Supporting Information

Facile Synthesis of Rhodium and Iridium Complexes Bearing a [PEP]-Type Ligand (E = Ge or Sn) via E–C Bond Cleavage

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Contents

Synthesis

Preparation of {*o*-(Ph_2P)C_6H_4}$_2SnMe_2$ (2)

A 1.00-g portion of *o*-$Ph_2P(C_6H_4)Br$ (2.93 mmol) was dissolved in 15 mL of diethylether, and the solution was cooled to −78 ºC. *n*-BuLi (1.96 mL, 1.65 M in hexane, 3.22 mmol) was added slowly to this cold solution, and the mixture was gradually warmed to room temperature. The solution was stirred at room temperature for 1 h, and then the volatile materials were removed under vacuum. The white residue was washed with 3 mL of Et_2O and dried in vacuo to afford 986 mg of {*o*-$PPh_2(C_6H_4)$}Li·Et_2O (2.88 mmol) as a white solid in 98% yield. {*o*-$PPh_2(C_6H_4)$}Li·Et_2O (986 mg, 2.88 mmol) was dissolved in toluene (10 mL), and the solution was cooled to −78 ºC. $SnMe_2Cl_2$ (316 mg, 1.44 mmol) was added slowly to the prepared reaction solution, and the mixture was allowed to warm to room temperature. The reaction mixture was stirred at ambient temperature for 15 h. The resulting solution was filtered through a Celite pad. Removal of the volatile materials in vacuo gave a white solid. The residue was washed with hexane (5 mL × 3), and dried under vacuum to afford **2** (886 mg, 1.32 mmol) in 92% yield as a white powder.

Preparation of {*o*-(Cy_2P)C_6H_4}$_2GeMe_2$ (16)

A 300-mg portion of *o*-$Cy_2P(C_6H_4)Br$ (0.849 mmol) was dissolved in 5 mL of diethylether, and the solution was cooled to −78 ºC. *n*-BuLi (0.56 mL, 1.65 M in hexane, 0.934 mmol) was added slowly to this cold solution, and the mixture was gradually warmed to room temperature. The solution was stirred at room temperature for 1 h, and then the volatile materials were removed under vacuum. The white residue was washed with 1 mL of Et_2O and dried in vacuo to afford 233 mg of {*o*-$PPh_2(C_6H_4)$}Li·Et_2O (0.656 mmol) as a white solid in 77% yield. {*o*-$PPh_2(C_6H_4)$}Li·Et_2O (233 mg, 0.656 mmol) was dissolved in toluene (4 mL), and the solution was cooled to −78 ºC. $GeMe_2Cl_2$ (37.8 μL, 0.328 mmol) was added slowly to the prepared reaction solution, and the mixture was allowed to warm to room temperature. The reaction mixture was stirred at 80 °C for 15 h. The mixture was then allowed to cool to room temperature, and the resulting solution was filtered through a Celite pad. Removal of the volatile materials in vacuo gave a white solid. The residue was washed with Et_2O (1 mL × 2), and dried under vacuum to afford **16** (156 mg, 0.240 mmol) in 73% yield as a white powder.

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90 (s, 6H, GeMe), 0.97–1.27 (m, 20H, Cy), 1.49–1.91 (m, 24H, Cy), 7.17–7.24 (m, 4H, Ar), 7.34–7.44 (m, 2H, Ar), 7.61–7.62 (m, 2H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$): δ 5.25, 26.6, 27.3, 27.5, 30.5, 30.6, 36.1, 127.6, 127.8, 132.5, 135.8, 135.9, 143.5. ^{31}P NMR (163 MHz, $CDCl_3$): δ −5.84 (s). Anal. Calc. for $C_{38}H_{58}P_2Ge$: C, 70.28; H, 9.00. Found: C, 70.28; H 9.03.

Preparation of {*o*-(Cy_2P)C_6H_4}$_2SnMe_2$

A 300-mg portion of *o*-$Cy_2P(C_6H_4)Br$ (0.849 mmol) was dissolved in 5 mL of diethylether, and the solution was cooled to −78 ºC. *n*-BuLi (0.56 mL, 1.65 M in hexane, 0.934 mmol) was added slowly to this cold solution, and the mixture was gradually warmed to room temperature. The solution was stirred at room temperature for 1 h, and then the volatile materials were removed under vacuum. The white residue was washed with 1 mL of Et_2O and dried in vacuo to afford 288 mg of {*o*-$PPh_2(C_6H_4)$}Li·Et_2O (0.813 mmol) as a white solid in 96% yield.

{*o*-$PPh_2(C_6H_4)$}Li·Et_2O (288 mg, 0.813 mmol) was dissolved in toluene (5 mL), and the solution was cooled to −78 ºC. $SnMe_2Cl_2$ (89.3 mg, 0.407 mmol) was added slowly to the prepared reaction solution, and the mixture was allowed to warm to room temperature. The reaction mixture was stirred at ambient temperature for 15 h. The resulting solution was filtered through a Celite pad. Removal of the volatile materials in vacuo gave a white solid. The residue was washed with Et_2O (1 mL × 2), and dried under vacuum to afford $\{(Cy_2P)C_6H_4\}_2SnMe_2$ (226 mg, 0.326 mmol) in 80% yield as a white powder.

^{1}H NMR (400 MHz, C_6D_6): δ 0.98 (s, 6H, SnMe), 1.05–1.29 (m, 20H, Cy), 1.55–1.92 (m, 24H, Cy), 7.18–7.22 (m, 4H, Ar), 7.44–7.46 (m, 2H, Ar), 7.81–7.82 (m, 2H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$): δ –0.93, 26.6, 27.3, 27.4, 30.3, 30.5, 35.8, 127.6, 128.2, 132.1, 137.3, 137.5, 144.9. ^{31}P NMR (163 MHz, C_6D_6): δ –3.75 (s, $J_{P\text{-}119Sn}$ = 40.4 Hz). Anal. Calc. for $C_{38}H_{58}P_2Sn$: C, 65.62; H, 8.41. Found: C, 65.18; H, 8.27.

Preparation of {(*o*-$Ph_2PC_6H_4)_2$(Me)Sn}Rh(CO)(PPh_3) (5)

A 50-mL Schlenk tube was filled with **2** (169.5 mg, 0.252 mmol), $RhH(CO)(PPh_3)_3$ (**3**) (252.5 mg, 0.252 mmol), and toluene (15 mL), and the reaction mixture was stirred at ambient temperature. After 12 h, the solvent was removed under reduced pressure to give a pale orange solid. The residue was washed with a 2/1 mixture of hexane/Et_2O (3 mL × 3) and dried under vacuum to afford 198.6 mg of **5**(0.189 mmol) as an orange powder in 75% yield.

Preparation of {(*o*-$Ph_2PC_6H_4)_2$(Me)Sn}Ir(CO)(PPh_3) (9)

A 50-mL Schlenk tube was filled with **2** (55.7 mg, 0.0830 mmol), $IrH(CO)(PPh_3)_3$ (**7**) (83.6 mg, 0.0830 mmol), and toluene (5 mL), and the reaction mixture was stirred at 80 °C. After 4 h, the solvent was removed under reduced pressure to give a yellow solid. The residue was washed with a 2/1 mixture of hexane/Et_2O (2 mL × 3) and dried under vacuum to afford 68.9 mg of **9**(0.0605 mmol) as a pale yellow powder in 73% yield.

Preparation of {(*o*-$Ph_2PC_6H_4)_2$(Me)Sn}Rh(PPh_3) (12)

A 50-mL Schlenk tube was filled with **2**(39.4 mg, 0.0586 mmol), $RhH(PPh_3)_4$ (67.6 mg, 0.0586 mmol), and toluene (5 mL), and the reaction mixture was stirred at 50 °C. After 3 h, the solvent was removed under reduced pressure to give a pale orange solid. The residue was washed with a 2/1 mixture of hexane/Et_2O (2 mL × 3) and dried under vacuum to afford 46.3 mg of **12**(0.0453 mmol) as an orange powder in 77% yield.

Result of X-ray diffraction study of [PSnP]Rh(CO)(PPh_3) (**5**)

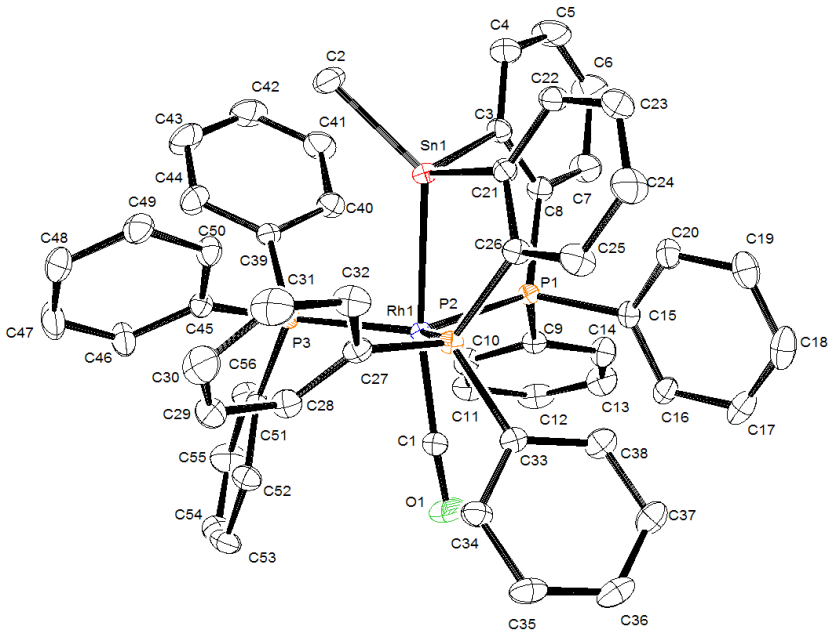

Figure S1. Molecular structure of **5** (40% probability).

Table S1. Crystallographic data for **5**.

(a) Crystal data		(b) Intensity measurements	
Empirical formula	$C_{56}H_{46}OP_3RhSn$, C_6H_6	Diffractometer	Rigaku/MSC Mercury CCD
Formula weight	1127.61	Radiation	MoKα (λ = 0.71069 Å)
Crystal description	Platelet	Monochrometer	Graphite
Crystal color	Pale Yellow	2θ max (°)	55
Crystal size (mm)	0.15 × 0.13 × 0.05	Reflections collected	38959
Crystalizing solution	Benzene, *n*-hexane (23 °C)	Independent reflections	11538 (R_{int} = 0.039)
Crystal system	Monoclinic	Reflections observed (> 2σ)	10401
Space group	$P2_1/n$ (#14)	Abs. correction type	Multi-scan
a (Å)	12.0309(7)	Abs. transmission	0.761 (min.), 0.954 (max.)
b (Å)	11.3392(5)	(c) Refinement (CrystalStructure 3.8)	
c (Å)	38.540(2)	R_1 ($I > 2\sigma(I)$)	0.0428
β (º)	103.348(2)	wR_2 ($I > 2\sigma(I)$)	0.1331
Volume (Å^3)	5115.7(5)	Data	11538
Z value	4	Restraints	0
D_{calc} (g/cm^3)	1.464	Parameters	665
Mesurement temp. (K)	200	Goodness of fit on F^2	1.006
μ (MoKα) (mm^{-1})	0.946	Largest diff. peak and hole	0.67 and −0.97 e.Å^{-3}

Table S2. Selected bond lengths (Å) and angles (°).

Rh1-P1	2.3395(8)	Rh1-P2	2.3228(9)	Rh1-P3	2.3200(8)	Rh1-Sn1	2.6034(4)
Rh1-C1	1.893(3)	C1-O1	1.137(4)	Sn1-C2	2.148(3)	Sn1-C3	2.168(3)
Sn1-C21	2.189(3)						

P1-Rh1-P2	115.07(3)	P1-Rh1-P3	120.92(3)	P2-Rh1-P3	121.27(2)
P1-Rh1-C1	93.03(10)	P2-Rh1-C1	94.85(11)	P3-Rh1-C1	98.46(10)
P1-Rh1-Sn1	80.90(2)	P2-Rh1-Sn1	81.99(2)	P3-Rh1-Sn1	90.27(2)
C1-Rh1-Sn1	171.10(10)	Rh1-C1-O1	177.1(3)	Rh1-Sn1-C2	132.51(11)
Rh1-Sn1-C3	102.83(9)	Rh1-Sn1-C21	99.42(8)		

Result of X-ray diffraction study of [PGeP]Ir(CO)(PPh_3) (**8**)

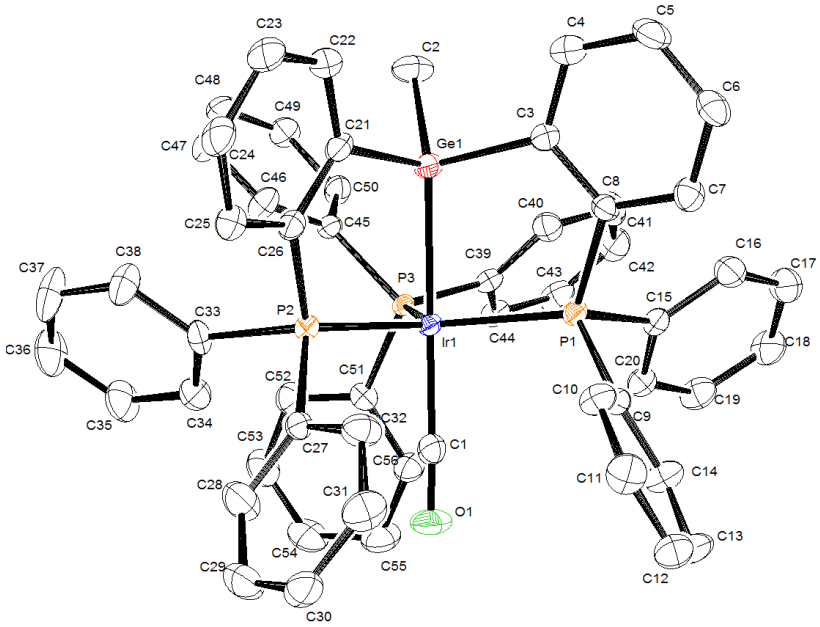

Figure S2. Molecular structure of **8** (40% probability).

Table S3. Crystallographic data for **8**.

(a) Crystal data		(b) Intensity measurements	
Empirical formula	$C_{56}H_{46}GeIrOP_3$	Diffractometer	Rigaku/MSC Mercury CCD
Formula weight	1092.71	Radiation	MoKα (λ = 0.71069 Å)
Crystal description	Prism	Monochrometer	Graphite
Crystal color	Pale Yellow	2θ max (°)	55
Crystal size (mm)	0.20 × 0.15 × 0.10	Reflections collected	36271
Crystalizing solution	Et_2O (23 °C)	Independent reflections	10457 (R_{int} = 0.041)
Crystal system	Monoclinic	Reflections observed (> 2σ)	9642
Space group	$P2_1/c$ (#14)	Abs. correction type	Multi-scan
a (Å)	11.6489(5)	Abs. transmission	0.498 (min.), 0.691 (max.)
b (Å)	20.5910(10)	(c) Refinement (CrystalStructure 3.8)	
c (Å)	19.4199(11)	R_1 ($I > 2\sigma(I)$)	0.0439
β (°)	98.772(3)	wR_2 ($I > 2\sigma(I)$)	0.0880
Volume (Å^3)	4603.6(4)	Data	10457
Z value	4	Restraints	0
D_{calc} (g/cm^3)	1.576	Parameters	560
Mesurement temp. (K)	200	Goodness of fit on F^2	1.185
μ (MoKα) (mm^{-1})	3.693	Largest diff. peak and hole	1.22 and −1.13 e.Å^{-3}

Table S4. Selected bond lengths (Å) and angles (°).

Ir1-P1	2.3107(10)	Ir1-P2	2.2958(9)	Ir1-P3	2.3340(10)	Ir1-Ge1	2.4716(4)
Ir1-C1	1.907(4)	C1-O1	1.124(6)	Ge1-C2	1.978(5)	Ge1-C3	1.988(4)
Ge1-C21	1.994(4)						

P1-Ir1-P2	125.06(3)	P1-Ir1-P3	117.49(3)	P2-Ir1-P3	116.24(3)
P1-Ir1-C1	93.17(13)	P2-Ir1-C1	88.69(13)	P3-Ir1-C1	99.49(15)
P1-Ir1-Ge1	82.27(2)	P2-Ir1-Ge1	82.77(2)	P3-Ir1-Ge1	94.84(2)
C1-Ir1-Ge1	165.46(14)	Ir1-C1-O1	173.7(4)	Ir1-Ge1-C2	130.21(15)
Ir1-Ge1-C3	106.14(12)	Ir1-Ge1-C21	105.23(12)		

Result of X-ray diffraction study of [PSnP]Ir(CO)(PPh_3) (**9**)

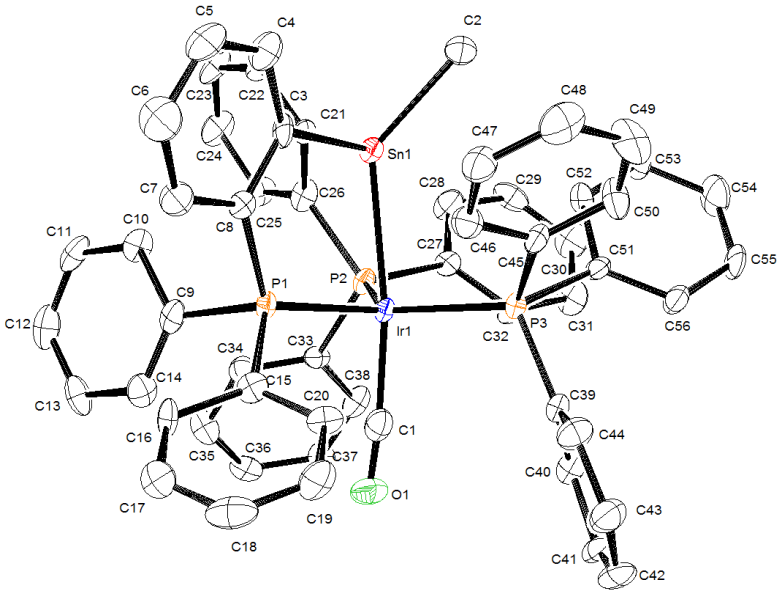

Figure S3. Molecular structure of **9** (40% probability)

Table S5. Crystallographic data for **9**.

(a) Crystal data		(b) Intensity measurements	
Empirical formula	$C_{56}H_{46}IrOP_3Sn$, C_6H_6	Diffractometer	Rigaku/MSC Mercury CCD
Formula weight	1216.92	Radiation	MoKα (λ = 0.71069 Å)
Crystal description	Platelet	Monochrometer	Graphite
Crystal color	Pale Yellow	2θ max (°)	55
Crystal size (mm)	0.30 × 0.10 × 0.03	Reflections collected	37977
Crystalizing solution	Benzene, *n*-hexane (23 °C)	Independent reflections	11551 (R_{int} = 0.0843)
Crystal system	Monoclinic	Reflections observed (> 2σ)	10950
Space group	$P2_1/n$ (#14)	Abs. correction type	Multi-scan
a (Å)	12.055(8)	Abs. transmission	0.4469 (min.), 0.9101 (max.)
b (Å)	11.354(8)	(c) Refinement (Shelxl-97)	
c (Å)	37.77(3)	R_1 ($I > 2\sigma(I)$)	0.0975
β (°)	94.839(6)	wR_2 ($I > 2\sigma(I)$)	0.2157
Volume (Å^3)	5151(6)	R_1 (all data)	0.1019
Z value	4	wR_2 (all data)	0.2173
D_{calc} (g/cm^3)	1.569	Data / Restraints / Parameters	11551 / 0 / 584
Mesurement temp. (K)	200	Goodness of fit on F^2	1.590
μ (MoKα) (mm^{-1})	3.201	Largest diff. peak and hole	3.667 and −3.920 e.Å^{-3}

Table S6. Selected bond lengths (Å) and angles (°).

Ir1-P1	2.328(3)	Ir1-P2	2.314(3)	Ir1-P3	2.309(3)	Ir1-Sn1	2.6384(17)
Ir1-C1	1.889(12)	C1-O1	1.142(15)	Sn1-C2	2.160(14)	Sn1-C3	2.174(10)
Sn1-C21	2.197(11)						

P1-Ir1-P2	115.21(10)	P1-Ir1-P3	121.09(11)	P2-Ir1-P3	121.09(10)
P1-Ir1-C1	93.3(4)	P2-Ir1-C1	94.8(4)	P3-Ir1-C1	97.8(4)
P1-Ir1-Sn1	81.13(8)	P2-Ir1-Sn1	82.08(8)	P3-Ir1-Sn1	90.38(9)
C1-Ir1-Sn1	171.7(4)	Ir1-C1-O1	176.5(11)	Ir1-Sn1-C2	132.8(4)
Ir1-Sn1-C3	102.1(3)	Ir1-Sn1-C21	99.0(3)		

Result of X-ray diffraction study of **17**

Suitable single crystals were obtained from a saturated *n*-pentane solution of **17**.

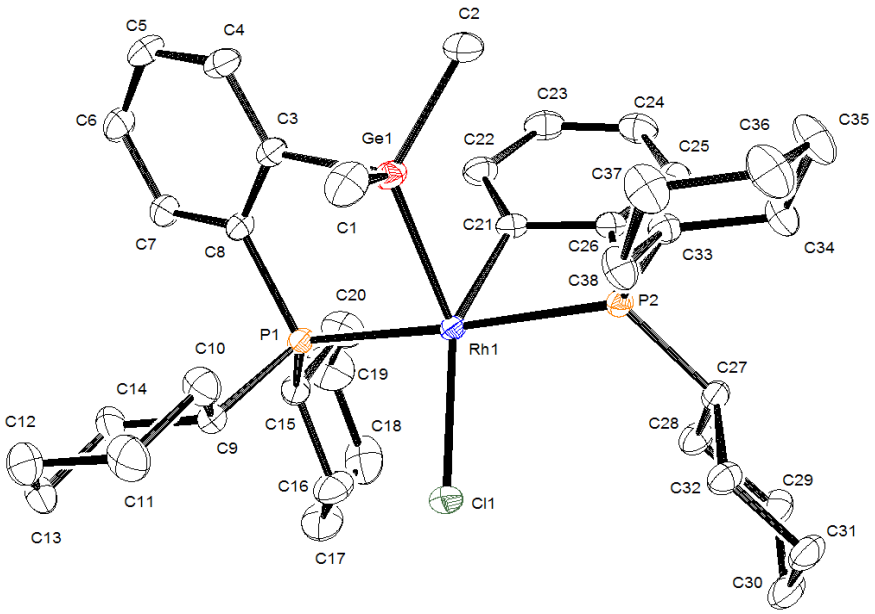

Figure S4. Molecular structure of **17** (40% probability)

Table S7. Crystallographic data for **17**.

(a) Crystal data		(b) Intensity measurements	
Empirical formula	$C_{38}H_{58}ClGeP_2Rh$, 1/2(C_5H_{12})	Diffractometer	Rigaku/MSC Mercury CCD
Formula weight	823.81	Radiation	MoKα (λ = 0.71069 Å)
Crystal description	Prism	Monochrometer	Graphite
Crystal color	Orange	2θ max (°)	55
Crystal size (mm)	0.40 × 0.30 × 0.20	Reflections collected	30941
Crystalizing solution	*n*-Pentane (23 °C)	Independent reflections	9126 (R_{int} = 0.0330)
Crystal system	Monoclinic	Reflections observed (> 2σ)	8701
Space group	$P2_1/c$ (#14)	Abs. correction type	Multi-scan
a (Å)	14.955(3)	Abs. transmission	0.6194 (min.), 0.7776 (max.)
b (Å)	14.070(3)	(c) Refinement (Shelxl-97)	
c (Å)	19.454(4)	R_1 ($I > 2\sigma(I)$)	0.0306
β (º)	99.418(3)	wR_2 ($I > 2\sigma(I)$)	0.0706
Volume (Å^3)	4038.6(13)	R_1 (all data)	0.0335
Z value	4	wR_2 (all data)	0.0719
D_{calc} (g/cm^3)	1.355	Data / Restraints / Parameters	9126 / 0 / 437
Mesurement temp. (K)	200	Goodness of fit on F^2	1.118
μ (MoKα) (mm^{-1})	1.325	Largest diff. peak and hole	0.584 and −0.542 e.Å^{-3}

Table S8. Selected bond lengths (Å) and angles (°).

Rh1-P1	2.3184(6)	Rh1-P2	2.3426(6)	Rh1-Ge1	2.3997(4)	Rh1-Cl1	2.4038(6)
Rh1-C21	2.0268(19)						
P1-Rh1-P2	170.668(17)	P1-Rh1-Ge1	84.136(18)	P1-Rh1-Cl1	89.24(2)		
P1-Rh1-C21	102.09(6)	P2-Rh1-Ge1	96.892(18)	P2-Rh1-Cl1	96.36(2)		
P2-Rh1-C21	69.33(6)	Ge1-Rh1-Cl1	135.685(17)	Ge1-Rh1-C21	75.90(5)		
Cl1-Rh1-C21	147.88(5)						