)
N(6)-Rh(1)-C(21)-C(28)	89.7(4)
N(8)-Rh(1)-C(21)-C(28)	172.0(5)
C(24)-Rh(1)-C(21)-C(28)	-110.8(4)
C(25)-Rh(1)-C(21)-C(28)	-73.7(4)
Rh(2)-Rh(1)-C(21)-C(28)	30.1(4)
N(6)-Rh(1)-C(21)-C(22)	-151.9(5)
N(8)-Rh(1)-C(21)-C(22)	-69.7(8)
C(24)-Rh(1)-C(21)-C(22)	7.5(5)
C(28)-Rh(1)-C(21)-C(22)	118.4(7)
C(25)-Rh(1)-C(21)-C(22)	44.6(5)
Rh(2)-Rh(1)-C(21)-C(22)	148.5(4)
C(13)-C(20)-C(19)-C(18)	91.2(7)
Rh(2)-C(20)-C(19)-C(18)	10.5(7)

N(6)-Rh(1)-C(24)-C(25)	-174.8(5)
N(8)-Rh(1)-C(24)-C(25)	-98.8(4)
C(28)-Rh(1)-C(24)-C(25)	65.9(4)
C(21)-Rh(1)-C(24)-C(25)	100.5(4)
Rh(2)-Rh(1)-C(24)-C(25)	-41.5(4)
N(6)-Rh(1)-C(24)-C(23)	63.6(8)
N(8)-Rh(1)-C(24)-C(23)	139.6(5)
C(28)-Rh(1)-C(24)-C(23)	-55.7(5)
C(25)-Rh(1)-C(24)-C(23)	-121.6(6)
C(21)-Rh(1)-C(24)-C(23)	-21.1(5)
Rh(2)-Rh(1)-C(24)-C(23)	-163.0(4)
C(23)-C(24)-C(25)-C(26)	-2.7(9)
Rh(1)-C(24)-C(25)-C(26)	-104.5(5)
C(23)-C(24)-C(25)-Rh(1)	101.7(6)
N(6)-Rh(1)-C(25)-C(24)	173.9(6)
N(8)-Rh(1)-C(25)-C(24)	84.6(4)
C(28)-Rh(1)-C(25)-C(24)	-113.2(4)
C(21)-Rh(1)-C(25)-C(24)	-77.2(4)
Rh(2)-Rh(1)-C(25)-C(24)	149.5(3)
N(6)-Rh(1)-C(25)-C(26)	-67.6(9)
N(8)-Rh(1)-C(25)-C(26)	-156.8(5)
C(24)-Rh(1)-C(25)-C(26)	118.6(6)
C(28)-Rh(1)-C(25)-C(26)	5.4(5)
C(21)-Rh(1)-C(25)-C(26)	41.3(5)
Rh(2)-Rh(1)-C(25)-C(26)	-92.0(5)
C(16)-C(17)-C(18)-C(19)	-50.0(9)
Rh(2)-C(17)-C(18)-C(19)	31.3(7)
C(20)-C(19)-C(18)-C(17)	-27.7(8)
C(28)-C(21)-C(22)-C(23)	88.5(8)
Rh(1)-C(21)-C(22)-C(23)	8.0(8)
C(18)-C(17)-C(16)-C(15)	-1.4(10)
Rh(2)-C(17)-C(16)-C(15)	-103.8(6)
C(18)-C(17)-C(16)-Rh(2)	102.4(6)
N(5)-Rh(2)-C(16)-C(17)	173.4(5)
N(7)-Rh(2)-C(16)-C(17)	85.4(4)
C(13)-Rh(2)-C(16)-C(17)	-113.0(4)
C(20)-Rh(2)-C(16)-C(17)	-75.5(4)
Rh(1)-Rh(2)-C(16)-C(17)	24.2(5)
N(5)-Rh(2)-C(16)-C(15)	-67.5(8)
N(7)-Rh(2)-C(16)-C(15)	-155.5(5)
C(13)-Rh(2)-C(16)-C(15)	6.1(5)
C(17)-Rh(2)-C(16)-C(15)	119.1(7)
C(20)-Rh(2)-C(16)-C(15)	43.6(5)
Rh(1)-Rh(2)-C(16)-C(15)	143.3(4)
C(19)-C(20)-C(13)-C(14)	-3.4(9)
Rh(2)-C(20)-C(13)-C(14)	101.4(6)
C(19)-C(20)-C(13)-Rh(2)	-104.8(5)
C(15)-C(14)-C(13)-C(20)	-48.4(9)
C(15)-C(14)-C(13)-Rh(2)	31.9(8)
N(5)-Rh(2)-C(13)-C(20)	-98.5(4)
N(7)-Rh(2)-C(13)-C(20)	-173.3(6)
C(17)-Rh(2)-C(13)-C(20)	65.7(4)
C(16)-Rh(2)-C(13)-C(20)	100.3(4)
Rh(1)-Rh(2)-C(13)-C(20)	-40.4(5)
N(5)-Rh(2)-C(13)-C(14)	141.0(5)
N(7)-Rh(2)-C(13)-C(14)	66.2(9)
C(17)-Rh(2)-C(13)-C(14)	-54.8(5)
C(20)-Rh(2)-C(13)-C(14)	-120.5(7)
C(16)-Rh(2)-C(13)-C(14)	-20.3(5)
Rh(1)-Rh(2)-C(13)-C(14)	-160.9(4)
C(28)-C(27)-C(26)-C(25)	-24.2(9)

C(24)-C(25)-C(26)-C(27)	88.1(8)
Rh(1)-C(25)-C(26)-C(27)	8.4(8)
C(21)-C(22)-C(23)-C(24)	-26.9(9)
C(25)-C(24)-C(23)-C(22)	-49.8(9)
Rh(1)-C(24)-C(23)-C(22)	32.1(7)
C(13)-C(14)-C(15)-C(16)	-27.7(9)
C(17)-C(16)-C(15)-C(14)	90.0(9)
Rh(2)-C(16)-C(15)-C(14)	9.3(8)
N(2)-Rh(3)-Rh(4)-N(3)	93.6(2)
N(4)-Rh(3)-Rh(4)-N(3)	-1.26(18)
C(52)-Rh(3)-Rh(4)-N(3)	-69.7(3)
C(49)-Rh(3)-Rh(4)-N(3)	165.8(3)
C(56)-Rh(3)-Rh(4)-N(3)	-176.5(2)
C(53)-Rh(3)-Rh(4)-N(3)	-94.5(2)
N(2)-Rh(3)-Rh(4)-N(1)	-1.36(17)
N(4)-Rh(3)-Rh(4)-N(1)	-96.2(2)
C(52)-Rh(3)-Rh(4)-N(1)	-164.7(3)
C(49)-Rh(3)-Rh(4)-N(1)	70.8(3)
C(56)-Rh(3)-Rh(4)-N(1)	88.6(2)
C(53)-Rh(3)-Rh(4)-N(1)	170.5(2)
N(2)-Rh(3)-Rh(4)-C(41)	-70.0(3)
N(4)-Rh(3)-Rh(4)-C(41)	-164.9(3)
C(52)-Rh(3)-Rh(4)-C(41)	126.7(3)
C(49)-Rh(3)-Rh(4)-C(41)	2.1(3)
C(56)-Rh(3)-Rh(4)-C(41)	19.9(3)
C(53)-Rh(3)-Rh(4)-C(41)	101.9(3)
N(2)-Rh(3)-Rh(4)-C(45)	-176.25(19)
N(4)-Rh(3)-Rh(4)-C(45)	88.9(2)
C(52)-Rh(3)-Rh(4)-C(45)	20.4(3)
C(49)-Rh(3)-Rh(4)-C(45)	-104.1(3)
C(56)-Rh(3)-Rh(4)-C(45)	-86.3(3)
C(53)-Rh(3)-Rh(4)-C(45)	-4.3(2)
N(2)-Rh(3)-Rh(4)-C(44)	164.9(2)
N(4)-Rh(3)-Rh(4)-C(44)	70.0(3)
C(52)-Rh(3)-Rh(4)-C(44)	1.6(3)
C(49)-Rh(3)-Rh(4)-C(44)	-122.9(3)
C(56)-Rh(3)-Rh(4)-C(44)	-105.2(3)
C(53)-Rh(3)-Rh(4)-C(44)	-23.2(3)
N(2)-Rh(3)-Rh(4)-C(48)	-94.1(2)
N(4)-Rh(3)-Rh(4)-C(48)	171.0(2)
C(52)-Rh(3)-Rh(4)-C(48)	102.6(3)
C(49)-Rh(3)-Rh(4)-C(48)	-21.9(3)
C(56)-Rh(3)-Rh(4)-C(48)	-4.2(2)
C(53)-Rh(3)-Rh(4)-C(48)	77.8(3)
N(3)-Rh(4)-N(1)-C(30)	101.9(5)
C(41)-Rh(4)-N(1)-C(30)	-56.1(5)
C(45)-Rh(4)-N(1)-C(30)	-175.8(6)
C(44)-Rh(4)-N(1)-C(30)	19.3(9)
C(48)-Rh(4)-N(1)-C(30)	-93.6(5)
Rh(3)-Rh(4)-N(1)-C(30)	167.5(5)
N(3)-Rh(4)-N(1)-N(2)	-63.5(3)
C(41)-Rh(4)-N(1)-N(2)	138.5(4)
C(45)-Rh(4)-N(1)-N(2)	18.8(8)
C(44)-Rh(4)-N(1)-N(2)	-146.1(5)
C(48)-Rh(4)-N(1)-N(2)	101.0(4)
Rh(3)-Rh(4)-N(1)-N(2)	2.1(3)
N(1)-Rh(4)-N(3)-C(38)	-104.5(6)
C(41)-Rh(4)-N(3)-C(38)	-23.2(9)
C(45)-Rh(4)-N(3)-C(38)	93.3(6)
C(44)-Rh(4)-N(3)-C(38)	55.8(6)
C(48)-Rh(4)-N(3)-C(38)	160.6(7)

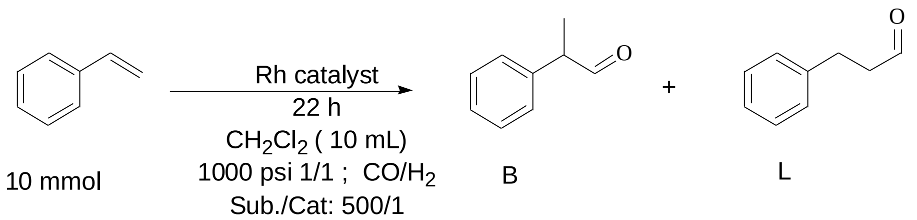
Rh(3)-Rh(4)-N(3)-C(38)	-169.8(6)
N(1)-Rh(4)-N(3)-N(4)	67.2(4)
C(41)-Rh(4)-N(3)-N(4)	148.5(5)
C(45)-Rh(4)-N(3)-N(4)	-95.0(4)
C(44)-Rh(4)-N(3)-N(4)	-132.5(4)
C(48)-Rh(4)-N(3)-N(4)	-27.7(9)
Rh(3)-Rh(4)-N(3)-N(4)	1.9(3)
C(38)-N(3)-N(4)-C(36)	1.2(5)
Rh(4)-N(3)-N(4)-C(36)	-172.9(3)
C(38)-N(3)-N(4)-Rh(3)	171.3(3)
Rh(4)-N(3)-N(4)-Rh(3)	-2.9(4)
N(2)-Rh(3)-N(4)-C(36)	102.8(5)
C(52)-Rh(3)-N(4)-C(36)	-55.6(5)
C(49)-Rh(3)-N(4)-C(36)	18.1(9)
C(56)-Rh(3)-N(4)-C(36)	-176.5(6)
C(53)-Rh(3)-N(4)-C(36)	-93.5(5)
Rh(4)-Rh(3)-N(4)-C(36)	168.2(5)
N(2)-Rh(3)-N(4)-N(3)	-63.6(4)
C(52)-Rh(3)-N(4)-N(3)	138.1(4)
C(49)-Rh(3)-N(4)-N(3)	-148.2(6)
C(56)-Rh(3)-N(4)-N(3)	17.1(8)
C(53)-Rh(3)-N(4)-N(3)	100.2(4)
Rh(4)-Rh(3)-N(4)-N(3)	1.9(3)
C(34)-O(6)-C(33)-O(5)	-1.2(7)
C(34)-O(6)-C(33)-C(32)	-178.3(4)
N(2)-N(1)-C(30)-C(31)	-0.5(6)
Rh(4)-N(1)-C(30)-C(31)	-166.6(4)
N(2)-N(1)-C(30)-C(29)	176.4(4)
Rh(4)-N(1)-C(30)-C(29)	10.4(8)
N(3)-N(4)-C(36)-C(37)	-1.9(6)
Rh(3)-N(4)-C(36)-C(37)	-168.8(4)
N(3)-N(4)-C(36)-C(35)	175.6(5)
Rh(3)-N(4)-C(36)-C(35)	8.7(8)
O(5)-C(33)-C(32)-N(2)	8.8(8)
O(6)-C(33)-C(32)-N(2)	-174.2(4)
O(5)-C(33)-C(32)-C(31)	-164.1(5)
O(6)-C(33)-C(32)-C(31)	12.9(7)
N(4)-N(3)-C(38)-C(37)	-0.1(6)
Rh(4)-N(3)-C(38)-C(37)	172.0(4)
N(4)-N(3)-C(38)-C(39)	-174.1(5)
Rh(4)-N(3)-C(38)-C(39)	-2.0(8)
N(2)-Rh(3)-C(53)-C(52)	177.1(6)
N(4)-Rh(3)-C(53)-C(52)	83.8(4)
C(49)-Rh(3)-C(53)-C(52)	-77.9(4)
C(56)-Rh(3)-C(53)-C(52)	-114.7(4)
Rh(4)-Rh(3)-C(53)-C(52)	149.7(3)
N(2)-Rh(3)-C(53)-C(54)	-63.7(9)
N(4)-Rh(3)-C(53)-C(54)	-156.9(4)
C(52)-Rh(3)-C(53)-C(54)	119.2(6)
C(49)-Rh(3)-C(53)-C(54)	41.4(5)
C(56)-Rh(3)-C(53)-C(54)	4.5(4)
Rh(4)-Rh(3)-C(53)-C(54)	-91.1(4)
C(31)-C(32)-N(2)-N(1)	-0.2(5)
C(33)-C(32)-N(2)-N(1)	-174.4(4)
C(31)-C(32)-N(2)-Rh(3)	170.0(4)
C(33)-C(32)-N(2)-Rh(3)	-4.2(8)
C(30)-N(1)-N(2)-C(32)	0.4(5)
Rh(4)-N(1)-N(2)-C(32)	169.6(3)
C(30)-N(1)-N(2)-Rh(3)	-172.3(3)
Rh(4)-N(1)-N(2)-Rh(3)	-3.1(4)
N(4)-Rh(3)-N(2)-C(32)	-102.4(5)

C(52)-Rh(3)-N(2)-C(32)	-22.3(8)
C(49)-Rh(3)-N(2)-C(32)	58.0(5)
C(56)-Rh(3)-N(2)-C(32)	95.9(5)
C(53)-Rh(3)-N(2)-C(32)	162.5(6)
Rh(4)-Rh(3)-N(2)-C(32)	-167.6(5)
N(4)-Rh(3)-N(2)-N(1)	67.4(3)
C(52)-Rh(3)-N(2)-N(1)	147.4(5)
C(49)-Rh(3)-N(2)-N(1)	-132.3(4)
C(56)-Rh(3)-N(2)-N(1)	-94.4(4)
C(53)-Rh(3)-N(2)-N(1)	-27.8(8)
Rh(4)-Rh(3)-N(2)-N(1)	2.1(3)
N(3)-Rh(4)-C(45)-C(44)	-90.8(4)
N(1)-Rh(4)-C(45)-C(44)	-171.6(5)
C(41)-Rh(4)-C(45)-C(44)	69.3(4)
C(48)-Rh(4)-C(45)-C(44)	103.6(4)
Rh(3)-Rh(4)-C(45)-C(44)	-156.4(3)
N(3)-Rh(4)-C(45)-C(46)	146.6(4)
N(1)-Rh(4)-C(45)-C(46)	65.8(8)
C(41)-Rh(4)-C(45)-C(46)	-53.3(5)
C(44)-Rh(4)-C(45)-C(46)	-122.6(6)
C(48)-Rh(4)-C(45)-C(46)	-19.0(4)
Rh(3)-Rh(4)-C(45)-C(46)	81.0(4)
C(43)-C(42)-C(41)-C(48)	-48.7(9)
C(43)-C(42)-C(41)-Rh(4)	32.3(7)
N(3)-Rh(4)-C(41)-C(48)	-178.4(5)
N(1)-Rh(4)-C(41)-C(48)	-98.6(4)
C(45)-Rh(4)-C(41)-C(48)	65.8(4)
C(44)-Rh(4)-C(41)-C(48)	100.7(4)
Rh(3)-Rh(4)-C(41)-C(48)	-40.9(5)
N(3)-Rh(4)-C(41)-C(42)	58.4(8)
N(1)-Rh(4)-C(41)-C(42)	138.1(5)
C(45)-Rh(4)-C(41)-C(42)	-57.5(5)
C(44)-Rh(4)-C(41)-C(42)	-22.6(5)
C(48)-Rh(4)-C(41)-C(42)	-123.3(6)
Rh(3)-Rh(4)-C(41)-C(42)	-164.2(4)
N(2)-Rh(3)-C(49)-C(56)	89.6(4)
N(4)-Rh(3)-C(49)-C(56)	172.5(5)
C(52)-Rh(3)-C(49)-C(56)	-112.3(4)
C(53)-Rh(3)-C(49)-C(56)	-74.8(4)
Rh(4)-Rh(3)-C(49)-C(56)	29.6(5)
N(2)-Rh(3)-C(49)-C(50)	-151.9(5)
N(4)-Rh(3)-C(49)-C(50)	-69.0(8)
C(52)-Rh(3)-C(49)-C(50)	6.2(5)
C(56)-Rh(3)-C(49)-C(50)	118.5(6)
C(53)-Rh(3)-C(49)-C(50)	43.7(5)
Rh(4)-Rh(3)-C(49)-C(50)	148.1(4)
C(40)-O(7)-C(39)-O(8)	1.0(8)
C(40)-O(7)-C(39)-C(38)	-177.6(5)
N(3)-C(38)-C(39)-O(8)	12.7(9)
C(37)-C(38)-C(39)-O(8)	-160.0(6)
N(3)-C(38)-C(39)-O(7)	-168.8(5)
C(37)-C(38)-C(39)-O(7)	18.4(8)
C(50)-C(49)-C(56)-C(55)	0.5(9)
Rh(3)-C(49)-C(56)-C(55)	104.2(6)
C(50)-C(49)-C(56)-Rh(3)	-103.7(5)
N(2)-Rh(3)-C(56)-C(49)	-92.8(4)
N(4)-Rh(3)-C(56)-C(49)	-172.0(5)
C(52)-Rh(3)-C(56)-C(49)	67.8(4)
C(53)-Rh(3)-C(56)-C(49)	102.2(4)
Rh(4)-Rh(3)-C(56)-C(49)	-158.1(3)
N(2)-Rh(3)-C(56)-C(55)	146.1(5)

N(4)-Rh(3)-C(56)-C(55)	66.8(9)
C(52)-Rh(3)-C(56)-C(55)	-53.4(5)
C(49)-Rh(3)-C(56)-C(55)	-121.2(7)
C(53)-Rh(3)-C(56)-C(55)	-19.0(5)
Rh(4)-Rh(3)-C(56)-C(55)	80.7(5)
N(1)-C(30)-C(31)-C(32)	0.4(6)
C(29)-C(30)-C(31)-C(32)	-176.3(5)
N(2)-C(32)-C(31)-C(30)	-0.1(6)
C(33)-C(32)-C(31)-C(30)	173.5(5)
C(52)-C(53)-C(54)-C(55)	90.9(7)
Rh(3)-C(53)-C(54)-C(55)	10.5(7)
C(42)-C(41)-C(48)-C(47)	-4.9(9)
Rh(4)-C(41)-C(48)-C(47)	-105.2(5)
C(42)-C(41)-C(48)-Rh(4)	100.3(6)
N(3)-Rh(4)-C(48)-C(41)	177.7(6)
N(1)-Rh(4)-C(48)-C(41)	84.5(4)
C(45)-Rh(4)-C(48)-C(41)	-113.5(4)
C(44)-Rh(4)-C(48)-C(41)	-77.3(4)
Rh(3)-Rh(4)-C(48)-C(41)	150.4(4)
N(3)-Rh(4)-C(48)-C(47)	-64.2(10)
N(1)-Rh(4)-C(48)-C(47)	-157.4(5)
C(41)-Rh(4)-C(48)-C(47)	118.1(7)
C(45)-Rh(4)-C(48)-C(47)	4.6(5)
C(44)-Rh(4)-C(48)-C(47)	40.8(5)
Rh(3)-Rh(4)-C(48)-C(47)	-91.5(5)
C(49)-C(56)-C(55)-C(54)	-51.4(8)
Rh(3)-C(56)-C(55)-C(54)	30.3(7)
C(53)-C(54)-C(55)-C(56)	-26.7(8)
C(41)-C(42)-C(43)-C(44)	-25.7(9)
C(44)-C(45)-C(46)-C(47)	-52.1(8)
Rh(4)-C(45)-C(46)-C(47)	30.5(7)
C(54)-C(53)-C(52)-C(51)	-4.2(9)
Rh(3)-C(53)-C(52)-C(51)	100.3(6)
C(54)-C(53)-C(52)-Rh(3)	-104.5(5)
N(2)-Rh(3)-C(52)-C(53)	-177.8(4)
N(4)-Rh(3)-C(52)-C(53)	-99.3(4)
C(49)-Rh(3)-C(52)-C(53)	99.7(4)
C(56)-Rh(3)-C(52)-C(53)	64.8(4)
Rh(4)-Rh(3)-C(52)-C(53)	-41.8(4)
N(2)-Rh(3)-C(52)-C(51)	60.1(7)
N(4)-Rh(3)-C(52)-C(51)	138.5(5)
C(49)-Rh(3)-C(52)-C(51)	-22.4(5)
C(56)-Rh(3)-C(52)-C(51)	-57.3(5)
C(53)-Rh(3)-C(52)-C(51)	-122.1(6)
Rh(4)-Rh(3)-C(52)-C(51)	-163.9(4)
N(3)-C(38)-C(37)-C(36)	-1.0(6)
C(39)-C(38)-C(37)-C(36)	172.5(5)
N(4)-C(36)-C(37)-C(38)	1.7(6)
C(35)-C(36)-C(37)-C(38)	-175.5(6)
C(45)-C(46)-C(47)-C(48)	-26.8(8)
C(41)-C(48)-C(47)-C(46)	91.2(7)
Rh(4)-C(48)-C(47)-C(46)	10.6(7)
C(46)-C(45)-C(44)-C(43)	0.7(9)
Rh(4)-C(45)-C(44)-C(43)	-103.4(6)
C(46)-C(45)-C(44)-Rh(4)	104.2(6)
C(42)-C(43)-C(44)-C(45)	86.8(8)
C(42)-C(43)-C(44)-Rh(4)	5.6(7)
N(3)-Rh(4)-C(44)-C(45)	91.4(4)
N(1)-Rh(4)-C(44)-C(45)	172.4(5)
C(41)-Rh(4)-C(44)-C(45)	-110.6(4)
C(48)-Rh(4)-C(44)-C(45)	-73.7(4)

Rh(3)-Rh(4)-C(44)-C(45)	31.8(4)
N(3)-Rh(4)-C(44)-C(43)	-148.5(5)
N(1)-Rh(4)-C(44)-C(43)	-67.4(8)
C(41)-Rh(4)-C(44)-C(43)	9.6(5)
C(45)-Rh(4)-C(44)-C(43)	120.2(6)
C(48)-Rh(4)-C(44)-C(43)	46.5(5)
Rh(3)-Rh(4)-C(44)-C(43)	151.9(4)
C(53)-C(52)-C(51)-C(50)	-45.0(9)
Rh(3)-C(52)-C(51)-C(50)	35.6(7)
C(56)-C(49)-C(50)-C(51)	91.9(7)
Rh(3)-C(49)-C(50)-C(51)	11.2(7)
C(52)-C(51)-C(50)-C(49)	-31.6(9)

The studies of the X-ray spectrum (Tablse 1-6) shows that we have selective coordination with the rhodium COD just the *head-to-tail* was observed no *head-to-head.* The distance spearing the Rh(1)-Rh(2) is 3.170 A, means formation of pyrazolate-bridge rhodium comparing with other works in the literature. New pyrazolate-bridge rhodium(I) complexe was prepared. Several studies have been carried out in the last years in order to test the catalytic activity of some pyrazolte-bridge complexes in various reaction such as oligomerization and Polymerization of alkynes, in this context we tray the hydroformylation of styrene, using (substrate/cat : 500/1 in 1000psi of CO/H2 **:** 1/1 in dichloromethane as solvent for 22 hours. With changing the temperature reaction (**Scheme 2**) we found very interesting results. The selectivity for the branched aldehyde is increasing with the decreases of temperature.



Entry	T (oC)	Conv%	Distribution * L / B
1	25	14	0/100
2	45	100	1/17
3	65	100	1/7

* Determined by GC and proton NMR

Scheme 2: Catalytic test of the bridging pyrazolate Rh(1) complex in hydroformylation reaction of styrene

Conclusion

New pyrazolate-bridge rhodium (I) complex was prepared with head to tail system. The hydroformylation reaction of styrene for this complex shows that the temperature plays a huge importance in this case.

Acknowledgment

We are grateful to Professor Howard Alper, University of Ottawa – Canada for his support.

References

1. Z. Krausová, P. Sehnal, B.P. Bondzic, D. Šaman, I. Starý, Helicene-based phosphite ligands in asymmetric transition-metal catalysis: Exploring Rh-catalyzed hydroformylation and Ir-catalyzed allylic amination. *Eur. J. Org. Chem.*, 20-21, 3849 (2011).
2. W. Alsalahi, A.M. Trzeciak, Advantages of the solventless hydroformylation of olefins. *J. Mol. Cat. Chem.*, 408, 147 (2015).
3. S. Siangwata, N. Baartzes, B.C.E. Makhubela, G.S. Smith, Synthesis, characterisation and reactivity of water-soluble ferrocenylimine-Rh(I) complexes as aqueous-biphasic hydroformylation catalyst precursors. *J. Organam. Chem.*, 796, 26-32 (2015). https://doi.org/10.1016/j.jorganchem.2015.04.029
4. S. Paganelli, O. Piccolo, F. Baldi, M. Gallo, R. Tassini, M. Rancan, L. Armelao, A new biogenerated Rh-based catalyst for aqueous biphasic hydroformylation. *Cat. Commun.*, 71, 32 (2015).
5. G. Achonduh, Q. Yang, H. Alper, From alkenes to alcohols by cobalt-catalyzed hydroformylation-reduction. *Tetrahedron*, 71, 1241-1246 (2015).
6. P. J. Baricelli, M. Rodriguez, L.G. Melean, M. M. Alonso, M. Borusiak, M. Rosales, B. Gonzalez, K.C.B. de Oliveira, E.V. Gusevskaya, E. N. dos Santos, Rhodium catalyzed aqueous biphasic hydroformylation of naturally occurring allylbenzenes in the presence of water-soluble phosphorus ligands. *Applied Catalysis A: General*, 490, 163-169 (2015).
7. M. Jiang, Y. Ding, L. Yan, X. Song, R. Lin, *Chinese J. Catal.*, 35, 1456-1464 (2014).
8. S.H. Chikkali, J. I. van der Vlugt, J.N.H. Reek, Hybrid diphosphorus ligands in rhodium catalysed asymmetric hydroformylation. *Coord. Chem. Rev.*, 262, 1-15 (2014).
9. Yanyan Diao, Jing Li, Ling Wang, Pu Yang, Ruiyi Yan, Li Jiang, Heng Zhang, Suojiang Zhang, *Catalysis Today*, 200, 54-62 (2013).

10. D.G. Hanna, S. Shylesh, S. Werner, A.T. The kinetics of gas-phase propene hydroformylation over a supported ionic liquid-phase (SILP) rhodium catalyst. Bell, *J. Catal.*, 292, 166-172 (2012).
11. A. Peschel, B. Hentschel, H. Freund, K. Sundmacher, Design of optimal multiphase reactors exemplified on the hydroformylation of long chain alkenes. *Chem. Engin. J.*, 188, 126-141 (2012).
12. M. Beller, B. Cornils, C.D. Frohning, C.W. Kohlpaintner, Progress in hydroformylation and carbonylation. *J. Mol. Catal.* A 104, 17 (1995).
13. M.E. Broussard, B. Juma, S.G. Train, W.-J. Peng, S.A. Laneman, G.G. Stanley, A bimetallic hydroformylation catalyst: High regioselectivity and reactivity through homobimetallic cooperativity. *Science* 260, 1784 (1993).
14. R.C. Matthews D.K. Howell, W.-P. Peng, S.G. Train, T.W Dale, G.G. Stanley, Bimetallic hydroformylation catalysis: In situ characterization of a dinuclear rhodium(ii) dihydrido complex with the largest Rh-H NMR coupling constant. *Angew. Chem. Int. Ed. Engl.* 35, 2253 (1996).
15. M. El Kodadi F. Malek, R. Touzani, A. Ramdani, Synthesis of new tripodal ligand 5-(bis(3,5-dimethyl-1H-pyrazol-1-ylmethyl)amino)pentan-1-ol, catecholase activities studies of three functional tripodal pyrazolyl N-donor ligands, with different copper (II) salts, *Catal. Commun.*, 9, 966-969 (2008).
16. I. Bouabdallah, R. Touzani, I. Zidane, A. Ramdani, Synthesis of new tripodal ligand: N,N-bis[(1,5-dimethylpyrazol-3-yl)methyl]benzylamine.: Catecholase activity of two series of tripodal ligands with some copper (II) salts, *Catal. Commun.*, 8, 707-712 (2007). https://doi.org/10.1016/j.catcom.2006.08.034
17. N. Boussalah, R. Touzani, T. Bouabdallah, S. El Kadiri, S. Ghalem, Oxidation catalytic properties of new amino acid based on pyrazole tripodal ligands *Int. J. Aca. Res.*, 2 137 (2009).
18. N. Boussalah, R. Touzani, T. Bouabdallah, S. El Kadiri, S. Ghalem, Synthesis, structure and catalytic properties of tripodal amino-acid derivatized pyrazole-based ligands. *J. Mol. Cat. Chem.*, 306, 113-117 (2009). https://doi.org/10.1016/j.molcata.2009.02.031
19. A. Mouadili, A. Attayibat, S. El Kadiri, S. Radi, R. Touzani, Catecholase activity investigations using in situ copper complexes with pyrazole and pyridine based ligands. *Appl. Cata. Gen.*, 454, 93 (2013).
20. A. Zerrouki, R. Touzani, S. El Kadiri, Synthesis of new derivatized pyrazole based ligands and their catecholase activity studies. *Arab. J. Chem.*, 4, 459-464 (2011). https://doi.org/10.1016/j.arabjc.2010.07.013

21. A. Mouadili, F. Abrigach, M. Khoutoul, A. Zarrouk, N. Benchat, R. Touzani, Catecholase activity investigations using in situ copper complexes with pyrazole and pyridine based ligands. *J. Chem. Pharm. Res.*, 7, 968 (2015).
22. A. Takfaoui, I. Lakehal , I. Bouabdallah, F. Halaimia, H. Nacer, B. Hammouti, R. Touzani, New imines bearing alkyl armed for catecholase activity, *J. Mater. Environ. Sci.* 5, 753 (2014).
23. A. Mouadili, A. Zerrouki, L. Herrag, R. Touzani, B. Hammouti, S. El Kadiri, Catechol oxidation: Activity studies using electron rich nitrogen based ligands. *Res. Chem. Inter.*, 9, 2427 (2012).
24. S. Radi, A. Attayibat, A. Ramdani, M. Bacquet, Synthesis and characterization of novel silica gel supported N-pyrazole ligand for selective elimination of Hg(II) . *Eur. Polym. J.*, 44, 3163 (2008).
25. M. El Kodadi, F. Malek, R. Touzani, A. Ramdani, S. El Kadiri, D. Eddike, Synthesis and X-ray structure of [N,N-Bis(3,5-dimethylpyrazol-1-ylmethyl)- 1-hydroxy-2-aminoethane](3,5-dimethylpyrazole) copper(II) dinitrate. *Molecules* 8 (11), 780 (2003).

(2014) ; www.mocedes.org/ajcer