Mechanistic investigation on the generation of a Pd(0) catalyst from a Pd(II) allyl complex: a combined experimental and DFT study.

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Supporting Information

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Experimental Details

All experiments were performed under an atmosphere of dry nitrogen or argon using standard schlenk and glove box techniques. Complex **1** was synthesized according to ref 1.

Synthesis of complex $\mathbf{2_K}$: Potassium carbonate (14 mg, 0.1 mmol) was added to a solution of complex **1** (52.7 mg, 0.1 mmol) in toluene. The pale yellow reaction mixture was stirred for 30 min. at room temperature. The resulting suspension was filtered over celite. The pale yellow product was isolated by evaporation of the solvent under vacuum Yield: 53 mg (0.083 mmol, 83 %). ^{1}H NMR(C_6D_6): δ 0.40 (s, 9H, $SiMe_3$), 0.47 (s, 9H, $SiMe_3$), 2.00 (br, 6H, Me), 2.64 (d, J_{HH}=12.3 Hz, 1H, CH_2 of allyl *trans* to carbonate), 3.61 (dd, J_{HH}=10.5 Hz, $^{3}J_{HH}$=13.8 Hz, 1H, CH_2 of allyl *trans* to P), 4.14 (d, J_{HH}=6.3 Hz, 1H, CH_2 of allyl *trans* to carbonate), 4.65 (d, 1H), 4.72 (*pseudo*-t, Σ(J_{PH},J_{HH})=7.5 Hz, 1H, CH_2 of allyl *trans* to P), 5.10 (m, 1H, CH of allyl), 6.87-7.00 (m, 2H), 7.06 (d, *J*=6.9 Hz, 1H), 7.76 (m, 1H). ^{13}C NMR (C_6D_6): δ 2.4 (s, $SiMe_3$), 23.2 (s, allyl CH), 25.5 (d, J_{PC}=9.1 Hz, Me), 48.9 (s, allyl CH_2 *trans* to carbonate), 69.5 (d, J_{PC}=27.1 Hz), 76.8 (d, J_{PC}=34.7 Hz, allyl CH_2 *trans* to P), 115.2 (d, J_{PC}=5.5 Hz, CH of allyl), 123.8 (d, J_{PC}=2.2 Hz), 125.0 (d, J_{PC}=11.9 Hz), 127.6 (s), 129.2 (m), 134.0 (m), 139.7 (d, J_{PC}=24.6 Hz), 147.5 (d, J_{PC}=2.1 Hz), 168.6 8 (d, J_{PC}=10.7 Hz). ^{31}P NMR (C_6D_6): δ -11.0 (s).

Synthesis of complex **3**: phenylboronic acid (12 mg, 0.1 mmol) was added to a solution of $\mathbf{2_K}$ obtained as above (0.1 mmol) in toluene (2 mL), and the color of the initially pale yellow solution changed to bright yellow. The resulting suspension was filtered over celite and the product could be isolated as a bright yellow solid after evaporation of the solvent under vacuum. Yield: 44.8 mg (0.079 mmol, 79 %) ^{1}H NMR (C_6D_6): δ 0.43 (s, 9H, $SiMe_3$), 0.47 (s, 9H, $SiMe_3$), 1.95-2.10 (m, 8H, Me, CH_2), 3.17 (d, J_{PH}= 7.2 Hz, 1H), 3.82 (q, J_{PH}=7.2 Hz, 1H), 4.61 (s, 1H), 4.95 (d, J_{HH} =13.8 Hz, 1H), 6.90- 7.18 (m, 8H), 8.21 (m, 1H). ^{31}P NMR (C_6D_6): δ -22.0 (s).

Synthesis of complex **4**: The crude solution of **3**, obtained as above, was stirred at room temperature for 5 min and dvds (50 µl, 0.2 mmol) was added. The reaction mixture was then stirred for 2 h at room temperature. The light yellow solution was taken to dryness and the resulting residue was washed with

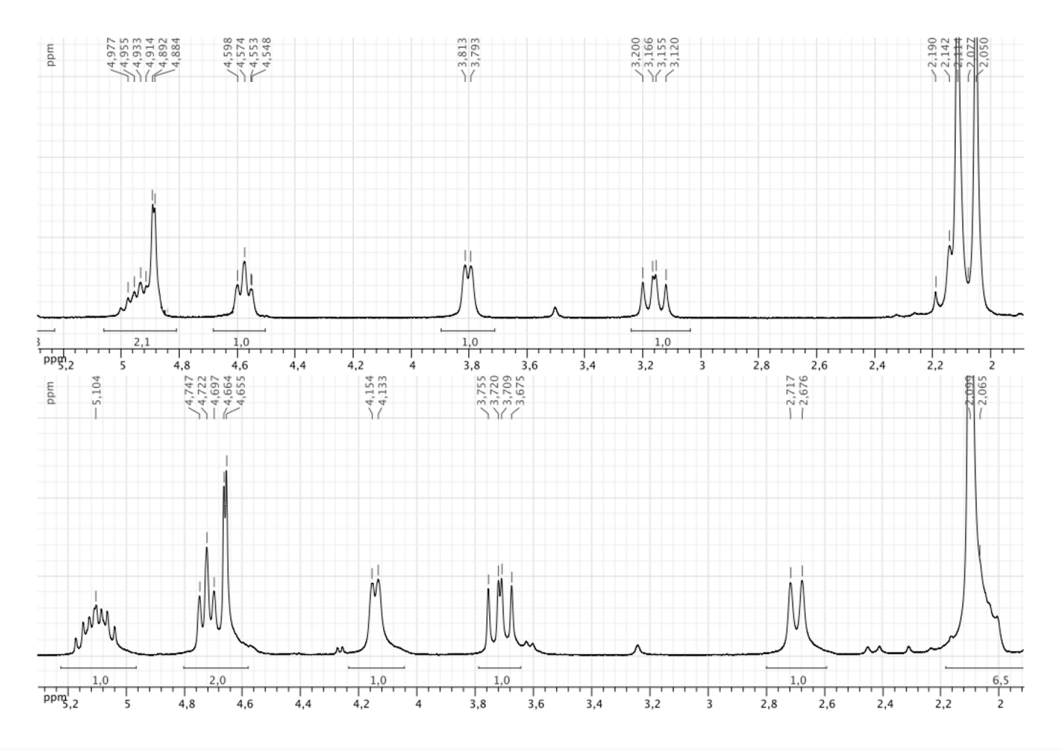
MeOH (3 x 1 mL). Crystals of **4** were obtained by slow evaporation of a diethylether solution. Yield: 41 mg (0.065 mmol, 65 %) Elemental analysis ($C_{27}H_{47}OPPdSi_4$) calculated: C: 50.9 % H: 7.44%; found: C: 51.0 % H: 7.42 %; 1H NMR (C_6D_6): δ 0.3 (br, $SiMe_2$, $SiMe_3$, 24H), 0.4 (s, $SiMe_2$, 6H) 2.05 (d, JPC= 2.0 Hz, 6H, Me), 3.51 (ddd, J_{PH}=5.3 Hz, J_{HH}=12.6 Hz, J_{PH}=16.2 Hz, $CHSiMe_2$), 3.82 (ddd, J_{PH}=1.4 Hz, J_{HH}=4.7 Hz, J_{PH}=16.2 Hz, CH_2), 4.18 (ddd, J_{PH}=1.4 Hz, J_{HH}=7.9 Hz, J_{HH}=12.6 Hz, CH_2), 4.65 (d, J_{PH}=2.0 Hz, 1H), 7.00-7.08 (m, 2H), 7.17-7.23 (m, 1H), 8.05 (m, 1H).^{13}C NMR (C_6D_6): δ 1.7 (br, $SiMe_2$, $SiMe_3$), 25.2 (d, J_{PC}=6.5 Hz, Me), 66.5-66.9 (m, $CH_2CHSiMe_2$),70.1 (d, J_{PC}=19.5 Hz), 123.7 (s), 124.8 (d, J_{PC}=11.9 Hz), 126.9 (s, C9H), 130.7(d, J_{PC}=24.9 Hz), 135.7 (d, J_{PC}=21.7 Hz), 142.7 (d, J_{PC}=16.2 Hz), 146.5 (s), 169.3 (d, J_{PC}=8.6 Hz). ^{31}P NMR (C_6D_6): δ-28.8 (s).

Experiments were performed using a Tandem mass spectrometer equipped with an Electrospray ionization source coupled with the Infrared Free Electron Laser (FEL) based in Orsay.[23] Details on the performance of this experimental setup have been given earlier.[24] The reactive solution was sprayed with conventional ESI conditions into a 3D quadrupole ion trap mass spectrometer (Bruker Esquire 3000+). Mass-selected complex ions were irradiated with the FEL IR beam. IR action spectra can be derived where the IRMPD efficiency is plotted against the photon energy.

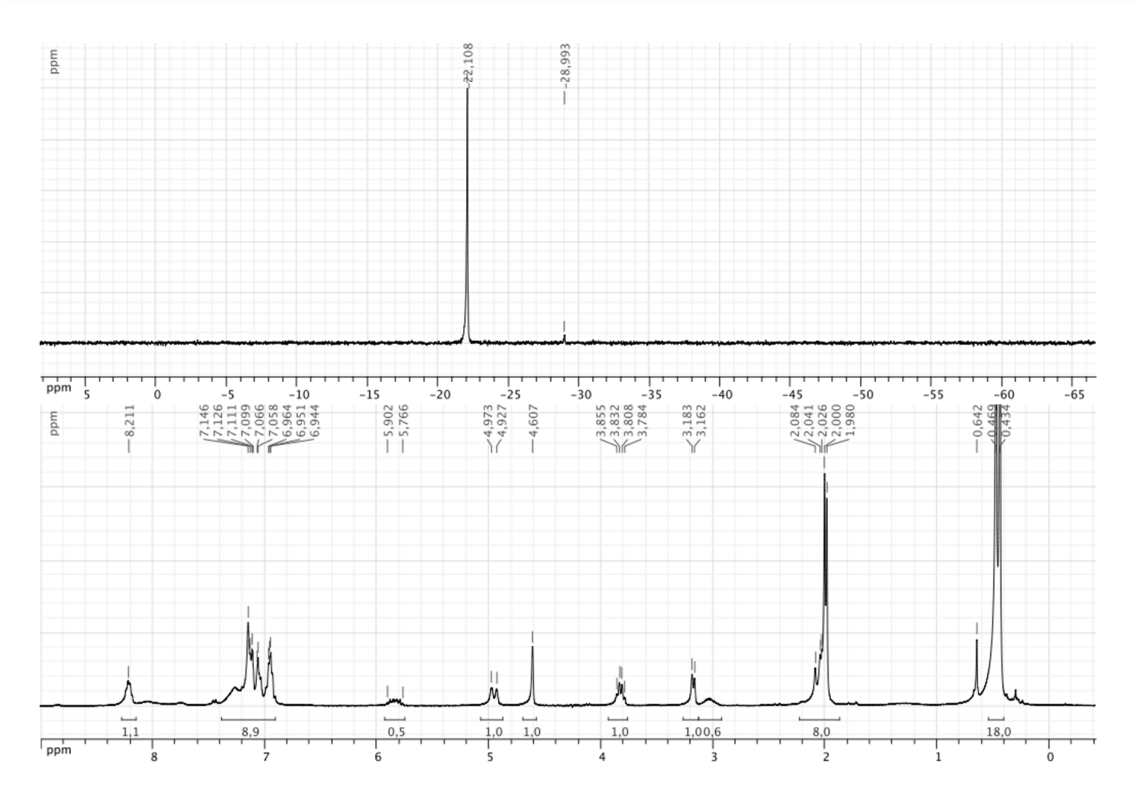
References:

1. Blug, M.; Guibert, C.; Le Goff, X. F.; Mezailles, N.; Le Floch, P. *Chem. Comm.* **2009**, 201-203.

1H NMR spectra of compounds **1** (top) and $\mathbf{2_K}$ (bottom).



31P (top) and 1H NMR (bottom) spectra of compound **3.**



X-Ray Structure data

Table 1. Crystal data for complex **4**

Compound	**4**
Molecular formula	$C_{27}H_{47}OPPdSi_4$
Molecular weight	637.38
Crystal habit	White Needle
Crystal dimensions(mm)	0.22x0.08x0.06
Crystal system	monoclinic
Space group	$P2_1/c$
a(Å)	9.218(1)
b(Å)	22.874(1)
c(Å)	16.629(1)
α(°)	90.00
β(°)	108.854(4)
γ(°)	90.00
V(Å^3)	3318.1(4)
Z	4
d(g-cm^{-3})	1.276
F(000)	1336
μ(cm^{-1})	0.769
Absorption corrections	multi-scan ; 0.8490 min, 0.9553 max
Diffractometer	KappaCCD
X-ray source	MoKα
λ(Å)	0.71069
Monochromator	graphite
T (K)	150.0(1)
Scan mode	phi and omega scans
Maximum θ	30.03
HKL ranges	-12 10 ; -32 28 ; -23 23
Reflections measured	38552
Unique data	9676
Rint	0.0393
Reflections used	7443
Criterion	I > 2σI)
Refinement type	Fsqd
Hydrogen atoms	constr
Parameters refined	319
Reflections / parameter	23
wR2	0.0777
R1	0.0308
Weights a, b	0.0358 ; 0.2713
GoF	1.031
difference peak / hole (e Å^{-3})	0.471(0.068) / -0.577(0.068)

Table 2. Atomic Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for complex **4**

atom	x	y	z	U(eq)
Pd(1)	2169(1)	-861(1)	3172(1)	23(1)
P(1)	2774(1)	-1772(1)	3857(1)	21(1)
Si(1)	6277(1)	-2012(1)	3970(1)	29(1)
Si(2)	2765(1)	-1197(1)	5681(1)	28(1)
Si(3)	-1057(1)	-212(1)	1901(1)	29(1)
Si(4)	1848(1)	12(1)	1495(1)	29(1)
O(1)	53(1)	115(1)	1438(1)	32(1)
C(1)	4450(2)	-2288(1)	4105(1)	26(1)
C(2)	4172(2)	-2790(1)	4435(1)	31(1)
C(3)	2622(2)	-2880(1)	4575(1)	28(1)
C(4)	2406(2)	-2384(1)	5149(1)	25(1)
C(5)	2526(2)	-1828(1)	4918(1)	23(1)
C(6)	1339(2)	-2316(1)	3292(1)	23(1)
C(7)	277(2)	-2239(1)	2490(1)	30(1)
C(8)	-751(2)	-2687(1)	2126(1)	37(1)
C(9)	-692(2)	-3210(1)	2551(1)	39(1)
C(10)	376(2)	-3292(1)	3347(1)	33(1)
C(11)	1389(2)	-2843(1)	3718(1)	26(1)
C(12)	5213(3)	-3311(1)	4706(2)	53(1)
C(13)	2102(2)	-2590(1)	5936(1)	35(1)
C(14)	6738(2)	-1313(1)	4584(1)	37(1)
C(15)	8001(2)	-2489(1)	4411(1)	44(1)
C(16)	5980(2)	-1924(1)	2814(1)	43(1)
C(17)	4353(3)	-1384(1)	6681(1)	48(1)
C(18)	960(2)	-1051(1)	5935(1)	44(1)
C(19)	3351(3)	-505(1)	5280(1)	42(1)
C(20)	4133(2)	-588(1)	2812(2)	42(1)
C(21)	3056(2)	-137(1)	2599(1)	31(1)
C(22)	2497(2)	704(1)	1132(1)	40(1)
C(23)	1980(3)	-598(1)	788(2)	48(1)
C(24)	-2680(2)	298(1)	1811(1)	46(1)
C(25)	-1855(3)	-894(1)	1315(1)	47(1)
C(26)	29(2)	-371(1)	3025(1)	27(1)
C(27)	-16(2)	-900(1)	3430(1)	28(1)

U(eq) is defined as 1/3 the trace of the Uij tensor.

Table 3. Bond lengths (A) and angles (deg) for complex **4**

Pd(1)-C(20)	2.174(2)	Pd(1)-C(27)	2.193(2)
Pd(1)-C(21)	2.196(2)	Pd(1)-C(26)	2.213(2)
Pd(1)-P(1)	2.3527(5	P(1)-C(6)	1.838(2)
P(1)-C(5)	1.856(2)	P(1)-C(1)	1.882(2)
Si(1)-C(16)	1.863(2)	Si(1)-C(14)	1.869(2)
Si(1)-C(15)	1.872(2)	Si(1)-C(1)	1.879(2)
Si(2)-C(19)	1.864(2)	Si(2)-C(18)	1.874(2)
Si(2)-C(17)	1.875(2)	Si(2)-C(5)	1.886(2)
Si(3)-O(1)	1.645(1)	Si(3)-C(26)	1.849(2)
Si(3)-C(25)	1.859(2)	Si(3)-C(24)	1.865(2)
Si(4)-O(1)	1.644(1)	Si(4)-C(21)	1.845(2)
Si(4)-C(23)	1.855(2)	Si(4)-C(22)	1.860(2)
C(1)-C(2)	1.333(3)	C(2)-C(12)	1.505(3)
C(2)-C(3)	1.534(2)	C(3)-C(11)	1.510(3)
C(3)-C(4)	1.537(3)	C(3)-H(3)	1.0000
C(4)-C(5)	1.342(3)	C(4)-C(13)	1.501(3)
C(6)-C(7)	1.387(2)	C(6)-C(11)	1.392(3)
C(7)-C(8)	1.394(3)	C(7)-H(7)	0.9500
C(8)-C(9)	1.382(3)	C(8)-H(8)	0.9500
C(9)-C(10)	1.384(3)	C(9)-H(9)	0.9500
C(10)-C(11)	1.391(3)	C(10)-H(10)	0.9500
C(12)-H(12A)	0.9800	C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800	C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800	C(13)-H(13C)	0.9800
C(14)-H(14A)	0.9800	C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800	C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800	C(15)-H(15C)	0.9800
C(16)-H(16A)	0.9800	C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800	C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800	C(17)-H(17C)	0.9800
C(18)-H(18A)	0.9800	C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800	C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800	C(19)-H(19C)	0.9800
C(20)-C(21)	1.396(3)	C(20)-H(20A)	0.9900
C(20)-H(20B)	0.9900	C(21)-H(21)	0.9500
C(22)-H(22A)	0.9800	C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800	C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800	C(23)-H(23C)	0.9800
C(24)-H(24A)	0.9800	C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800	C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800	C(25)-H(25C)	0.9800
C(26)-C(27)	1.391(3)	C(26)-H(26)	0.9499
C(27)-H(27A)	0.9899	C(27)-H(27B)	0.9900

C(20)-Pd(1)-C(27)	164.77(8)	C(20)-Pd(1)-C(21)	37.27(8)
C(27)-Pd(1)-C(21)	127.55(7)	C(20)-Pd(1)-C(26)	128.05(8)
C(27)-Pd(1)-C(26)	36.80(7)	C(21)-Pd(1)-C(26)	90.79(7)
C(20)-Pd(1)-P(1)	107.43(6)	C(27)-Pd(1)-P(1)	87.61(5)
C(21)-Pd(1)-P(1)	144.55(5)	C(26)-Pd(1)-P(1)	124.39(5)
C(6)-P(1)-C(5)	98.60(8)	C(6)-P(1)-C(1)	95.22(8)
C(5)-P(1)-C(1)	95.32(8)	C(6)-P(1)-Pd(1)	109.47(6)
C(5)-P(1)-Pd(1)	116.07(6)	C(1)-P(1)-Pd(1)	135.32(6)
C(16)-Si(1)-C(14)	113.8(1)	C(16)-Si(1)-C(15)	106.9(1)
C(14)-Si(1)-C(15)	105.7(1)	C(16)-Si(1)-C(1)	108.7(1)
C(14)-Si(1)-C(1)	106.1(1)	C(15)-Si(1)-C(1)	115.9(1)
C(19)-Si(2)-C(18)	108.0(1)	C(19)-Si(2)-C(17)	106.1(1)
C(18)-Si(2)-C(17)	109.7(1)	C(19)-Si(2)-C(5)	113.1(1)
C(18)-Si(2)-C(5)	111.6(1)	C(17)-Si(2)-C(5)	108.1(1)
O(1)-Si(3)-C(26)	110.29(8)	O(1)-Si(3)-C(25)	109.7(1)
C(26)-Si(3)-C(25)	111.0(1)	O(1)-Si(3)-C(24)	106.4(1)
C(26)-Si(3)-C(24)	111.2(1)	C(25)-Si(3)-C(24)	108.2(1)
O(1)-Si(4)-C(21)	110.87(8)	O(1)-Si(4)-C(23)	110.0(1)
C(21)-Si(4)-C(23)	110.5(1)	O(1)-Si(4)-C(22)	106.44(8)
C(21)-Si(4)-C(22)	109.0(1)	C(23)-Si(4)-C(22)	109.9(1)
Si(4)-O(1)-Si(3)	132.4(1)	C(2)-C(1)-Si(1)	129.6(1)
C(2)-C(1)-P(1)	112.2(1)	Si(1)-C(1)-P(1)	117.8(1)
C(1)-C(2)-C(12)	128.1(2)	C(1)-C(2)-C(3)	119.3(2)
C(12)-C(2)-C(3)	112.6(2)	C(11)-C(3)-C(2)	107.7(2)
C(11)-C(3)-C(4)	109.6(1)	C(2)-C(3)-C(4)	108.0(2)

C(11)-C(3)-H(3)	110.5	C(2)-C(3)-H(3)	110.5
C(4)-C(3)-H(3)	110.5	C(5)-C(4)-C(13)	127.1(2)
C(5)-C(4)-C(3)	118.8(2)	C(13)-C(4)-C(3)	114.1(2)
C(4)-C(5)-P(1)	112.6(1)	C(4)-C(5)-Si(2)	122.3(1)
P(1)-C(5)-Si(2)	124.3(1)	C(7)-C(6)-C(11)	119.7(2)
C(7)-C(6)-P(1)	125.0(2)	C(11)-C(6)-P(1)	115.3(1)
C(6)-C(7)-C(8)	119.7(2)	C(6)-C(7)-H(7)	120.2
C(8)-C(7)-H(7)	120.2	C(9)-C(8)-C(7)	120.3(2)
C(9)-C(8)-H(8)	119.9	C(7)-C(8)-H(8)	119.9
C(8)-C(9)-C(10)	120.4(2)	C(8)-C(9)-H(9)	119.8
C(10)-C(9)-H(9)	119.8	C(9)-C(10)-C(11)	119.5(2)
C(9)-C(10)-H(10)	120.3	C(11)-C(10)-H(10)	120.3
C(10)-C(11)-C(6)	120.5(2)	C(10)-C(11)-C(3)	124.7(2)
C(6)-C(11)-C(3)	114.8(2)	C(2)-C(12)-H(12A)	109.5
C(2)-C(12)-H(12B)	109.5	H(12A)-C(12)-H(12B)	109.5
C(2)-C(12)-H(12C)	109.5	H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5	C(4)-C(13)-H(13A)	109.5
C(4)-C(13)-H(13B)	109.5	H(13A)-C(13)-H(13B)	109.5
C(4)-C(13)-H(13C)	109.5	H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5	Si(1)-C(14)-H(14A)	109.5
Si(1)-C(14)-H(14B)	109.5	H(14A)-C(14)-H(14B)	109.5
Si(1)-C(14)-H(14C)	109.5	H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5	Si(1)-C(15)-H(15A)	109.5
Si(1)-C(15)-H(15B)	109.5	H(15A)-C(15)-H(15B)	109.5
Si(1)-C(15)-H(15C)	109.5	H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5	Si(1)-C(16)-H(16A)	109.5
Si(1)-C(16)-H(16B)	109.5	H(16A)-C(16)-H(16B)	109.5
Si(1)-C(16)-H(16C)	109.5	H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5	Si(2)-C(17)-H(17A)	109.5
Si(2)-C(17)-H(17B)	109.5	H(17A)-C(17)-H(17B)	109.5
Si(2)-C(17)-H(17C)	109.5	H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5	Si(2)-C(18)-H(18A)	109.5
Si(2)-C(18)-H(18B)	109.5	H(18A)-C(18)-H(18B)	109.5
Si(2)-C(18)-H(18C)	109.5	H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5	Si(2)-C(19)-H(19A)	109.5
Si(2)-C(19)-H(19B)	109.5	H(19A)-C(19)-H(19B)	109.5
Si(2)-C(19)-H(19C)	109.5	H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5	C(21)-C(20)-Pd(1)	72.2(1)
C(21)-C(20)-H(20A)	116.4	Pd(1)-C(20)-H(20A)	116.4
C(21)-C(20)-H(20B)	116.1	Pd(1)-C(20)-H(20B)	116.4
H(20A)-C(20)-H(20B)	113.4	C(20)-C(21)-Si(4)	122.6(2)
C(20)-C(21)-Pd(1)	70.5(1)	Si(4)-C(21)-Pd(1)	112.4(1)
C(20)-C(21)-H(21)	118.6	Si(4)-C(21)-H(21)	118.7
Pd(1)-C(21)-H(21)	86.9	Si(4)-C(22)-H(22A)	109.5
Si(4)-C(22)-H(22B)	109.5	H(22A)-C(22)-H(22B)	109.5
Si(4)-C(22)-H(22C)	109.5	H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5	Si(4)-C(23)-H(23A)	109.5
Si(4)-C(23)-H(23B)	109.5	H(23A)-C(23)-H(23B)	109.5
Si(4)-C(23)-H(23C)	109.5	H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5	Si(3)-C(24)-H(24A)	109.5
Si(3)-C(24)-H(24B)	109.5	H(24A)-C(24)-H(24B)	109.5
Si(3)-C(24)-H(24C)	109.5	H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5	Si(3)-C(25)-H(25A)	109.5
Si(3)-C(25)-H(25B)	109.5	H(25A)-C(25)-H(25B)	109.5
Si(3)-C(25)-H(25C)	109.5	H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5	C(27)-C(26)-Si(3)	124.7(2)
C(27)-C(26)-Pd(1)	70.8(1)	Si(3)-C(26)-Pd(1)	112.54(8)
C(27)-C(26)-H(26)	117.6	Si(3)-C(26)-H(26)	117.7
Pd(1)-C(26)-H(26)	86.2	C(26)-C(27)-Pd(1)	72.4(1)
C(26)-C(27)-H(27A)	116.1	Pd(1)-C(27)-H(27A)	116.3
C(26)-C(27)-H(27B)	116.5	Pd(1)-C(27)-H(27B)	116.5
H(27A)-C(27)-H(27B)	113.4		

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for complex **4**

atom	U11	U22	U33	U23	U13	U12
Pd(1)	22(1)	21(1)	26(1)	2(1)	7(1)	-1(1)
P(1)	19(1)	20(1)	27(1)	1(1)	11(1)	1(1)
Si(1)	18(1)	34(1)	37(1)	-4(1)	11(1)	0(1)
Si(2)	26(1)	30(1)	27(1)	-4(1)	6(1)	2(1)
Si(3)	26(1)	31(1)	28(1)	5(1)	7(1)	-1(1)
Si(4)	31(1)	26(1)	32(1)	5(1)	12(1)	1(1)
O(1)	30(1)	33(1)	32(1)	10(1)	9(1)	2(1)
C(1)	18(1)	25(1)	37(1)	-3(1)	12(1)	3(1)
C(2)	23(1)	25(1)	46(1)	0(1)	14(1)	5(1)
C(3)	26(1)	18(1)	41(1)	5(1)	13(1)	3(1)
C(4)	19(1)	27(1)	28(1)	3(1)	6(1)	2(1)
C(5)	18(1)	25(1)	24(1)	2(1)	7(1)	3(1)
C(6)	22(1)	22(1)	30(1)	-4(1)	14(1)	-1(1)
C(7)	31(1)	34(1)	28(1)	-3(1)	15(1)	-2(1)
C(8)	34(1)	48(1)	30(1)	-13(1)	12(1)	-9(1)
C(9)	36(1)	41(1)	46(1)	-20(1)	20(1)	-15(1)
C(10)	34(1)	25(1)	47(1)	-7(1)	22(1)	-4(1)
C(11)	24(1)	22(1)	37(1)	-4(1)	17(1)	0(1)
C(12)	36(1)	31(1)	99(2)	13(1)	29(1)	13(1)
C(13)	36(1)	35(1)	33(1)	10(1)	11(1)	1(1)
C(14)	27(1)	40(1)	40(1)	-5(1)	7(1)	-3(1)
C(15)	23(1)	49(2)	59(1)	-3(1)	14(1)	6(1)
C(16)	38(1)	52(2)	42(1)	-8(1)	18(1)	-6(1)
C(17)	44(1)	49(2)	39(1)	-6(1)	-4(1)	1(1)
C(18)	41(1)	56(2)	38(1)	-8(1)	16(1)	9(1)
C(19)	52(1)	29(1)	44(1)	-10(1)	14(1)	-9(1)
C(20)	23(1)	48(1)	54(1)	22(1)	12(1)	-4(1)
C(21)	29(1)	29(1)	35(1)	7(1)	10(1)	-9(1)
C(22)	40(1)	37(1)	49(1)	16(1)	22(1)	4(1)
C(23)	53(1)	44(2)	48(1)	-8(1)	17(1)	3(1)
C(24)	34(1)	57(2)	44(1)	15(1)	11(1)	12(1)
C(25)	54(1)	47(2)	30(1)	2(1)	1(1)	-17(1)
C(26)	24(1)	28(1)	28(1)	0(1)	7(1)	2(1)
C(27)	24(1)	35(1)	29(1)	4(1)	13(1)	4(1)

The anisotropic displacement factor exponent takes the form
2 pi^2 [h^2a*^2U(11) +...+ 2hka*b*U(12)]

Table 5. Hydrogen Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for complex **4**

atom	x	y	z	U(eq)
H(3)	2590	-3268	4844	33
H(7)	251	-1884	2191	36
H(8)	-1497	-2632.0002	1583	45
H(9)	-1388	-3515	2296	47
H(10)	418	-3652.0002	3638	40
H(12A)	6128	-3254	4538	80
H(12B)	4671	-3664	4433	80
H(12C)	5516	-3355	5325	80
H(13A)	1908	-2252	6250	52
H(13B)	2995	-2805	6296	52
H(13C)	1203	-2847	5778	52
H(14A)	5798	-1085	4488	55
H(14B)	7474	-1088	4396	55
H(14C)	7185	-1402	5191	55
H(15A)	8150	-2572	5011	65
H(15B)	8908	-2289	4361	65
H(15C)	7848	-2857	4092	65
H(16A)	6044	-2308	2563	64
H(16B)	6773	-1666	2736	64
H(16C)	4967	-1753	2533	64
H(17A)	5259	-1506	6539	72
H(17B)	4023	-1703.0001	6975	72
H(17C)	4605	-1039	7051	72
H(18A)	1161	-758	6387	66
H(18B)	605	-1414	6123	66
H(18C)	168	-905	5426	66
H(19A)	3490	-198	5709	63
H(19B)	2555	-387	4755	63
H(19C)	4318	-568	5165	63
H(20A)	5092	-509	3283	50
H(20B)	4301	-800	2330	50
H(21)	2938	102	3042	37
H(22A)	1766	818	582	61
H(22B)	3511	644	1073	61
H(22C)	2556	1013	1550	61
H(23A)	1713	-966.0001	1008	72
H(23B)	3028	-623	767	72
H(23C)	1268	-528	214	72
H(24A)	-2281	664	2106	68
H(24B)	-3388.0002	119	2069	68
H(24C)	-3224	379	1210	68
H(25A)	-2578.0002	-793	756	70
H(25B)	-2389	-1117	1637	70
H(25C)	-1018.9999	-1130	1243	70
H(26)	670	-72	3348	33
H(27A)	-770	-1190	3098	34
H(27B)	41	-877	4034	34

Theoretical part

Computational methodology:

All the calculations were performed using Gaussian03.[1] The IR absorption spectra where determined using the B3PW91 density functional. The following basis set was used: 6-31G* for all non-metallic atoms and LANLDZ+f for palladium. The associate pseudo-potential was used to describe the 28 electrons of the palladium core. This basis set is denoted as Basis1. The relative energies of κ^2 and κ^2 carbonate isomers were also calculated at the B3LYP level using the same basis set. Single point calculations on B3LYP optimized geometries were performed using the M06 and M06-2X functional together with the LANLTZ+f for Pd, 6-311+G(d,p) for all non metallic atoms. This basis set is denoted as Basis2.

Coordinates, frequencies and thermochemistry of optimized structures:

Cartesian coordinates, three lowest frequencies and thermochemistry of κ^1-carbonate isomer of complex 2 determined at the B3PW91/Basis1 level.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.053994	1.383623	-0.691032
2	6	0	2.270852	1.152449	-1.222549
3	6	0	3.024124	-0.125805	-0.817418
4	6	0	2.167217	-1.327829	-1.238783
5	6	0	0.931036	-1.455073	-0.716758
6	6	0	2.025099	-0.102611	1.429469
7	6	0	2.067708	-0.109806	2.819631
8	6	0	3.303623	-0.164149	3.472527
9	6	0	4.483298	-0.208795	2.731604
10	6	0	4.439928	-0.198958	1.333470
11	6	0	3.210068	-0.145851	0.684298
12	15	0	0.505000	-0.022504	0.390396
13	1	0	3.998269	-0.162445	-1.317980
14	1	0	1.138229	-0.071676	3.382723
15	1	0	3.343588	-0.170968	4.559708
16	1	0	5.444067	-0.250838	3.240691
17	1	0	5.363025	-0.231700	0.756517
18	14	0	-0.274506	-2.883383	-1.103277
19	6	0	-0.904842	-2.700348	-2.871296
20	6	0	-1.705761	-2.990743	0.108326
21	6	0	0.662297	-4.537667	-0.894516
22	14	0	-0.025071	2.921685	-1.044547
23	6	0	-0.752239	2.875181	-2.779399
24	6	0	1.133545	4.447660	-0.886418
25	6	0	-1.321230	3.303480	0.276532
26	1	0	0.028582	2.809423	-3.548558
27	1	0	-1.417951	2.000982	-2.870693
28	1	0	-1.331061	3.788960	-2.973102

[1] Gaussian 03, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.

29	1	0	1.919674	4.527857	-1.644153
30	1	0	1.620224	4.464665	0.097795
31	1	0	0.521049	5.356912	-0.960757
32	1	0	-1.583222	4.369470	0.224042
33	1	0	-0.947559	3.098275	1.287562
34	1	0	-2.213376	2.696609	0.111068
35	1	0	-1.370176	-2.889314	1.147944
36	1	0	-2.177298	-3.978585	0.001750
37	1	0	-2.465235	-2.221015	-0.107256
38	1	0	-1.447598	-1.749952	-2.979853
39	1	0	-0.092254	-2.719928	-3.608556
40	1	0	-1.599926	-3.514668	-3.114660
41	1	0	1.072780	-4.618466	0.120151
42	1	0	-0.052786	-5.361320	-1.023465
43	1	0	1.483736	-4.706318	-1.598807
44	46	0	-1.633747	0.120589	1.203102
45	6	0	-3.686480	0.557454	1.947959
46	6	0	-3.051836	-0.402401	2.740789
47	6	0	-1.800833	-0.118552	3.357670
48	1	0	-1.277283	-0.922797	3.870455
49	1	0	-1.609671	0.880590	3.750426
50	1	0	-3.356532	-1.443138	2.632148
51	1	0	-4.443578	0.265579	1.229321
52	1	0	-3.563810	1.619539	2.157080
53	6	0	-2.802754	-0.002937	-1.516419
54	8	0	-3.664338	-0.658183	-0.873380
55	8	0	-1.723746	0.513648	-0.808098
56	8	0	-2.760922	0.247959	-2.745738
57	6	0	2.821474	-2.222628	-2.253514
58	1	0	3.186959	-1.624075	-3.099546
59	1	0	3.697048	-2.731089	-1.823635
60	1	0	2.143913	-2.979306	-2.650352
61	6	0	2.992422	1.983255	-2.246873
62	1	0	3.894806	2.445826	-1.820313
63	1	0	3.325883	1.344867	-3.076951
64	1	0	2.366727	2.771203	-2.665934

Full mass-weighted force constant matrix:
Low frequencies --- -1.7717 -0.0007 0.0003 0.0006 7.4481 11.6916
Low frequencies --- 34.6488 42.6617 47.1853

	1	2	3
	A	A	A
Frequencies --	34.5770	42.6361	47.0456
Red. masses --	4.7177	4.6761	4.0209
Frc consts --	0.0033	0.0050	0.0052
IR Inten --	2.2683	1.2155	1.1508

Sum of electronic and zero-point Energies= -2168.762082
Sum of electronic and thermal Energies= -2168.724429
Sum of electronic and thermal Enthalpies= -2168.723485
Sum of electronic and thermal Free Energies= -2168.829426

Electronic energy of κ^1-carbonate isomer of complex 2 determined at the M06-2X/Basis2//B3PW91/Basis1 level.

SCF Done: E(RM062X) = -2169.49981558

Cartesian coordinates, three lowest frequencies and thermochemistry of κ^2-carbonate isomer of complex 2 determined at the B3PW91/Basis1 level.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.168288	-1.596773	3.398048
2	6	0	-1.815801	-1.417601	3.680062
3	6	0	-0.937784	-0.945646	2.696665
4	6	0	-1.446092	-0.654887	1.433491
5	6	0	-2.800778	-0.847760	1.138744
6	6	0	-3.666826	-1.316746	2.120804
7	1	0	-4.722155	-1.467045	1.896748
8	1	0	-1.431097	-1.653674	4.669573
9	1	0	-3.842144	-1.964900	4.169273
10	1	0	0.131779	-0.847065	2.879379
11	6	0	-3.220621	-0.526733	-0.287103
12	15	0	-0.462566	-0.016808	0.005854
13	6	0	-2.410788	-1.411348	-1.241949
14	6	0	-1.066797	-1.316878	-1.206145
15	6	0	-2.916944	0.944166	-0.565321
16	6	0	-1.650333	1.380006	-0.400906
17	1	0	-4.291692	-0.719855	-0.415361
18	14	0	0.244437	-2.504478	-1.908608
19	14	0	-1.126736	3.201866	-0.256273
20	6	0	1.559389	-1.584727	-2.895626
21	1	0	2.133873	-0.930206	-2.233384
22	1	0	2.251603	-2.304562	-3.351388
23	1	0	1.126071	-0.973689	-3.696620
24	6	0	-0.454596	-3.825931	-3.092464
25	1	0	0.395477	-4.442686	-3.415186
26	1	0	-1.176955	-4.499971	-2.618298
27	1	0	-0.907460	-3.406941	-3.999261
28	6	0	1.006214	-3.433848	-0.455482
29	1	0	0.265418	-4.094885	0.012611
30	1	0	1.836376	-4.059432	-0.810279
31	1	0	1.399789	-2.764437	0.322104
32	6	0	-0.488456	3.892254	-1.898889
33	1	0	-1.276810	3.851438	-2.661402
34	1	0	-0.192112	4.942738	-1.781280
35	1	0	0.376554	3.337894	-2.272829
36	6	0	-2.575543	4.329862	0.265736
37	1	0	-3.205304	3.866571	1.034186
38	1	0	-2.141757	5.238262	0.704913
39	1	0	-3.221674	4.649421	-0.559523
40	6	0	0.103904	3.366295	1.164764
41	1	0	0.584762	4.352970	1.141538
42	1	0	-0.426980	3.276343	2.121206
43	1	0	0.887476	2.600904	1.146892
44	6	0	-4.117507	1.747223	-0.979927
45	1	0	-3.867083	2.764675	-1.279305
46	1	0	-4.612894	1.256830	-1.829793
47	1	0	-4.859098	1.795274	-0.169552
48	6	0	-3.260849	-2.327023	-2.075826
49	1	0	-3.816830	-3.024628	-1.432394
50	1	0	-4.012901	-1.744070	-2.626621
51	1	0	-2.686272	-2.905793	-2.796296
52	46	0	1.773219	0.166734	0.354469
53	6	0	2.169640	1.547155	-1.182968
54	8	0	3.676415	-0.041685	1.070879
55	6	0	3.586318	1.471623	-1.586694
56	1	0	1.504414	1.327310	-2.028913

57	1	0	1.935920	2.544811	-0.794834
58	6	0	3.315824	-0.909485	2.012572
59	6	0	4.535215	2.384754	-1.330889
60	1	0	3.886252	0.574085	-2.132777
61	8	0	2.006645	-1.169759	1.962281
62	8	0	4.084730	-1.409706	2.823508
63	1	0	5.571180	2.232869	-1.625853
64	1	0	4.313580	3.291878	-0.769869

Full mass-weighted force constant matrix:
Low frequencies --- -10.7925 -5.9393 -0.0013 -0.0009 0.0003 6.5199
Low frequencies --- 21.5948 26.9953 37.7438

	1	2	3
	A	A	A
Frequencies --	21.5886	26.7194	37.6649
Red. masses --	4.8026	4.0921	3.7735
Frc consts --	0.0013	0.0017	0.0032
IR Inten --	1.2859	1.1346	0.3675

Sum of electronic and zero-point Energies= -2168.773504
Sum of electronic and thermal Energies= -2168.735672
Sum of electronic and thermal Enthalpies= -2168.734728
Sum of electronic and thermal Free Energies= -2168.842635

Electronic energy of κ^2-carbonate isomer of complex 2 determined at the M06-2X/Basis2//B3PW91/Basis1 level.

SCF Done: E(RM062X) = -2169.49873788

Cartesian coordinates, three lowest frequencies and thermochemistry of LPd(allyl)$^+$ complex determined at the B3PW91/Basis1 level.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.964166	-0.039409	3.822398
2	6	0	1.596641	-0.078755	4.086350
3	6	0	0.679289	-0.062040	3.032145
4	6	0	1.149999	-0.002442	1.724432
5	6	0	2.523130	0.024436	1.455581
6	6	0	3.434095	0.009056	2.506360
7	1	0	4.503053	0.030824	2.308359
8	1	0	1.241910	-0.124400	5.112041
9	1	0	3.674086	-0.051645	4.644632
10	1	0	-0.387942	-0.105762	3.233908
11	6	0	2.905216	0.058337	-0.016681
12	15	0	0.163644	0.018829	0.188637
13	6	0	2.292832	1.321166	-0.648776
14	6	0	0.948348	1.462296	-0.662826
15	6	0	2.333949	-1.192568	-0.699630
16	6	0	0.995545	-1.371607	-0.695673
17	1	0	3.993471	0.079907	-0.121511
18	14	0	-0.109744	2.845416	-1.433435
19	14	0	0.011173	-2.799303	-1.448870
20	46	0	-2.148670	-0.327102	0.438581
21	6	0	-3.647063	0.245053	1.922560
22	1	0	-3.594482	-0.309848	2.857585
23	6	0	-2.710252	1.290897	1.660277
24	6	0	-4.375480	-0.266208	0.852913

25	1	0	-2.019132	1.597121	2.440626
26	1	0	-4.934688	-1.191545	0.958417
27	1	0	-2.965410	2.064891	0.937440
28	1	0	-4.625054	0.358339	-0.004227
29	6	0	-1.802741	-2.377869	-1.044858
30	1	0	-2.073214	-1.402449	-1.501051
31	1	0	-2.540650	-3.089864	-1.430082
32	1	0	-1.935043	-2.409058	0.061423
33	6	0	0.427999	-4.444265	-0.632935
34	1	0	-0.221046	-5.239711	-1.019003
35	1	0	1.463181	-4.748328	-0.822367
36	1	0	0.293620	-4.397742	0.453866
37	6	0	0.212931	-2.872926	-3.319497
38	1	0	-0.438155	-3.646070	-3.745183
39	1	0	-0.046350	-1.918538	-3.791708
40	1	0	1.240731	-3.116409	-3.610466
41	6	0	-1.641584	2.040142	-2.201019
42	1	0	-2.290998	2.813247	-2.630423
43	1	0	-1.361881	1.361862	-3.016450
44	1	0	-2.243071	1.470162	-1.480847
45	6	0	-0.593649	4.075565	-0.085647
46	1	0	0.292169	4.598146	0.293842
47	1	0	-1.280133	4.834917	-0.479667
48	1	0	-1.078033	3.597955	0.772698
49	6	0	0.755119	3.766925	-2.837514
50	1	0	1.277066	3.094389	-3.526986
51	1	0	-0.011903	4.295101	-3.418220
52	1	0	1.465647	4.524515	-2.490819
53	6	0	3.311045	2.294606	-1.161205
54	1	0	3.998112	2.568185	-0.349182
55	1	0	3.923313	1.835267	-1.948721
56	1	0	2.870260	3.208304	-1.556086
57	6	0	3.351570	-2.116320	-1.296980
58	1	0	2.906585	-2.998892	-1.761239
59	1	0	3.947067	-1.593355	-2.056971
60	1	0	4.054450	-2.455277	-0.524296

Full mass-weighted force constant matrix:
Low frequencies --- -0.0016 -0.0015 -0.0004 3.1444 6.8777 10.1800
Low frequencies --- 31.6021 40.4882 46.6912

	1	2	3
	A	A	A
Frequencies --	31.5570	40.4757	46.6734
Red. masses --	3.5914	3.9809	3.2048
Frc consts --	0.0021	0.0038	0.0041
IR Inten --	0.0696	0.0470	0.0897

Sum of electronic and zero-point Energies= -1904.853752
Sum of electronic and thermal Energies= -1904.820303
Sum of electronic and thermal Enthalpies= -1904.819359
Sum of electronic and thermal Free Energies= -1904.916411