

Supporting Material

Gaël Ung, Daniel Mendoza-Espinosa, Guy Bertrand*

UCR-CNRS Joint Research Chemistry Laboratory, Department of Chemistry, University
of California Riverside, Riverside, CA 92521-0403

E-mail: guy.bertrand@ucr.edu

General Information

All manipulations were performed under an atmosphere of dry argon using standard Schlenk or dry box techniques. Solvents were dried by standard methods and distilled under argon. ^1H , ^{31}P , ^{19}F , ^{11}B and ^{13}C NMR spectra were recorded on Varian Inova 500, Varian Inova 400 and Bruker 300 spectrometers at 25°C. NMR multiplicities are abbreviated as follows: *s* = singlet, *d* = doublet, *t* = triplet, *sept* = septet, *m* = multiplet, *br* = broad signal. Chemical shifts are given in ppm. Coupling constants *J* are given in Hz. Mass spectra were performed at the UC Riverside Mass Spectrometry Laboratory. Melting points were measured with a Büchi melting point apparatus.

Synthesis and characterization

3-isopropyl-2,5-diphenyloxazolium trifluoromethanesulfonate 2

A Schlenk tube containing a CH_2Cl_2 solution (10 mL) of isopropanol (210 μL , 2.7 mmol) and pyridine (220 μL , 2.7 mmol) was cooled to -78°C , and trifluoromethanesulfonate anhydride (460 μL , 2.7 mmol) was added. The reaction mixture was stirred for 30 min at -78°C then for an additional 30 min at room temperature. Dry hexanes (10 mL) were added. The supernatant was filtered into a Schlenk tube containing a solution of 2,5-diphenyloxazole (300 mg, 1.35 mmol) in dry CH_2Cl_2 (5 mL). The reaction mixture was stirred for 14 hours at room temperature. All volatiles were removed under vacuum and the white residue was washed with diethyl ether. 826 mg (74% yield); **m.p.** 247 °C; ^1H (300 MHz, C_6D_6) δ 1.53 (d, *J* = 6.6 Hz, 6H), 4.89 (sept, *J* = 6.6 Hz, 1H), 7.45-7.53 (m, 3H), 7.53-7.70 (m, 2H), 7.71-7.80 (m, 3H), 7.84-7.89 (m, 2H), 8.22 (s, 1H); ^{13}C (75 MHz, C_6D_6) δ 22.3 ($\text{CH}(\text{CH}_3)_2$), 54.8 ($\text{CH}(\text{CH}_3)_2$), 115.1 (CH_{oxa}), 117.4 (C^{q}), 121.2 (C^{q}), 125.3 (C^{q}), 126.2 (CH_{ar}), 130.7 (CH_{ar}), 130.9 (CH_{ar}), 131.1 (CH_{ar}), 132.6 (CH_{ar}), 135.8 (CH_{ar}), 155.1 (C^{q}); $^{19}\text{F}\{^1\text{H}\}$ (282 MHz, C_6D_6) δ -78.4; **HRMS:** *m/z* calculated for $\text{C}_{18}\text{H}_{18}\text{NO} (\text{M}-\text{OTf})^+$ 264.1383, found 264.1391.

N-isopropyl-N-(phenylethynyl)benzamide 3

Diethyl ether (15 mL) was added to a cold (-78°C) solid mixture of potassium bis(trimethylsilyl)amide (48 mg, 0.242 mmol) and oxazolium salt (100 mg, 0.242 mmol). The solution was stirred for 15 min at -78°C , and then allowed to warm to room temperature. The diethyl ether was removed under vacuum, and the residue extracted with hexanes (30 mL). Removing the hexanes under vacuum yielded **3** as a white powder. 49 mg (77% yield); **m.p.** 74 °C (dec); ^1H (300 MHz, C_6D_6) δ 1.21 (d, *J* = 6.6 Hz, 6H), 4.93 (sept, *J* = 6.6 Hz, 1H), 6.86-6.98 (m, 3H), 7.00-7.17 (m, 5H), 8.14-8.21 (m, 2H); ^{13}C (75 MHz, C_6D_6) δ 20.5 ($\text{CH}(\text{CH}_3)_2$), 48.1 ($\text{CH}(\text{CH}_3)_2$), 75.7 ($\text{C}\equiv\text{C}$), 83.8 ($\text{C}\equiv\text{C}$), 124.3 (C^{q}), 127.7 (CH_{ar}), 128.7 (CH_{ar}), 128.9 (CH_{ar}), 129.5 (CH_{ar}), 130.9 (CH_{ar}), 131.5 (CH_{ar}), 135.5 (C^{q}), 170.4 ($\text{C}=\text{O}$); **HRMS:** *m/z* calculated for $\text{C}_{18}\text{H}_{18}\text{NO} (\text{M}+\text{H})^+$ 264.1383, found 264.1388.

L-RhCl(COD) 4

THF (5 mL) was added at room temperature to a solid mixture of ynamide **3** (52 mg, 0.197 mmol) and 1,5-cyclooctadiene rhodium chloride dimer (49 mg, 0.098 mmol). The solution was stirred for 14 hours at room temperature. The solvent was evaporated and the light yellow residue washed with diethyl ether (4x10 mL). The resulting light yellow powder was dried under vacuum. 81 mg (81 % yield); **m.p.** 164°C (dec); ^1H (500 MHz, CDCl_3) δ 1.56-1.67 (m, 1H), 1.69 (d, *J* = 7.0 Hz, 3H), 1.75 (d, *J* = 7.0 Hz, 3H), 1.77-1.90 (m, 3H), 2.10-2.20 (m, 1H), 2.20-

2.32 (m, 2H), 2.35-2.45 (m, 1H), 2.98-3.04 (m, 1H), 3.14-3.20 (m, 1H), 4.88-4.96 (m, 1H), 5.03-5.10 (m, 1H), 5.90 (sept, $J = 7.0$ Hz, 1H), 7.24 (t, $J = 7.5$ Hz, 1H), 7.36 (t, $J = 7.5$ Hz, 2H), 7.47-7.53 (m, 4H), 7.54-7.60 (m, 1H), 8.62 (d, $J = 7.5$ Hz, 2H); ^{13}C (125 MHz, CDCl_3) δ 22.9 ($\text{CH}(\text{CH}_3)_2$), 23.6 ($\text{CH}(\text{CH}_3)_2$), 29.2 (CH_2), 29.4 (CH_2), 32.5 (CH_2), 33.1 (CH_2), 57.3 ($\text{CH}(\text{CH}_3)_2$), 67.4 (d, $J_{\text{C-Rh}} = 14.4$ Hz, CH, COD), 71.3 (d, $J_{\text{C-Rh}} = 14.4$ Hz, CH, COD), 95.9 (d, $J_{\text{C-Rh}} = 6.3$ Hz, CH, COD), 96.4 (d, $J_{\text{C-Rh}} = 6.3$ Hz, CH, COD), 124.0 (C^q), 126.3 (CH_{ar}), 127.9 (CH_{ar}), 128.2 (CH_{ar}), 129.3 (CH_{ar}), 129.4 (CH_{ar}), 129.7 (C^q), 132.6 (CH_{ar}), 152.5 (C^q), 155.6 (d, $J_{\text{C-Rh}} = 47.5$ Hz, C-Rh), 158.8 (C^q).

L-RhCl(CO)₂ **5**

Carbon monoxide was bubbled through a solution of L-RhCl(COD) **4** (81 mg, 0.197 mmol) in CHCl_3 (5 mL) for 20 minutes. The solvent was evaporated and the residue washed with hexanes (2x10 mL). The resulting light yellow powder was dried under vacuum. Single crystals of **5** were obtained by slow evaporation of a saturated chloroform/hexanes (8:1) solution at room temperature. 88 mg (98 % yield); m.p. 178 °C (dec); ^1H (500 MHz, CDCl_3) δ 1.76 (br s, 3H), 1.83 (br s, 3H), 5.06 (sept, $J = 7.0$ Hz, 1H), 7.28 (t, $J = 7.5$ Hz, 1H), 7.36 (t, $J = 7.5$ Hz, 2H), 7.55-7.68 (m, 5H), 8.39 (d, $J = 7.5$ Hz, 2H); ^{13}C (125 MHz, CDCl_3) δ 23.2 ($\text{CH}(\text{CH}_3)_2$), 24.1 ($\text{CH}(\text{CH}_3)_2$), 54.9 ($\text{CH}(\text{CH}_3)_2$), 122.7 (C^q), 128.6 (CH_{ar}), 128.7 (C^q), 128.8 (CH_{ar}), 129.0 (CH_{ar}), 129.3 (CH_{ar}), 129.8 (CH_{ar}), 133.3 (CH_{ar}), 144.1 (d, $J_{\text{C-Rh}} = 39.3$ Hz, C-Rh), 155.8 (C^q), 159.4 (C^q), 183.7 (d, $J_{\text{C-Rh}} = 76.3$ Hz, CO), 185.9 (d, $J_{\text{C-Rh}} = 55.6$ Hz, CO); IR (CH_2Cl_2): ν (cm^{-1}) 2074.87 (CO), 1995.64 (CO).

L-AuCl **6**

THF (5 mL) was added at room temperature to a solid mixture of ynamide **3** (45 mg, 0.171 mmol) and tetrahydrothiophene gold chloride (54 mg, 0.171 mmol). The solution was stirred for 14 hours at room temperature. The solvent was evaporated and the light yellow residue washed with diethyl ether (4x10 mL). The resulting light pink powder was dried under vacuum. 65 mg (77 % yield); m.p. 155 °C; ^1H (300 MHz, CDCl_3) δ 1.96 (d, $J = 6.6$ Hz, 6H), 5.00 (sept, $J = 6.6$ Hz, 1H), 7.35-7.43 (m, 3H), 7.66-7.77 (m, 5H), 8.30-8.39 (m, 2H); ^{13}C (75 MHz, CDCl_3) δ 22.9 ($\text{CH}(\text{CH}_3)_2$), 53.3 ($\text{CH}(\text{CH}_3)_2$), 121.7 (C^q), 125.3 (CH_{ar}), 127.9 (C^q), 128.9 (CH_{ar}), 129.4 (CH_{ar}), 129.5 (CH_{ar}), 130.0 (CH_{ar}), 133.7 (CH_{ar}), 138.4 (C^q), 157.9 (C^q), 158.4 (C^q).

L-PdCl(η^3 -allyl) **7**

THF (5 mL) was added at room temperature to a solid mixture of ynamide **3** (49 mg, 0.186 mmol) and η^3 -allyl palladium chloride dimer (34 mg, 0.093 mmol). The solution was stirred for 14 hours at room temperature. The solvent was removed under vacuum, and the light yellow residue washed with diethyl ether (4x10 mL). The resulting white powder was dried under vacuum. 76 mg (91 % yield); m.p. 187 °C; ^1H (500 MHz, CDCl_3) δ 1.65-1.74 (m, 3H), 1.76 (d, $J = 7.0$ Hz, 3H), 2.25 (d, $J = 11.5$ Hz, 1H), 3.12 (d, $J = 7.0$ Hz, 1H), 3.30 (d, $J = 13.5$ Hz, 6H), 4.18 (d, $J = 7.0$ Hz, 1H), 4.90 (sept, $J = 7.0$ Hz, 1H), 5.17-5.28 (m, 1H), 7.15-7.20 (m, 1H), 7.24-7.30 (m, 2H), 7.50-7.60 (m, 5H), 8.22-8.28 (m, 2H); ^{13}C (125 MHz, CDCl_3) δ 22.9 ($\text{CH}(\text{CH}_3)_2$), 23.1 ($\text{CH}(\text{CH}_3)_2$), 49.5 (CH_2 -allyl), 53.7 ($\text{CH}(\text{CH}_3)_2$), 71.7 (CH_2 -allyl), 113.4 (CH -allyl), 122.8 (C^q), 125.6 (CH_{ar}), 128.1 (CH_{ar}), 128.4 (CH_{ar}), 129.0 (CH_{ar}), 129.7 (CH_{ar}), 129.8 (C^q), 132.9 (CH_{ar}), 146.3 (C-Pd), 154.8 (C^q), 159.1 (C^q).

Crystallographic Data and Summary of Data Collection and Structure Refinement

Table S1. Crystal data and structure refinement for 5.

Identification code	GU1188	
Empirical formula	C ₂₁ H ₁₈ Cl ₄ NO ₃ Rh	
Formula weight	577.07	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 14.7427(9) Å	α = 90°
	b = 19.1083(12) Å	β = 91.668(2)°
	c = 8.2340(5) Å	γ = 90°
Volume	2318.6(2) Å ³	
Z	4	
Density (calculated)	1.653 Mg/m ³	
Absorption coefficient	1.220 mm ⁻¹	
F(000)	1152	
Theta range for data collection	2.13 to 41.65°	
Index ranges	-20 ≤ h ≤ 27, -35 ≤ k ≤ 32, -12 ≤ l ≤ 15	
Reflections collected	33043	
Independent reflections	14858 [R(int) = 0.0406]	
Completeness to theta = 41.65°	93.6 %	
Absorption correction	Sadabs	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	14858 / 0 / 273	
Goodness-of-fit on F ²	1.005	
Final R indices [I > 2σ(I)]	R1 = 0.0419, wR2 = 0.0995	
R indices (all data)	R1 = 0.0737, wR2 = 0.1150	
Largest diff. peak and hole	2.028 and -1.808 e.Å ⁻³	

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 5. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Rh(1)	7052(1)	5073(1)	5760(1)	18(1)
Cl(1)	8255(1)	4755(1)	4049(1)	22(1)
O(1)	7896(1)	7214(1)	5474(1)	18(1)
O(2)	5561(1)	5530(1)	7855(2)	44(1)
O(3)	6194(2)	3642(1)	5283(3)	46(1)
N(1)	8309(1)	6330(1)	6967(2)	17(1)
C(1)	7588(1)	6074(1)	5957(2)	18(1)
C(2)	7345(1)	6645(1)	5049(2)	18(1)
C(3)	8478(1)	6992(1)	6621(2)	17(1)
C(4)	8760(1)	5945(1)	8343(2)	20(1)
C(5)	9415(1)	5405(1)	7713(2)	28(1)
C(6)	8056(1)	5627(1)	9433(2)	26(1)
C(7)	9155(1)	7480(1)	7270(2)	17(1)
C(8)	8909(1)	8186(1)	7409(2)	19(1)
C(9)	9523(1)	8667(1)	8059(2)	24(1)
C(10)	10385(1)	8452(1)	8554(2)	26(1)
C(11)	10641(1)	7757(1)	8376(2)	28(1)
C(12)	10032(1)	7271(1)	7732(2)	23(1)
C(13)	6641(1)	6775(1)	3809(2)	19(1)
C(14)	6249(1)	6214(1)	2945(2)	24(1)
C(15)	5529(1)	6331(1)	1852(2)	28(1)
C(16)	5195(1)	7004(1)	1598(2)	28(1)
C(17)	5603(1)	7562(1)	2406(2)	26(1)
C(18)	6322(1)	7454(1)	3500(2)	22(1)
C(19)	6132(1)	5351(1)	7050(2)	28(1)
C(20)	6524(1)	4170(1)	5473(2)	28(1)
C(21)	2691(1)	8711(1)	3882(2)	25(1)
Cl(2)	3584(1)	9292(1)	4304(1)	37(1)
Cl(3)	1970(1)	8643(1)	5541(1)	44(1)
Cl(4)	3111(1)	7883(1)	3371(1)	42(1)

Table S3. Bond lengths [\AA] and angles [$^\circ$] for 5.

Rh(1)-C(19)	1.8256(19)	Rh(1)-C(20)	1.9046(18)
Rh(1)-C(1)	2.0750(14)	Rh(1)-Cl(1)	2.3757(4)
O(1)-C(3)	1.3266(18)	O(1)-C(2)	1.3962(18)
O(2)-C(19)	1.139(2)	O(3)-C(20)	1.129(2)
N(1)-C(3)	1.3232(18)	N(1)-C(1)	1.4169(19)
N(1)-C(4)	1.4902(19)	C(1)-C(2)	1.363(2)
C(2)-C(13)	1.456(2)	C(3)-C(7)	1.456(2)
C(4)-C(5)	1.515(2)	C(4)-C(6)	1.520(2)
C(7)-C(12)	1.395(2)	C(7)-C(8)	1.402(2)
C(8)-C(9)	1.387(2)	C(9)-C(10)	1.387(3)
C(10)-C(11)	1.388(3)	C(11)-C(12)	1.387(2)
C(13)-C(18)	1.400(2)	C(13)-C(14)	1.401(2)
C(14)-C(15)	1.389(2)	C(15)-C(16)	1.390(3)
C(16)-C(17)	1.385(3)	C(17)-C(18)	1.386(2)
C(21)-Cl(2)	1.7491(18)	C(21)-Cl(4)	1.7546(18)
C(21)-Cl(3)	1.7599(18)		
C(19)-Rh(1)-C(20)	91.63(8)	C(19)-Rh(1)-C(1)	88.49(7)
C(20)-Rh(1)-C(1)	176.85(7)	C(19)-Rh(1)-Cl(1)	177.88(6)
C(20)-Rh(1)-Cl(1)	90.21(5)	C(1)-Rh(1)-Cl(1)	89.61(4)
C(3)-O(1)-C(2)	106.83(11)	C(3)-N(1)-C(1)	110.22(12)
C(3)-N(1)-C(4)	123.54(13)	C(1)-N(1)-C(4)	125.97(12)
C(2)-C(1)-N(1)	103.16(12)	C(2)-C(1)-Rh(1)	126.90(11)
N(1)-C(1)-Rh(1)	129.85(10)	C(1)-C(2)-O(1)	110.07(13)
C(1)-C(2)-C(13)	133.77(14)	O(1)-C(2)-C(13)	116.14(12)
N(1)-C(3)-O(1)	109.68(13)	N(1)-C(3)-C(7)	131.70(13)
O(1)-C(3)-C(7)	118.62(12)	N(1)-C(4)-C(5)	110.54(12)
N(1)-C(4)-C(6)	110.38(13)	C(5)-C(4)-C(6)	112.50(14)
C(12)-C(7)-C(8)	119.53(14)	C(12)-C(7)-C(3)	122.46(13)
C(8)-C(7)-C(3)	118.01(13)	C(9)-C(8)-C(7)	120.12(15)
C(8)-C(9)-C(10)	119.96(15)	C(9)-C(10)-C(11)	120.15(16)
C(12)-C(11)-C(10)	120.35(17)	C(11)-C(12)-C(7)	119.84(15)
C(18)-C(13)-C(14)	118.96(14)	C(18)-C(13)-C(2)	120.96(14)
C(14)-C(13)-C(2)	120.04(14)	C(15)-C(14)-C(13)	120.14(16)
C(14)-C(15)-C(16)	120.46(17)	C(17)-C(16)-C(15)	119.52(16)

C(16)-C(17)-C(18)	120.64(16)	C(17)-C(18)-C(13)	120.20(16)
O(2)-C(19)-Rh(1)	179.50(18)	O(3)-C(20)-Rh(1)	178.3(2)
Cl(2)-C(21)-Cl(4)	110.54(10)	Cl(2)-C(21)-Cl(3)	111.18(10)
Cl(4)-C(21)-Cl(3)	110.18(10)		

Table S4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 5. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

Rh(1)	19(1)	15(1)	21(1)	0(1)	1(1)	-1(1)
Cl(1)	21(1)	20(1)	25(1)	-4(1)	1(1)	0(1)
O(1)	19(1)	15(1)	19(1)	0(1)	0(1)	0(1)
O(2)	35(1)	41(1)	56(1)	-7(1)	19(1)	3(1)
O(3)	52(1)	23(1)	64(1)	-6(1)	17(1)	-14(1)
N(1)	19(1)	14(1)	18(1)	-1(1)	-1(1)	1(1)
C(1)	18(1)	16(1)	19(1)	-2(1)	0(1)	0(1)
C(2)	18(1)	16(1)	19(1)	-1(1)	0(1)	-1(1)
C(3)	18(1)	15(1)	17(1)	-1(1)	2(1)	1(1)
C(4)	24(1)	16(1)	19(1)	0(1)	-3(1)	2(1)
C(5)	33(1)	26(1)	27(1)	-4(1)	-8(1)	12(1)
C(6)	33(1)	25(1)	22(1)	4(1)	-2(1)	-6(1)
C(7)	19(1)	15(1)	18(1)	0(1)	1(1)	-1(1)
C(8)	20(1)	16(1)	22(1)	1(1)	3(1)	-1(1)
C(9)	29(1)	16(1)	26(1)	-2(1)	4(1)	-4(1)
C(10)	28(1)	23(1)	27(1)	1(1)	-3(1)	-8(1)
C(11)	22(1)	24(1)	36(1)	3(1)	-5(1)	-3(1)
C(12)	21(1)	19(1)	30(1)	0(1)	-1(1)	0(1)
C(13)	18(1)	19(1)	18(1)	1(1)	1(1)	0(1)
C(14)	27(1)	21(1)	24(1)	0(1)	-4(1)	0(1)
C(15)	28(1)	30(1)	24(1)	1(1)	-7(1)	-3(1)
C(16)	22(1)	36(1)	25(1)	7(1)	-3(1)	0(1)
C(17)	26(1)	27(1)	26(1)	7(1)	-1(1)	4(1)
C(18)	22(1)	21(1)	22(1)	2(1)	0(1)	1(1)
C(19)	27(1)	24(1)	34(1)	-2(1)	4(1)	-1(1)

		x	y	z	U(eq)	
C(20)	30(1)	20(1)	34(1)	0(1)	8(1)	-3(1)
C(21)	21(1)	23(1)	29(1)	3(1)	0(1)	1(1)
Cl(2)	25(1)	32(1)	54(1)	3(1)	-3(1)	-5(1)
Cl(3)	54(1)	32(1)	49(1)	-6(1)	26(1)	-10(1)
Cl(4)	37(1)	31(1)	59(1)	-11(1)	8(1)	4(1)

Table S5. *Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for 5.*

	x	y	z	U(eq)
H(4)	9113	6285	8990	24
H(5A)	9086	5063	7077	43
H(5B)	9721	5178	8614	43
H(5C)	9853	5631	7051	43
H(6A)	7628	5981	9729	40
H(6B)	8351	5443	10396	40
H(6C)	7743	5257	8863	40
H(8)	8333	8331	7065	23
H(9)	9356	9134	8163	28
H(10)	10793	8773	9006	31
H(11)	11224	7617	8690	33
H(12)	10207	6807	7608	28
H(14)	6471	5763	3104	29
H(15)	5269	5957	1287	33
H(16)	4702	7078	889	33
H(17)	5392	8014	2213	32
H(18)	6593	7833	4030	26
H(21)	2336	8891	2949	30