Phosphido Pincer Complexes of Platinum: Synthesis, Structure and Reactivity

Mina Mazzeo[a]*, Maria Strianese[a], Olaf Kühl[b] and Jonas C. Peters[c]*

[a] Department of Chemistry and Biology, University of Salerno, I-84084 Via Ponte don Melillo, Fisciano, Salerno, Italy;[b] Bioinorganic Research Group, Institute for Biochemistry, University of Greifswald, Felix-Hausdorff-Str. 4, 17489 Greifswald, Germany;[c] Division of Chemistry and Chemical Engineering, Arnold and Mabel Beckman Laboratories of Chemical Synthesis, California Institute of Technology, Pasadena, California 91125

Supporting Information

I. Experimental details for crystal structure determination

Spatial refinement details.

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles, and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Crystals for X-ray analysis of complex **1** were obtained via vapor diffusion of petroleum ether into a THF solution.
Single crystals of **3** were obtained via slow evaporation of a petroleum ether solution of the complex. X-ray diffraction studies were carried out in the Beckman Institute Crystallographic Facility on a Bruker Smart 1000 CCD diffractometer.

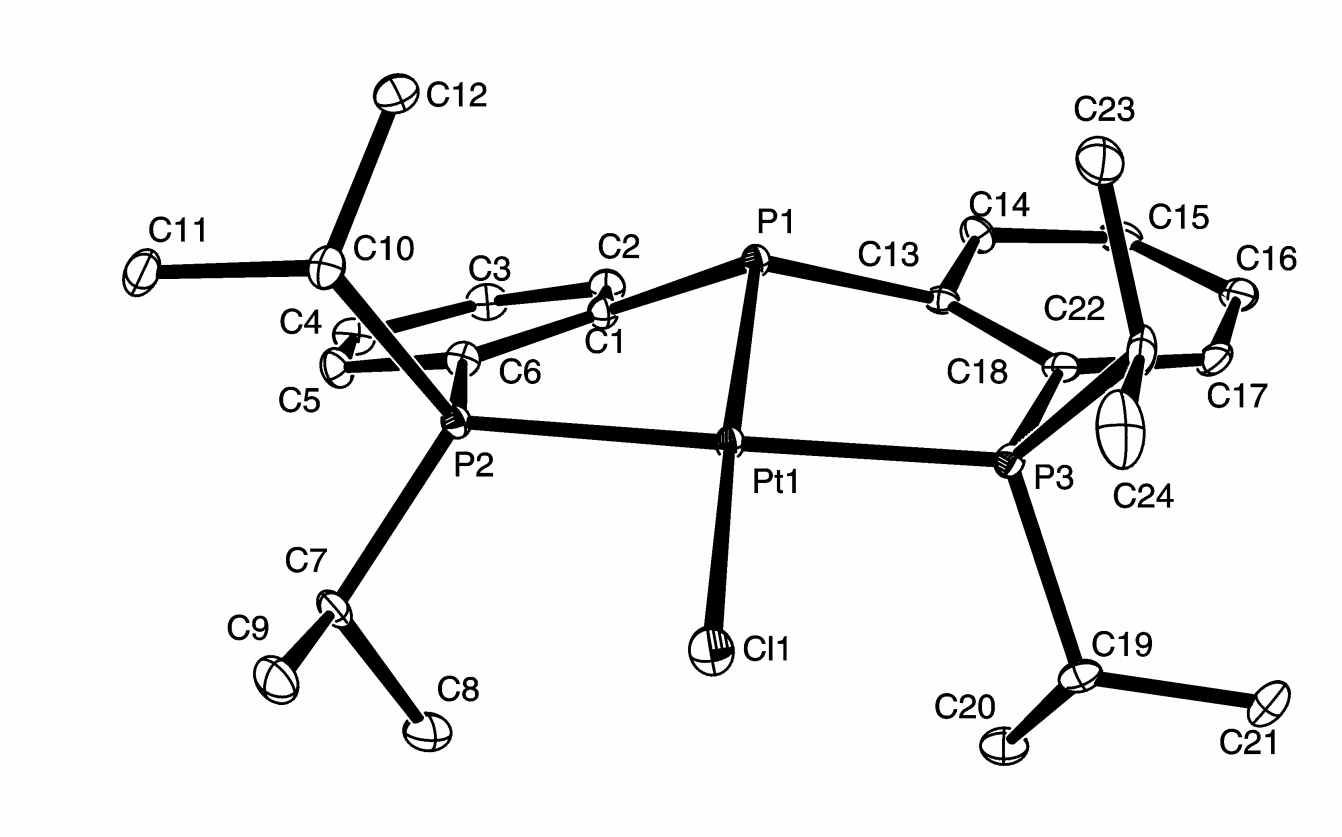

Figure S1. ORTEP diagram of complex **1** [^{i}Pr-PPP]PtCl with thermal ellipsoids drawn at 30% probability level. The crystal structure of **1** contains two independent molecules in the asymmetric unit. Hydrogen atoms are omitted for clarity.

Table S1. Crystal data and structure refinement for **1** [^{i}Pr-PPP]-Pt(Cl).

Identification code	mm02a	
Empirical formula	C24 H36 Cl P3 Pt	
Formula weight	647.98	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	P 1 21/c 1 (14)	
Space group	monoclinic	
Unit cell dimensions	a = 11.612(2) Å	α= 90°.
	b = 14.046(2) Å	β= 92.196(17)°.
	c = 30.941(5) Å	γ = 90°.
Volume	5042.7(14) Å^3	
Z	8	
Density (calculated)	1.707 Mg/m^3	
Absorption coefficient	5.871 mm^{-1}	
F(000)	2560	
Crystal size	? x ? x ? mm^3	
Theta range for data collection	1.59 to 36.17°.	
Index ranges	-19<=h<=18, -20<=k<=22, -41<=l<=46	
Reflections collected	89412	
Independent reflections	21280 [R(int) = 0.0712]	
Completeness to theta = 36.17°	87.9 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	21280 / 0 / 539	
Goodness-of-fit on F^2	1.504	
Final R indices [I>2sigma(I)]	R1 = 0.0551, wR2 = 0.0881	
R indices (all data)	R1 = 0.0792, wR2 = 0.0925	
Largest diff. peak and hole	3.982 and -6.829 e.Å^{-3}	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **1** [^{i}Pr-PPP]-Pt(Cl). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pt(1)	5574(1)	3234(1)	1011(1)	11(1)
P(1)	4752(1)	4485(1)	1339(1)	11(1)
P(2)	7067(1)	4282(1)	899(1)	11(1)
P(3)	4094(1)	2354(1)	1268(1)	12(1)
Cl(1)	6338(1)	1886(1)	645(1)	21(1)
C(1)	5984(3)	5131(3)	1586(1)	13(1)
C(2)	5965(4)	5710(3)	1950(2)	18(1)
C(3)	6880(4)	6309(3)	2062(2)	19(1)
C(4)	7825(4)	6368(3)	1805(2)	20(1)
C(5)	7884(3)	5782(3)	1449(2)	18(1)
C(6)	6981(3)	5145(3)	1337(1)	15(1)
C(7)	8550(3)	3823(3)	958(2)	17(1)
C(8)	8702(4)	3266(4)	1381(2)	28(1)
C(9)	8886(4)	3224(3)	565(2)	25(1)
C(10)	7008(3)	4965(3)	390(1)	16(1)
C(11)	8076(4)	5566(3)	310(2)	23(1)
C(12)	5935(4)	5602(3)	371(2)	24(1)
C(13)	3854(3)	3977(3)	1757(1)	12(1)
C(14)	3349(3)	4547(3)	2076(1)	16(1)
C(15)	2468(4)	4183(3)	2321(2)	21(1)
C(16)	2017(4)	3275(3)	2238(2)	21(1)
C(17)	2488(4)	2721(3)	1921(2)	18(1)
C(18)	3429(3)	3052(3)	1689(1)	15(1)
C(19)	4609(4)	1226(3)	1514(1)	15(1)
C(20)	5426(4)	1456(3)	1899(2)	21(1)
C(21)	3672(4)	522(3)	1647(2)	23(1)
C(22)	2902(4)	2056(3)	884(2)	20(1)
C(23)	2357(4)	2967(4)	711(2)	32(1)
C(24)	3318(4)	1416(4)	523(2)	32(1)
Pt(2)	126(1)	8226(1)	1096(1)	10(1)
P(4)	402(1)	8451(1)	1812(1)	13(1)

P(5)	1849(1)	7431(1)	1130(1)	13(1)
P(6)	-1240(1)	9407(1)	1126(1)	10(1)
Cl(2)	-241(1)	7815(1)	351(1)	16(1)
C(25)	1966(3)	8348(3)	1925(1)	13(1)
C(26)	2506(3)	8615(3)	2315(1)	16(1)
C(27)	3667(3)	8413(3)	2405(1)	17(1)
C(28)	4286(3)	7902(3)	2112(2)	19(1)
C(29)	3759(3)	7584(3)	1733(2)	19(1)
C(30)	2602(3)	7820(3)	1627(1)	14(1)
C(31)	1830(4)	6130(3)	1168(2)	20(1)
C(32)	1179(4)	5824(3)	1561(2)	22(1)
C(33)	1281(4)	5695(3)	753(2)	22(1)
C(34)	2727(3)	7733(3)	664(1)	16(1)
C(35)	3788(4)	7109(3)	594(2)	22(1)
C(36)	3061(4)	8786(3)	673(2)	20(1)
C(37)	-61(3)	9683(3)	1914(1)	13(1)
C(38)	274(4)	10246(3)	2273(1)	18(1)
C(39)	-282(4)	11100(3)	2358(1)	18(1)
C(40)	-1214(4)	11388(3)	2103(1)	17(1)
C(41)	-1540(3)	10857(3)	1740(1)	15(1)
C(42)	-958(3)	10029(3)	1638(1)	12(1)
C(43)	-2801(3)	9158(3)	1082(1)	13(1)
C(44)	-3047(4)	8364(4)	751(2)	27(1)
C(45)	-3303(4)	8889(3)	1514(2)	23(1)
C(46)	-1017(3)	10399(3)	744(1)	13(1)
C(47)	-1444(4)	10188(3)	283(1)	18(1)
C(48)	242(3)	10706(3)	764(2)	17(1)

Table S3. Bond lengths [Å] and angles [°] for **1** [^{i}Pr-PPP]-Pt(Cl).

Pt(1)-P(1)	2.2573(11)
Pt(1)-P(3)	2.2842(11)
Pt(1)-P(2)	2.3107(10)
Pt(1)-Cl(1)	2.3963(10)
P(1)-C(1)	1.837(4)
P(1)-C(13)	1.837(4)
P(2)-C(6)	1.824(4)
P(2)-C(7)	1.842(4)
P(2)-C(10)	1.843(4)
P(3)-C(18)	1.825(4)
P(3)-C(22)	1.837(4)
P(3)-C(19)	1.847(4)
C(1)-C(2)	1.389(6)
C(1)-C(6)	1.415(6)
C(2)-C(3)	1.389(6)
C(2)-H(2)	0.9500
C(3)-C(4)	1.384(7)
C(3)-H(3)	0.9500
C(4)-C(5)	1.379(6)
C(4)-H(4)	0.9500
C(5)-C(6)	1.410(5)
C(5)-H(5)	0.9500
C(7)-C(8)	1.531(6)
C(7)-C(9)	1.539(6)
C(7)-H(7)	1.0000
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-C(11)	1.528(6)
C(10)-C(12)	1.533(6)
C(10)-H(10)	1.0000

C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-C(18)	1.404(6)
C(13)-C(14)	1.414(6)
C(14)-C(15)	1.393(6)
C(14)-H(14)	0.9500
C(15)-C(16)	1.399(6)
C(15)-H(15)	0.9500
C(16)-C(17)	1.382(6)
C(16)-H(16)	0.9500
C(17)-C(18)	1.410(6)
C(17)-H(17)	0.9500
C(19)-C(20)	1.528(6)
C(19)-C(21)	1.537(6)
C(19)-H(19)	1.0000
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-C(23)	1.517(6)
C(22)-C(24)	1.528(7)
C(22)-H(22)	1.0000
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
Pt(2)-P(4)	2.2485(11)
Pt(2)-P(5)	2.2906(10)

Pt(2)-P(6)	2.2993(10)
Pt(2)-Cl(2)	2.3987(11)
P(4)-C(25)	1.842(4)
P(4)-C(37)	1.843(4)
P(5)-C(30)	1.823(4)
P(5)-C(31)	1.832(4)
P(5)-C(34)	1.846(4)
P(6)-C(42)	1.826(4)
P(6)-C(43)	1.846(4)
P(6)-C(46)	1.852(4)
C(25)-C(26)	1.391(6)
C(25)-C(30)	1.413(6)
C(26)-C(27)	1.395(6)
C(26)-H(26)	0.9500
C(27)-C(28)	1.380(6)
C(27)-H(27)	0.9500
C(28)-C(29)	1.376(6)
C(28)-H(28)	0.9500
C(29)-C(30)	1.411(5)
C(29)-H(29)	0.9500
C(31)-C(32)	1.518(6)
C(31)-C(33)	1.539(6)
C(31)-H(31)	1.0000
C(32)-H(32A)	0.9800
C(32)-H(32B)	0.9800
C(32)-H(32C)	0.9800
C(33)-H(33A)	0.9800
C(33)-H(33B)	0.9800
C(33)-H(33C)	0.9800
C(34)-C(36)	1.530(6)
C(34)-C(35)	1.533(6)
C(34)-H(34)	1.0000
C(35)-H(35A)	0.9800
C(35)-H(35B)	0.9800
C(35)-H(35C)	0.9800
C(36)-H(36A)	0.9800

C(36)-H(36B)	0.9800
C(36)-H(36C)	0.9800
C(37)-C(38)	1.407(6)
C(37)-C(42)	1.408(5)
C(38)-C(39)	1.392(6)
C(38)-H(38)	0.9500
C(39)-C(40)	1.377(6)
C(39)-H(39)	0.9500
C(40)-C(41)	1.389(6)
C(40)-H(40)	0.9500
C(41)-C(42)	1.387(6)
C(41)-H(41)	0.9500
C(43)-C(45)	1.526(6)
C(43)-C(44)	1.535(6)
C(43)-H(43)	1.0000
C(44)-H(44A)	0.9800
C(44)-H(44B)	0.9800
C(44)-H(44C)	0.9800
C(45)-H(45A)	0.9800
C(45)-H(45B)	0.9800
C(45)-H(45C)	0.9800
C(46)-C(47)	1.521(6)
C(46)-C(48)	1.523(5)
C(46)-H(46)	1.0000
C(47)-H(47A)	0.9800
C(47)-H(47B)	0.9800
C(47)-H(47C)	0.9800
C(48)-H(48A)	0.9800
C(48)-H(48B)	0.9800
C(48)-H(48C)	0.9800
P(1)-Pt(1)-P(3)	85.92(4)
P(1)-Pt(1)-P(2)	84.52(4)
P(3)-Pt(1)-P(2)	167.42(4)
P(1)-Pt(1)-Cl(1)	176.64(4)
P(3)-Pt(1)-Cl(1)	91.92(4)
P(2)-Pt(1)-Cl(1)	97.97(4)

C(1)-P(1)-C(13)	110.59(19)
C(1)-P(1)-Pt(1)	103.61(13)
C(13)-P(1)-Pt(1)	106.00(13)
C(6)-P(2)-C(7)	103.71(19)
C(6)-P(2)-C(10)	106.73(19)
C(7)-P(2)-C(10)	105.7(2)
C(6)-P(2)-Pt(1)	104.42(14)
C(7)-P(2)-Pt(1)	117.80(14)
C(10)-P(2)-Pt(1)	117.17(13)
C(18)-P(3)-C(22)	104.7(2)
C(18)-P(3)-C(19)	107.80(19)
C(22)-P(3)-C(19)	107.20(19)
C(18)-P(3)-Pt(1)	107.54(14)
C(22)-P(3)-Pt(1)	117.19(15)
C(19)-P(3)-Pt(1)	111.84(14)
C(2)-C(1)-C(6)	118.1(3)
C(2)-C(1)-P(1)	126.2(3)
C(6)-C(1)-P(1)	114.9(3)
C(1)-C(2)-C(3)	121.5(4)
C(1)-C(2)-H(2)	119.3
C(3)-C(2)-H(2)	119.3
C(4)-C(3)-C(2)	120.5(4)
C(4)-C(3)-H(3)	119.7
C(2)-C(3)-H(3)	119.7
C(5)-C(4)-C(3)	119.2(4)
C(5)-C(4)-H(4)	120.4
C(3)-C(4)-H(4)	120.4
C(4)-C(5)-C(6)	121.1(4)
C(4)-C(5)-H(5)	119.5
C(6)-C(5)-H(5)	119.5
C(5)-C(6)-C(1)	119.4(4)
C(5)-C(6)-P(2)	122.8(3)
C(1)-C(6)-P(2)	117.6(3)
C(8)-C(7)-C(9)	111.8(4)
C(8)-C(7)-P(2)	109.9(3)
C(9)-C(7)-P(2)	112.2(3)

C(8)-C(7)-H(7)	107.6
C(9)-C(7)-H(7)	107.6
P(2)-C(7)-H(7)	107.6
C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(7)-C(9)-H(9A)	109.5
C(7)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(7)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(11)-C(10)-C(12)	109.5(4)
C(11)-C(10)-P(2)	115.0(3)
C(12)-C(10)-P(2)	109.9(3)
C(11)-C(10)-H(10)	107.4
C(12)-C(10)-H(10)	107.4
P(2)-C(10)-H(10)	107.4
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(10)-C(12)-H(12A)	109.5
C(10)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(10)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(18)-C(13)-C(14)	118.4(4)
C(18)-C(13)-P(1)	117.3(3)
C(14)-C(13)-P(1)	122.3(3)

C(15)-C(14)-C(13)	120.3(4)
C(15)-C(14)-H(14)	119.8
C(13)-C(14)-H(14)	119.8
C(14)-C(15)-C(16)	120.8(4)
C(14)-C(15)-H(15)	119.6
C(16)-C(15)-H(15)	119.6
C(17)-C(16)-C(15)	119.2(4)
C(17)-C(16)-H(16)	120.4
C(15)-C(16)-H(16)	120.4
C(16)-C(17)-C(18)	120.8(4)
C(16)-C(17)-H(17)	119.6
C(18)-C(17)-H(17)	119.6
C(13)-C(18)-C(17)	120.2(4)
C(13)-C(18)-P(3)	116.7(3)
C(17)-C(18)-P(3)	122.9(3)
C(20)-C(19)-C(21)	110.7(4)
C(20)-C(19)-P(3)	108.8(3)
C(21)-C(19)-P(3)	116.1(3)
C(20)-C(19)-H(19)	106.9
C(21)-C(19)-H(19)	106.9
P(3)-C(19)-H(19)	106.9
C(19)-C(20)-H(20A)	109.5
C(19)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(19)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(19)-C(21)-H(21A)	109.5
C(19)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(19)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(23)-C(22)-C(24)	112.1(4)
C(23)-C(22)-P(3)	109.3(3)
C(24)-C(22)-P(3)	110.8(3)

C(23)-C(22)-H(22)	108.2
C(24)-C(22)-H(22)	108.2
P(3)-C(22)-H(22)	108.2
C(22)-C(23)-H(23A)	109.5
C(22)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(22)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(22)-C(24)-H(24A)	109.5
C(22)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
C(22)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
P(4)-Pt(2)-P(5)	86.07(4)
P(4)-Pt(2)-P(6)	86.02(4)
P(5)-Pt(2)-P(6)	162.27(4)
P(4)-Pt(2)-Cl(2)	173.72(4)
P(5)-Pt(2)-Cl(2)	92.84(4)
P(6)-Pt(2)-Cl(2)	96.68(4)
C(25)-P(4)-C(37)	109.42(18)
C(25)-P(4)-Pt(2)	106.17(14)
C(37)-P(4)-Pt(2)	105.60(13)
C(30)-P(5)-C(31)	104.53(19)
C(30)-P(5)-C(34)	109.17(19)
C(31)-P(5)-C(34)	106.7(2)
C(30)-P(5)-Pt(2)	106.43(13)
C(31)-P(5)-Pt(2)	118.45(14)
C(34)-P(5)-Pt(2)	111.09(13)
C(42)-P(6)-C(43)	107.29(18)
C(42)-P(6)-C(46)	99.77(18)
C(43)-P(6)-C(46)	104.84(18)
C(42)-P(6)-Pt(2)	106.25(13)
C(43)-P(6)-Pt(2)	122.49(14)
C(46)-P(6)-Pt(2)	113.73(13)

C(26)-C(25)-C(30)	118.6(3)
C(26)-C(25)-P(4)	123.5(3)
C(30)-C(25)-P(4)	116.9(3)
C(25)-C(26)-C(27)	121.3(4)
C(25)-C(26)-H(26)	119.4
C(27)-C(26)-H(26)	119.4
C(28)-C(27)-C(26)	119.8(4)
C(28)-C(27)-H(27)	120.1
C(26)-C(27)-H(27)	120.1
C(29)-C(28)-C(27)	120.3(4)
C(29)-C(28)-H(28)	119.9
C(27)-C(28)-H(28)	119.9
C(28)-C(29)-C(30)	120.7(4)
C(28)-C(29)-H(29)	119.7
C(30)-C(29)-H(29)	119.7
C(29)-C(30)-C(25)	119.2(4)
C(29)-C(30)-P(5)	123.2(3)
C(25)-C(30)-P(5)	117.5(3)
C(32)-C(31)-C(33)	110.8(4)
C(32)-C(31)-P(5)	110.0(3)
C(33)-C(31)-P(5)	110.3(3)
C(32)-C(31)-H(31)	108.6
C(33)-C(31)-H(31)	108.6
P(5)-C(31)-H(31)	108.6
C(31)-C(32)-H(32A)	109.5
C(31)-C(32)-H(32B)	109.5
H(32A)-C(32)-H(32B)	109.5
C(31)-C(32)-H(32C)	109.5
H(32A)-C(32)-H(32C)	109.5
H(32B)-C(32)-H(32C)	109.5
C(31)-C(33)-H(33A)	109.5
C(31)-C(33)-H(33B)	109.5
H(33A)-C(33)-H(33B)	109.5
C(31)-C(33)-H(33C)	109.5
H(33A)-C(33)-H(33C)	109.5
H(33B)-C(33)-H(33C)	109.5

C(36)-C(34)-C(35)	110.5(3)
C(36)-C(34)-P(5)	110.8(3)
C(35)-C(34)-P(5)	116.8(3)
C(36)-C(34)-H(34)	106.0
C(35)-C(34)-H(34)	106.0
P(5)-C(34)-H(34)	106.0
C(34)-C(35)-H(35A)	109.5
C(34)-C(35)-H(35B)	109.5
H(35A)-C(35)-H(35B)	109.5
C(34)-C(35)-H(35C)	109.5
H(35A)-C(35)-H(35C)	109.5
H(35B)-C(35)-H(35C)	109.5
C(34)-C(36)-H(36A)	109.5
C(34)-C(36)-H(36B)	109.5
H(36A)-C(36)-H(36B)	109.5
C(34)-C(36)-H(36C)	109.5
H(36A)-C(36)-H(36C)	109.5
H(36B)-C(36)-H(36C)	109.5
C(38)-C(37)-C(42)	117.4(4)
C(38)-C(37)-P(4)	126.1(3)
C(42)-C(37)-P(4)	115.7(3)
C(39)-C(38)-C(37)	121.2(4)
C(39)-C(38)-H(38)	119.4
C(37)-C(38)-H(38)	119.4
C(40)-C(39)-C(38)	120.3(4)
C(40)-C(39)-H(39)	119.9
C(38)-C(39)-H(39)	119.9
C(39)-C(40)-C(41)	119.4(4)
C(39)-C(40)-H(40)	120.3
C(41)-C(40)-H(40)	120.3
C(42)-C(41)-C(40)	120.9(4)
C(42)-C(41)-H(41)	119.5
C(40)-C(41)-H(41)	119.5
C(41)-C(42)-C(37)	120.5(4)
C(41)-C(42)-P(6)	121.7(3)
C(37)-C(42)-P(6)	117.7(3)

C(45)-C(43)-C(44)	109.8(4)
C(45)-C(43)-P(6)	112.9(3)
C(44)-C(43)-P(6)	110.1(3)
C(45)-C(43)-H(43)	108.0
C(44)-C(43)-H(43)	108.0
P(6)-C(43)-H(43)	108.0
C(43)-C(44)-H(44A)	109.5
C(43)-C(44)-H(44B)	109.5
H(44A)-C(44)-H(44B)	109.5
C(43)-C(44)-H(44C)	109.5
H(44A)-C(44)-H(44C)	109.5
H(44B)-C(44)-H(44C)	109.5
C(43)-C(45)-H(45A)	109.5
C(43)-C(45)-H(45B)	109.5
H(45A)-C(45)-H(45B)	109.5
C(43)-C(45)-H(45C)	109.5
H(45A)-C(45)-H(45C)	109.5
H(45B)-C(45)-H(45C)	109.5
C(47)-C(46)-C(48)	111.8(3)
C(47)-C(46)-P(6)	113.9(3)
C(48)-C(46)-P(6)	110.1(3)
C(47)-C(46)-H(46)	106.9
C(48)-C(46)-H(46)	106.9
P(6)-C(46)-H(46)	106.9
C(46)-C(47)-H(47A)	109.5
C(46)-C(47)-H(47B)	109.5
H(47A)-C(47)-H(47B)	109.5
C(46)-C(47)-H(47C)	109.5
H(47A)-C(47)-H(47C)	109.5
H(47B)-C(47)-H(47C)	109.5
C(46)-C(48)-H(48A)	109.5
C(46)-C(48)-H(48B)	109.5
H(48A)-C(48)-H(48B)	109.5
C(46)-C(48)-H(48C)	109.5
H(48A)-C(48)-H(48C)	109.5
H(48B)-C(48)-H(48C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **1** [^{i}Pr-PPP]-Pt(Cl). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pt(1)	11(1)	10(1)	11(1)	-2(1)	2(1)	-1(1)
P(1)	11(1)	11(1)	12(1)	-1(1)	2(1)	-1(1)
P(2)	11(1)	12(1)	12(1)	-2(1)	2(1)	-1(1)
P(3)	13(1)	12(1)	11(1)	1(1)	1(1)	-2(1)
Cl(1)	22(1)	15(1)	28(1)	-9(1)	7(1)	-1(1)
C(1)	14(2)	12(2)	14(2)	-1(1)	2(1)	-1(1)
C(2)	19(2)	14(2)	19(2)	-5(2)	4(2)	1(2)
C(3)	25(2)	17(2)	15(2)	-6(2)	-2(2)	2(2)
C(4)	19(2)	17(2)	21(3)	-6(2)	-7(2)	-2(2)
C(5)	14(2)	17(2)	22(2)	-4(2)	0(2)	-4(2)
C(6)	16(2)	16(2)	12(2)	-1(1)	-1(2)	-1(1)
C(7)	9(2)	17(2)	24(2)	-3(2)	3(2)	1(1)
C(8)	23(2)	31(3)	30(3)	10(2)	-1(2)	7(2)
C(9)	20(2)	24(2)	33(3)	-3(2)	10(2)	3(2)
C(10)	18(2)	18(2)	11(2)	0(2)	1(2)	-3(2)
C(11)	23(2)	23(2)	23(3)	8(2)	3(2)	-6(2)
C(12)	22(2)	27(2)	21(3)	9(2)	-1(2)	2(2)
C(13)	13(2)	13(2)	10(2)	0(1)	0(1)	4(1)
C(14)	14(2)	19(2)	17(2)	-4(2)	3(2)	2(2)
C(15)	21(2)	24(2)	17(2)	0(2)	2(2)	8(2)
C(16)	17(2)	26(2)	19(2)	11(2)	7(2)	6(2)
C(17)	21(2)	14(2)	19(2)	7(2)	6(2)	2(2)
C(18)	16(2)	16(2)	13(2)	3(1)	3(2)	5(1)
C(19)	21(2)	10(2)	13(2)	-2(1)	2(2)	4(2)
C(20)	24(2)	21(2)	17(2)	-1(2)	-2(2)	5(2)
C(21)	30(2)	14(2)	24(3)	4(2)	4(2)	-4(2)
C(22)	18(2)	25(2)	17(2)	6(2)	-3(2)	-12(2)
C(23)	22(2)	42(3)	31(3)	17(2)	-10(2)	-6(2)
C(24)	32(2)	50(3)	14(3)	-6(2)	-2(2)	-20(2)
Pt(2)	11(1)	12(1)	9(1)	-1(1)	0(1)	3(1)
P(4)	12(1)	15(1)	10(1)	-1(1)	0(1)	3(1)

P(5)	13(1)	14(1)	11(1)	-1(1)	1(1)	3(1)
P(6)	11(1)	12(1)	8(1)	0(1)	1(1)	1(1)
Cl(2)	19(1)	18(1)	11(1)	-4(1)	0(1)	3(1)
C(25)	12(2)	15(2)	11(2)	3(1)	1(1)	2(1)
C(26)	16(2)	18(2)	13(2)	0(2)	-1(2)	1(2)
C(27)	19(2)	14(2)	16(2)	4(2)	-6(2)	0(1)
C(28)	15(2)	23(2)	17(2)	8(2)	-3(2)	2(2)
C(29)	13(2)	24(2)	18(2)	5(2)	0(2)	5(2)
C(30)	13(2)	16(2)	14(2)	2(2)	-1(2)	2(1)
C(31)	15(2)	19(2)	25(3)	-1(2)	1(2)	5(2)
C(32)	20(2)	22(2)	24(3)	8(2)	2(2)	2(2)
C(33)	25(2)	16(2)	25(3)	-3(2)	0(2)	0(2)
C(34)	13(2)	22(2)	12(2)	-1(2)	3(2)	4(2)
C(35)	19(2)	22(2)	25(3)	-1(2)	8(2)	1(2)
C(36)	20(2)	19(2)	20(2)	2(2)	1(2)	1(2)
C(37)	13(2)	16(2)	11(2)	-1(1)	4(1)	1(1)
C(38)	19(2)	23(2)	12(2)	-4(2)	-2(2)	0(2)
C(39)	23(2)	17(2)	14(2)	-6(2)	1(2)	3(2)
C(40)	24(2)	15(2)	11(2)	-2(2)	4(2)	3(2)
C(41)	20(2)	15(2)	11(2)	0(1)	4(2)	2(2)
C(42)	14(2)	14(2)	8(2)	-2(1)	0(1)	-1(1)
C(43)	13(2)	17(2)	8(2)	2(1)	-1(1)	0(1)
C(44)	19(2)	32(3)	30(3)	-11(2)	3(2)	-7(2)
C(45)	20(2)	29(3)	22(3)	2(2)	7(2)	-3(2)
C(46)	14(2)	13(2)	12(2)	1(1)	2(1)	1(1)
C(47)	22(2)	21(2)	10(2)	3(2)	-1(2)	3(2)
C(48)	17(2)	18(2)	17(2)	2(2)	4(2)	-3(2)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **1** [^{i}Pr-PPP]-Pt(Cl).

	x	y	z	U(eq)
H(2)	5312	5695	2125	21
H(3)	6856	6681	2318	23
H(4)	8427	6808	1872	23
H(5)	8542	5807	1276	21
H(7)	9081	4383	977	20
H(8A)	8150	2738	1382	42
H(8B)	8566	3690	1626	42
H(8C)	9489	3013	1408	42
H(9A)	9691	3021	603	38
H(9B)	8794	3608	302	38
H(9C)	8387	2663	541	38
H(10)	6924	4497	148	19
H(11A)	8009	5845	20	34
H(11B)	8764	5163	334	34
H(11C)	8139	6077	526	34
H(12A)	5995	6076	603	35
H(12B)	5247	5211	407	35
H(12C)	5878	5926	91	35
H(14)	3612	5180	2123	20
H(15)	2170	4557	2547	25
H(16)	1395	3042	2398	25
H(17)	2174	2109	1859	21
H(19)	5076	897	1295	18
H(20A)	4995	1762	2127	31
H(20B)	6033	1887	1806	31
H(20C)	5776	866	2011	31
H(21A)	4025	-95	1716	34
H(21B)	3103	445	1407	34
H(21C)	3291	768	1901	34
H(22)	2307	1699	1045	24
H(23A)	2949	3365	584	48
H(23B)	2008	3314	947	48
H(23C)	1762	2811	489	48
H(24A)	2654	1198	344	48
H(24B)	3722	864	649	48
H(24C)	3843	1775	343	48
H(26)	2076	8940	2525	19
H(27)	4030	8626	2668	20
H(28)	5078	7770	2172	22
H(29)	4180	7202	1541	22
H(31)	2642	5898	1203	23

H(32A)	393	6077	1539	33
H(32B)	1573	6070	1824	33
H(32C)	1151	5127	1574	33
H(33A)	1219	5004	787	33
H(33B)	1764	5839	508	33
H(33C)	512	5966	699	33
H(34)	2211	7647	401	19
H(35A)	4387	7256	815	33
H(35B)	4081	7237	307	33
H(35C)	3573	6436	614	33
H(36A)	3630	8899	910	30
H(36B)	2375	9174	718	30
H(36C)	3394	8961	398	30
H(38)	890	10039	2461	21
H(39)	-16	11486	2594	22
H(40)	-1630	11945	2174	20
H(41)	-2171	11063	1559	18
H(43)	-3200	9748	975	15
H(44A)	-2734	7761	863	40
H(44B)	-2682	8522	479	40
H(44C)	-3881	8302	698	40
H(45A)	-4127	8752	1472	35
H(45B)	-3198	9419	1718	35
H(45C)	-2906	8324	1631	35
H(46)	-1477	10950	847	15
H(47A)	-1286	10735	98	27
H(47B)	-2275	10067	278	27
H(47C)	-1045	9625	175	27
H(48A)	731	10161	697	26
H(48B)	448	10940	1055	26
H(48C)	356	11214	553	26

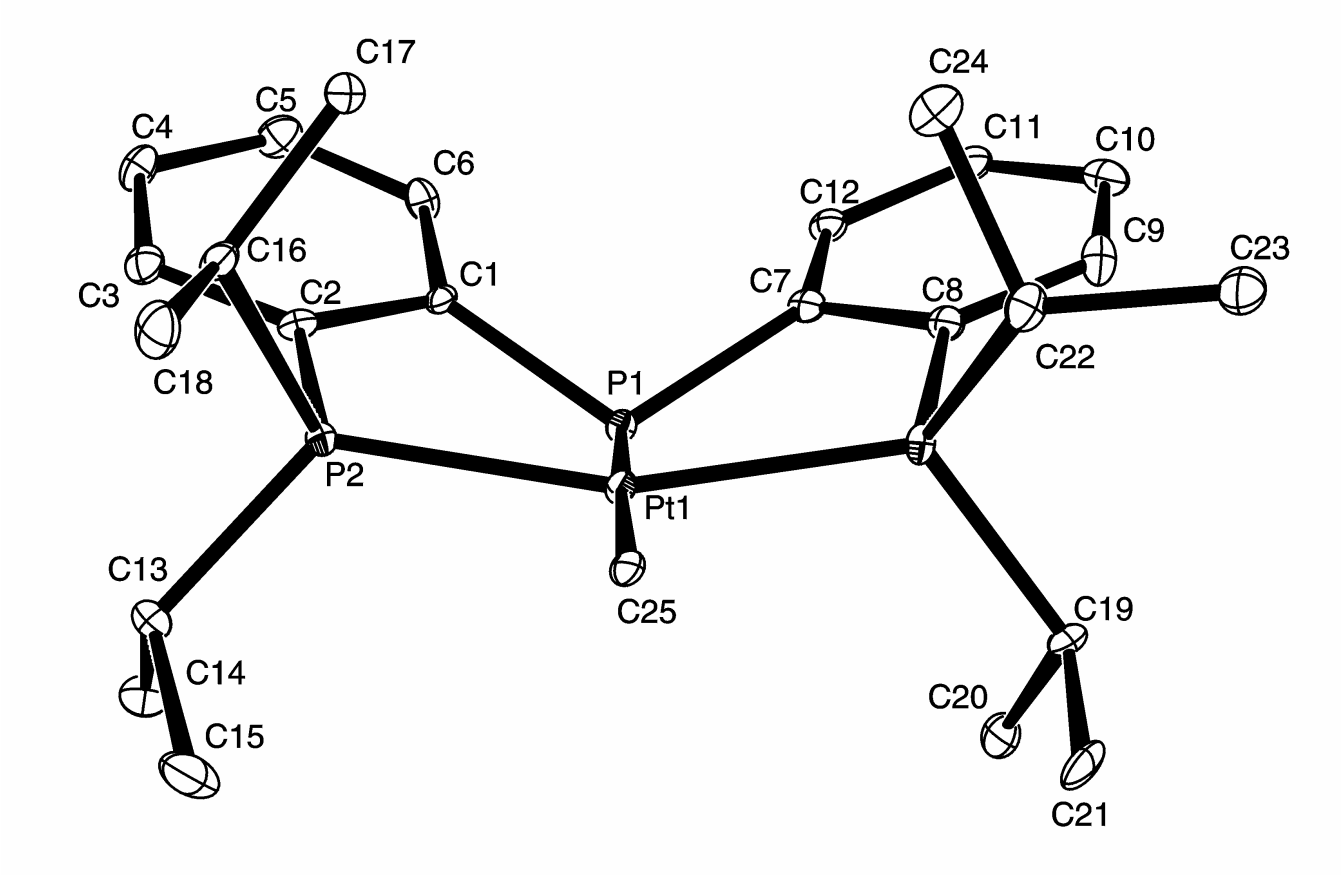

Figure S2. ORTEP diagram of complex **3** [^{i}Pr-PPP]PtCH$_3$ with thermal ellipsoids drawn at 30% probability level. The crystal structure of **3** contains two independent molecules in the asymmetric unit. Hydrogen atoms are omitted for clarity.

Table S6. Crystal data and structure refinement for 3 [^{i}Pr-PPP]-Pt(CH_3).

Identification code	mm05	
Empirical formula	C25 H39 P3 Pt	
Formula weight	627.56	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 11.7084(6) Å	α= 90°.
	b = 13.9668(7) Å	β= 91.280(2)°.
	c = 31.1141(16) Å	γ = 90°.
Volume	5086.8(4) Å^3	
Z	8	
Density (calculated)	1.639 Mg/m^3	
Absorption coefficient	5.715 mm^{-1}	
F(000)	2496	
Crystal size	? x ? x ? mm^3	
Theta range for data collection	1.60 to 42.99°.	
Index ranges	-14<=h<=20, -17<=k<=21, -41<=l<=59	
Reflections collected	56422	
Independent reflections	20231 [R(int) = 0.1043]	
Completeness to theta = 42.99°	53.8 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	20231 / 0 / 541	
Goodness-of-fit on F^2	0.872	
Final R indices [I>2sigma(I)]	R1 = 0.0529, wR2 = 0.1013	
R indices (all data)	R1 = 0.1247, wR2 = 0.1199	
Largest diff. peak and hole	3.568 and -3.246 e.Å^{-3}	

Table S7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for [^{i}Pr-PPP]-Pt(CH_3) (3). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pt(1)	103(1)	6882(1)	6111(1)	11(1)
Pt(2)	5556(1)	1815(1)	5987(1)	11(1)
P(1)	384(1)	6637(1)	6840(1)	11(1)
P(2)	-1232(1)	5698(1)	6154(1)	12(1)
P(3)	1798(1)	7681(1)	6150(1)	13(1)
P(4)	4731(1)	544(1)	6339(1)	13(1)
P(5)	4100(1)	2695(1)	6248(1)	12(1)
P(6)	7041(1)	767(1)	5898(1)	13(1)
C(1)	-71(5)	5402(4)	6930(2)	13(1)
C(2)	-951(5)	5054(4)	6661(2)	15(1)
C(3)	-1542(5)	4224(4)	6755(2)	17(1)
C(4)	-1212(6)	3659(4)	7108(2)	20(1)
C(5)	-283(6)	3955(5)	7358(2)	23(1)
C(6)	262(5)	4811(4)	7281(2)	18(1)
C(7)	1937(5)	6740(4)	6939(2)	14(1)
C(8)	2546(5)	7295(4)	6643(2)	15(1)
C(9)	3677(5)	7548(4)	6741(2)	20(1)
C(10)	4229(5)	7226(4)	7110(2)	21(1)
C(11)	3639(5)	6676(4)	7396(2)	18(1)
C(12)	2502(5)	6442(4)	7317(2)	16(1)
C(13)	-2791(5)	5918(4)	6123(2)	16(1)
C(14)	-3273(6)	6205(5)	6554(2)	25(2)
C(15)	-3080(6)	6691(5)	5787(2)	29(2)
C(16)	-1018(5)	4688(4)	5776(2)	15(1)
C(17)	221(5)	4395(4)	5777(2)	20(1)
C(18)	-1494(5)	4871(4)	5325(2)	21(1)
C(19)	1787(5)	9007(4)	6180(2)	17(1)
C(20)	1128(5)	9321(4)	6574(2)	23(1)
C(21)	1303(6)	9446(4)	5774(2)	23(2)
C(22)	2708(5)	7393(4)	5690(2)	16(1)
C(23)	3783(5)	7985(4)	5632(2)	22(1)
C(24)	3004(6)	6319(4)	5690(2)	24(2)
C(25)	-176(5)	7188(4)	5437(2)	13(1)
C(26)	3822(5)	1068(4)	6753(2)	16(1)
C(27)	3416(5)	2014(4)	6672(2)	16(1)
C(28)	2479(5)	2353(4)	6896(2)	22(2)
C(29)	1999(6)	1806(5)	7221(2)	24(2)
C(30)	2442(6)	915(5)	7316(2)	23(1)
C(31)	3316(6)	553(5)	7081(2)	23(1)
C(32)	5949(5)	-84(4)	6586(2)	13(1)
C(33)	6949(5)	-93(4)	6340(2)	15(1)
C(34)	7858(5)	-700(4)	6453(2)	18(1)
C(35)	7805(6)	-1267(4)	6816(2)	21(2)

C(36)	6867(6)	-1217(4)	7076(2)	21(1)
C(37)	5952(5)	-649(4)	6955(2)	20(1)
C(38)	4598(5)	3832(4)	6499(2)	17(1)
C(39)	5424(6)	3575(5)	6875(2)	23(2)
C(40)	3687(6)	4539(4)	6644(2)	25(2)
C(41)	2911(5)	3015(4)	5886(2)	20(1)
C(42)	2342(6)	2096(5)	5709(2)	33(2)
C(43)	3281(6)	3658(5)	5517(2)	29(2)
C(44)	8520(5)	1209(4)	5954(2)	16(1)
C(45)	8668(6)	1767(5)	6375(2)	26(2)
C(46)	8886(6)	1813(5)	5567(2)	31(2)
C(47)	7023(5)	58(4)	5390(2)	18(1)
C(48)	8088(6)	-556(5)	5320(2)	24(2)
C(49)	5934(5)	-566(5)	5380(2)	25(2)
C(50)	6268(5)	3002(4)	5646(2)	18(1)

Table S8. Bond lengths [Å] and angles [°] for 3 [^{i}Pr-PPP]-Pt(CH_3).

Pt(1)-C(25)	2.156(5)
Pt(1)-P(3)	2.2780(15)
Pt(1)-P(2)	2.2822(15)
Pt(1)-P(1)	2.3088(15)
Pt(2)-C(50)	2.145(6)
Pt(2)-P(5)	2.2679(16)
Pt(2)-P(6)	2.2945(15)
Pt(2)-P(4)	2.3090(15)
P(1)-C(1)	1.829(6)
P(1)-C(7)	1.843(6)
P(2)-C(2)	1.839(6)
P(2)-C(13)	1.851(6)
P(2)-C(16)	1.855(6)
P(3)-C(8)	1.831(6)
P(3)-C(22)	1.848(6)
P(3)-C(19)	1.854(6)
P(4)-C(32)	1.829(6)
P(4)-C(26)	1.840(6)
P(5)-C(41)	1.826(6)
P(5)-C(27)	1.825(6)
P(5)-C(38)	1.858(6)
P(6)-C(33)	1.832(6)
P(6)-C(44)	1.844(6)
P(6)-C(47)	1.864(6)
C(1)-C(2)	1.402(8)
C(1)-C(6)	1.415(8)
C(2)-C(3)	1.384(8)
C(3)-C(4)	1.400(8)
C(3)-H(3)	0.9500
C(4)-C(5)	1.385(8)
C(4)-H(4)	0.9500
C(5)-C(6)	1.380(9)
C(5)-H(5)	0.9500
C(6)-H(6)	0.9500
C(7)-C(12)	1.400(8)
C(7)-C(8)	1.409(8)
C(8)-C(9)	1.398(8)
C(9)-C(10)	1.381(8)
C(9)-H(9)	0.9500
C(10)-C(11)	1.375(9)
C(10)-H(10)	0.9500
C(11)-C(12)	1.387(8)
C(11)-H(11)	0.9500
C(12)-H(12)	0.9500
C(13)-C(14)	1.518(9)
C(13)-C(15)	1.536(8)
C(13)-H(13)	1.0000
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)-C(17)	1.508(8)
C(16)-C(18)	1.522(8)
C(16)-H(16)	1.0000
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)-C(21)	1.504(8)
C(19)-C(20)	1.528(9)
C(19)-H(19)	1.0000
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-C(23)	1.520(8)
C(22)-C(24)	1.538(8)
C(22)-H(22)	1.0000
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(31)	1.391(9)
C(26)-C(27)	1.425(8)
C(27)-C(28)	1.395(8)
C(28)-C(29)	1.396(9)
C(28)-H(28)	0.9500
C(29)-C(30)	1.377(9)
C(29)-H(29)	0.9500
C(30)-C(31)	1.368(9)
C(30)-H(30)	0.9500
C(31)-H(31)	0.9500
C(32)-C(37)	1.394(8)
C(32)-C(33)	1.412(8)
C(33)-C(34)	1.400(8)
C(34)-C(35)	1.382(8)
C(34)-H(34)	0.9500
C(35)-C(36)	1.379(9)
C(35)-H(35)	0.9500
C(36)-C(37)	1.378(8)

C(36)-H(36)	0.9500
C(37)-H(37)	0.9500
C(38)-C(40)	1.530(9)
C(38)-C(39)	1.542(8)
C(38)-H(38)	1.0000
C(39)-H(39A)	0.9800
C(39)-H(39B)	0.9800
C(39)-H(39C)	0.9800
C(40)-H(40A)	0.9800
C(40)-H(40B)	0.9800
C(40)-H(40C)	0.9800
C(41)-C(43)	1.530(9)
C(41)-C(42)	1.541(8)
C(41)-H(41)	1.0000
C(42)-H(42A)	0.9800
C(42)-H(42B)	0.9800
C(42)-H(42C)	0.9800
C(43)-H(43A)	0.9800
C(43)-H(43B)	0.9800
C(43)-H(43C)	0.9800
C(44)-C(45)	1.531(8)
C(44)-C(46)	1.539(9)
C(44)-H(44)	1.0000
C(45)-H(45A)	0.9800
C(45)-H(45B)	0.9800
C(45)-H(45C)	0.9800
C(46)-H(46A)	0.9800
C(46)-H(46B)	0.9800
C(46)-H(46C)	0.9800
C(47)-C(48)	1.533(8)
C(47)-C(49)	1.544(8)
C(47)-H(47)	1.0000
C(48)-H(48A)	0.9800
C(48)-H(48B)	0.9800
C(48)-H(48C)	0.9800
C(49)-H(49A)	0.9800
C(49)-H(49B)	0.9800
C(49)-H(49C)	0.9800
C(50)-H(50A)	0.9801
C(50)-H(50B)	0.9801
C(50)-H(50C)	0.9801
C(25)-Pt(1)-P(3)	93.86(15)
C(25)-Pt(1)-P(2)	96.38(15)
P(3)-Pt(1)-P(2)	161.66(5)
C(25)-Pt(1)-P(1)	177.04(15)
P(3)-Pt(1)-P(1)	85.17(5)
P(2)-Pt(1)-P(1)	85.30(5)
C(50)-Pt(2)-P(5)	93.56(17)
C(50)-Pt(2)-P(6)	97.44(17)
P(5)-Pt(2)-P(6)	165.23(5)
C(50)-Pt(2)-P(4)	177.98(17)
P(5)-Pt(2)-P(4)	85.42(5)

P(6)-Pt(2)-P(4)	83.87(5)
C(1)-P(1)-C(7)	109.7(3)
C(1)-P(1)-Pt(1)	104.84(19)
C(7)-P(1)-Pt(1)	105.72(19)
C(2)-P(2)-C(13)	106.4(3)
C(2)-P(2)-C(16)	98.5(3)
C(13)-P(2)-C(16)	104.0(3)
C(2)-P(2)-Pt(1)	107.14(19)
C(13)-P(2)-Pt(1)	123.5(2)
C(16)-P(2)-Pt(1)	114.3(2)
C(8)-P(3)-C(22)	108.2(3)
C(8)-P(3)-C(19)	104.8(3)
C(22)-P(3)-C(19)	105.2(3)
C(8)-P(3)-Pt(1)	107.4(2)
C(22)-P(3)-Pt(1)	111.65(19)
C(19)-P(3)-Pt(1)	119.0(2)
C(32)-P(4)-C(26)	110.8(3)
C(32)-P(4)-Pt(2)	103.73(19)
C(26)-P(4)-Pt(2)	106.3(2)
C(41)-P(5)-C(27)	103.5(3)
C(41)-P(5)-C(38)	106.1(3)
C(27)-P(5)-C(38)	106.3(3)
C(41)-P(5)-Pt(2)	118.7(2)
C(27)-P(5)-Pt(2)	108.81(19)
C(38)-P(5)-Pt(2)	112.5(2)
C(33)-P(6)-C(44)	102.7(3)
C(33)-P(6)-C(47)	106.8(3)
C(44)-P(6)-C(47)	104.6(3)
C(33)-P(6)-Pt(2)	105.7(2)
C(44)-P(6)-Pt(2)	119.18(19)
C(47)-P(6)-Pt(2)	116.5(2)
C(2)-C(1)-C(6)	116.4(5)
C(2)-C(1)-P(1)	116.6(4)
C(6)-C(1)-P(1)	126.4(4)
C(3)-C(2)-C(1)	121.9(5)
C(3)-C(2)-P(2)	120.7(4)
C(1)-C(2)-P(2)	117.3(4)
C(2)-C(3)-C(4)	120.6(6)
C(2)-C(3)-H(3)	119.7
C(4)-C(3)-H(3)	119.7
C(5)-C(4)-C(3)	118.1(6)
C(5)-C(4)-H(4)	120.9
C(3)-C(4)-H(4)	121.0
C(4)-C(5)-C(6)	121.5(6)
C(4)-C(5)-H(5)	119.3
C(6)-C(5)-H(5)	119.3
C(5)-C(6)-C(1)	121.3(6)
C(5)-C(6)-H(6)	119.4
C(1)-C(6)-H(6)	119.4
C(12)-C(7)-C(8)	118.4(5)
C(12)-C(7)-P(1)	124.3(5)
C(8)-C(7)-P(1)	116.5(4)

C(9)-C(8)-C(7)	119.2(5)
C(9)-C(8)-P(3)	122.7(5)
C(7)-C(8)-P(3)	118.0(4)
C(10)-C(9)-C(8)	121.5(6)
C(10)-C(9)-H(9)	119.3
C(8)-C(9)-H(9)	119.2
C(9)-C(10)-C(11)	119.2(6)
C(9)-C(10)-H(10)	120.2
C(11)-C(10)-H(10)	120.6
C(10)-C(11)-C(12)	120.6(6)
C(10)-C(11)-H(11)	119.5
C(12)-C(11)-H(11)	119.9
C(11)-C(12)-C(7)	120.9(6)
C(11)-C(12)-H(12)	119.3
C(7)-C(12)-H(12)	119.8
C(14)-C(13)-C(15)	109.6(5)
C(14)-C(13)-P(2)	112.6(4)
C(15)-C(13)-P(2)	110.7(4)
C(14)-C(13)-H(13)	107.8
C(15)-C(13)-H(13)	108.0
P(2)-C(13)-H(13)	107.9
C(13)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.3
H(14A)-C(14)-H(14B)	109.5
C(13)-C(14)-H(14C)	109.6
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(13)-C(15)-H(15A)	109.5
C(13)-C(15)-H(15B)	109.2
H(15A)-C(15)-H(15B)	109.5
C(13)-C(15)-H(15C)	109.7
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(17)-C(16)-C(18)	112.3(5)
C(17)-C(16)-P(2)	110.4(4)
C(18)-C(16)-P(2)	113.9(4)
C(17)-C(16)-H(16)	106.5
C(18)-C(16)-H(16)	106.6
P(2)-C(16)-H(16)	106.7
C(16)-C(17)-H(17A)	109.5
C(16)-C(17)-H(17B)	109.8
H(17A)-C(17)-H(17B)	109.5
C(16)-C(17)-H(17C)	109.1
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(16)-C(18)-H(18A)	109.3
C(16)-C(18)-H(18B)	109.6
H(18A)-C(18)-H(18B)	109.5
C(16)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(21)-C(19)-C(20)	111.7(5)

C(21)-C(19)-P(3)	111.6(4)
C(20)-C(19)-P(3)	109.4(4)
C(21)-C(19)-H(19)	107.9
C(20)-C(19)-H(19)	108.1
P(3)-C(19)-H(19)	108.0
C(19)-C(20)-H(20A)	109.5
C(19)-C(20)-H(20B)	109.4
H(20A)-C(20)-H(20B)	109.5
C(19)-C(20)-H(20C)	109.6
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(19)-C(21)-H(21A)	109.3
C(19)-C(21)-H(21B)	109.6
H(21A)-C(21)-H(21B)	109.5
C(19)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(23)-C(22)-C(24)	110.1(5)
C(23)-C(22)-P(3)	117.8(4)
C(24)-C(22)-P(3)	110.2(4)
C(23)-C(22)-H(22)	106.1
C(24)-C(22)-H(22)	105.9
P(3)-C(22)-H(22)	105.9
C(22)-C(23)-H(23A)	109.8
C(22)-C(23)-H(23B)	109.3
H(23A)-C(23)-H(23B)	109.5
C(22)-C(23)-H(23C)	109.2
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(22)-C(24)-H(24A)	109.5
C(22)-C(24)-H(24B)	109.3
H(24A)-C(24)-H(24B)	109.5
C(22)-C(24)-H(24C)	109.6
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
Pt(1)-C(25)-H(25A)	109.5
Pt(1)-C(25)-H(25B)	109.4
H(25A)-C(25)-H(25B)	109.5
Pt(1)-C(25)-H(25C)	109.6
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
C(31)-C(26)-C(27)	117.5(6)
C(31)-C(26)-P(4)	124.8(5)
C(27)-C(26)-P(4)	116.2(5)
C(28)-C(27)-C(26)	119.4(6)
C(28)-C(27)-P(5)	123.1(5)
C(26)-C(27)-P(5)	117.4(5)
C(29)-C(28)-C(27)	120.6(6)
C(29)-C(28)-H(28)	119.6
C(27)-C(28)-H(28)	119.8
C(30)-C(29)-C(28)	119.6(6)
C(30)-C(29)-H(29)	120.2

C(28)-C(29)-H(29)	120.2
C(31)-C(30)-C(29)	120.1(6)
C(31)-C(30)-H(30)	119.8
C(29)-C(30)-H(30)	120.1
C(30)-C(31)-C(26)	122.5(6)
C(30)-C(31)-H(31)	118.9
C(26)-C(31)-H(31)	118.6
C(37)-C(32)-C(33)	117.0(5)
C(37)-C(32)-P(4)	127.3(5)
C(33)-C(32)-P(4)	115.2(4)
C(34)-C(33)-C(32)	120.3(5)
C(34)-C(33)-P(6)	121.9(5)
C(32)-C(33)-P(6)	117.6(4)
C(35)-C(34)-C(33)	120.3(6)
C(35)-C(34)-H(34)	119.8
C(33)-C(34)-H(34)	119.9
C(36)-C(35)-C(34)	120.1(5)
C(36)-C(35)-H(35)	119.8
C(34)-C(35)-H(35)	120.1
C(35)-C(36)-C(37)	119.6(6)
C(35)-C(36)-H(36)	120.3
C(37)-C(36)-H(36)	120.1
C(36)-C(37)-C(32)	122.6(6)
C(36)-C(37)-H(37)	118.7
C(32)-C(37)-H(37)	118.8
C(40)-C(38)-C(39)	110.9(5)
C(40)-C(38)-P(5)	117.5(4)
C(39)-C(38)-P(5)	107.8(4)
C(40)-C(38)-H(38)	106.7
C(39)-C(38)-H(38)	106.8
P(5)-C(38)-H(38)	106.7
C(38)-C(39)-H(39A)	109.6
C(38)-C(39)-H(39B)	109.4
H(39A)-C(39)-H(39B)	109.5
C(38)-C(39)-H(39C)	109.4
H(39A)-C(39)-H(39C)	109.5
H(39B)-C(39)-H(39C)	109.5
C(38)-C(40)-H(40A)	109.4
C(38)-C(40)-H(40B)	109.4
H(40A)-C(40)-H(40B)	109.5
C(38)-C(40)-H(40C)	109.6
H(40A)-C(40)-H(40C)	109.5
H(40B)-C(40)-H(40C)	109.5
C(43)-C(41)-C(42)	110.4(6)
C(43)-C(41)-P(5)	112.5(4)
C(42)-C(41)-P(5)	109.5(4)
C(43)-C(41)-H(41)	108.2
C(42)-C(41)-H(41)	108.0
P(5)-C(41)-H(41)	108.1
C(41)-C(42)-H(42A)	109.3
C(41)-C(42)-H(42B)	109.6
H(42A)-C(42)-H(42B)	109.5

C(41)-C(42)-H(42C)	109.4
H(42A)-C(42)-H(42C)	109.5
H(42B)-C(42)-H(42C)	109.5
C(41)-C(43)-H(43A)	109.5
C(41)-C(43)-H(43B)	109.8
H(43A)-C(43)-H(43B)	109.5
C(41)-C(43)-H(43C)	109.1
H(43A)-C(43)-H(43C)	109.5
H(43B)-C(43)-H(43C)	109.5
C(45)-C(44)-C(46)	111.3(5)
C(45)-C(44)-P(6)	109.9(4)
C(46)-C(44)-P(6)	112.7(4)
C(45)-C(44)-H(44)	107.7
C(46)-C(44)-H(44)	107.5
P(6)-C(44)-H(44)	107.5
C(44)-C(45)-H(45A)	109.5
C(44)-C(45)-H(45B)	109.4
H(45A)-C(45)-H(45B)	109.5
C(44)-C(45)-H(45C)	109.5
H(45A)-C(45)-H(45C)	109.5
H(45B)-C(45)-H(45C)	109.5
C(44)-C(46)-H(46A)	109.4
C(44)-C(46)-H(46B)	109.7
H(46A)-C(46)-H(46B)	109.5
C(44)-C(46)-H(46C)	109.3
H(46A)-C(46)-H(46C)	109.5
H(46B)-C(46)-H(46C)	109.5
C(48)-C(47)-C(49)	110.8(5)
C(48)-C(47)-P(6)	115.1(4)
C(49)-C(47)-P(6)	108.1(4)
C(48)-C(47)-H(47)	107.6
C(49)-C(47)-H(47)	107.5
P(6)-C(47)-H(47)	107.5
C(47)-C(48)-H(48A)	109.6
C(47)-C(48)-H(48B)	109.4
H(48A)-C(48)-H(48B)	109.5
C(47)-C(48)-H(48C)	109.3
H(48A)-C(48)-H(48C)	109.5
H(48B)-C(48)-H(48C)	109.5
C(47)-C(49)-H(49A)	109.4
C(47)-C(49)-H(49B)	109.5
H(49A)-C(49)-H(49B)	109.5
C(47)-C(49)-H(49C)	109.5
H(49A)-C(49)-H(49C)	109.5
H(49B)-C(49)-H(49C)	109.5
Pt(2)-C(50)-H(50A)	109.4
Pt(2)-C(50)-H(50B)	109.5
H(50A)-C(50)-H(50B)	109.5
Pt(2)-C(50)-H(50C)	109.5
H(50A)-C(50)-H(50C)	109.5
H(50B)-C(50)-H(50C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S9. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **3** [^{i}Pr-PPP]-Pt(CH_3). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pt(1)	12(1)	9(1)	11(1)	1(1)	0(1)	-1(1)
Pt(2)	11(1)	10(1)	13(1)	2(1)	1(1)	1(1)
P(1)	12(1)	11(1)	11(1)	-1(1)	0(1)	-1(1)
P(2)	10(1)	11(1)	14(1)	0(1)	-1(1)	-1(1)
P(3)	12(1)	12(1)	14(1)	-1(1)	0(1)	-4(1)
P(4)	12(1)	11(1)	15(1)	0(1)	0(1)	0(1)
P(5)	14(1)	8(1)	14(1)	-1(1)	-2(1)	0(1)
P(6)	13(1)	10(1)	16(1)	1(1)	-1(1)	0(1)
C(1)	13(3)	8(3)	19(3)	-1(2)	7(2)	0(2)
C(2)	17(3)	11(3)	15(3)	1(2)	0(2)	3(2)
C(3)	19(3)	16(3)	17(3)	-5(2)	2(3)	-1(2)
C(4)	27(4)	15(3)	18(3)	2(2)	3(3)	-6(3)
C(5)	29(4)	19(3)	20(3)	3(3)	-2(3)	1(3)
C(6)	14(3)	23(3)	16(3)	1(2)	-2(2)	-3(2)
C(7)	15(3)	13(3)	14(3)	-6(2)	-4(2)	1(2)
C(8)	14(3)	13(3)	17(3)	-5(2)	-4(2)	0(2)
C(9)	21(3)	23(3)	15(3)	-3(2)	3(3)	-9(3)
C(10)	17(3)	22(3)	22(3)	-9(3)	-6(3)	4(2)
C(11)	20(3)	14(3)	21(3)	-4(2)	-7(3)	1(2)
C(12)	17(3)	13(3)	17(3)	-2(2)	-4(2)	1(2)
C(13)	11(3)	18(3)	19(3)	0(2)	1(2)	1(2)
C(14)	23(4)	22(3)	30(4)	3(3)	-3(3)	4(3)
C(15)	16(3)	34(4)	37(4)	14(3)	4(3)	7(3)
C(16)	18(3)	9(3)	17(3)	-1(2)	-3(2)	-1(2)
C(17)	14(3)	15(3)	29(3)	-4(3)	-2(3)	0(2)
C(18)	22(4)	22(3)	20(3)	-3(3)	-6(3)	-5(3)
C(19)	17(3)	7(3)	26(3)	-2(2)	0(3)	1(2)
C(20)	20(3)	15(3)	34(4)	-8(3)	-1(3)	-4(2)
C(21)	32(4)	9(3)	28(4)	4(3)	19(3)	-2(3)
C(22)	20(3)	16(3)	12(3)	1(2)	2(2)	-3(2)
C(23)	23(4)	17(3)	25(3)	-5(3)	7(3)	-1(3)
C(24)	29(4)	17(3)	25(4)	-1(3)	-1(3)	-1(3)
C(25)	12(3)	8(2)	18(3)	-3(2)	-4(2)	-1(2)
C(26)	10(3)	20(3)	17(3)	-8(2)	0(2)	1(2)
C(27)	10(3)	13(3)	24(3)	-3(2)	-2(2)	-2(2)
C(28)	22(4)	10(3)	35(4)	-10(3)	1(3)	6(2)
C(29)	22(4)	26(4)	24(3)	-8(3)	8(3)	-9(3)
C(30)	25(4)	23(3)	20(3)	4(3)	6(3)	-4(3)
C(31)	28(4)	21(3)	21(3)	5(3)	-5(3)	1(3)
C(32)	9(3)	11(3)	18(3)	2(2)	-2(2)	-4(2)
C(33)	22(3)	12(3)	9(3)	0(2)	-4(2)	0(2)
C(34)	14(3)	20(3)	21(3)	2(2)	0(2)	5(2)
C(35)	27(4)	11(3)	25(3)	3(2)	-9(3)	6(2)
C(36)	31(4)	14(3)	18(3)	6(2)	-6(3)	1(3)

C(37)	17(3)	14(3)	29(4)	0(3)	2(3)	-6(2)
C(38)	22(4)	12(3)	17(3)	2(2)	0(3)	-6(2)
C(39)	22(4)	25(3)	22(3)	0(3)	-9(3)	-6(3)
C(40)	32(4)	15(3)	28(4)	-6(3)	-1(3)	2(3)
C(41)	19(3)	16(3)	24(3)	-7(2)	-1(3)	4(2)
C(42)	26(4)	36(4)	37(4)	-16(3)	-12(3)	5(3)
C(43)	29(4)	37(4)	21(3)	7(3)	-6(3)	10(3)
C(44)	10(3)	14(3)	24(3)	-4(2)	3(3)	-1(2)
C(45)	21(4)	29(4)	27(4)	-9(3)	-6(3)	0(3)
C(46)	21(4)	25(4)	46(4)	-1(3)	4(3)	-3(3)
C(47)	24(4)	17(3)	13(3)	-2(2)	-3(3)	2(2)
C(48)	25(4)	20(3)	28(4)	-5(3)	-5(3)	7(3)
C(49)	23(4)	21(3)	31(4)	-6(3)	-8(3)	-2(3)
C(50)	18(3)	8(3)	29(3)	2(2)	1(3)	-1(2)

Table S10. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **3** [^{i}Pr-PPP]-Pt(CH_3).

	x	y	z	U(eq)
H(3)	-2176	4037	6579	21
H(4)	-1613	3088	7174	24
H(5)	-16	3559	7587	27
H(6)	872	5009	7467	21
H(9)	4075	7950	6549	24
H(10)	5008	7383	7165	25
H(11)	4013	6453	7651	22
H(12)	2101	6076	7522	19
H(13)	-3173	5310	6030	19
H(14A)	-2889	6785	6658	38
H(14B)	-3149	5685	6761	38
H(14C)	-4094	6328	6519	38
H(15A)	-3911	6759	5758	44
H(15B)	-2770	6504	5509	44
H(15C)	-2744	7302	5878	44
H(16)	-1452	4132	5892	18
H(17A)	305	3808	5608	29
H(17B)	489	4278	6073	29
H(17C)	677	4907	5651	29
H(18A)	-1135	5444	5206	32
H(18B)	-2322	4967	5335	32
H(18C)	-1331	4319	5141	32
H(19)	2594	9230	6218	21
H(20A)	1197	10016	6610	34
H(20B)	1444	9000	6830	34
H(20C)	321	9149	6535	34
H(21A)	512	9234	5729	34
H(21B)	1760	9245	5529	34
H(21C)	1323	10145	5798	34
H(22)	2223	7504	5426	19
H(23A)	4352	7810	5854	33
H(23B)	3597	8667	5658	33
H(23C)	4092	7860	5348	33
H(24A)	3406	6160	5427	35
H(24B)	2299	5943	5703	35
H(24C)	3494	6172	5941	35
H(25A)	80	7841	5376	19
H(25B)	-991	7129	5365	19
H(25C)	258	6733	5265	19
H(28)	2165	2963	6827	26
H(29)	1370	2046	7376	29
H(30)	2139	550	7544	27
H(31)	3588	-73	7144	28
H(34)	8515	-723	6280	22

H(35)	8414	-1691	6887	26
H(36)	6852	-1571	7336	25
H(37)	5298	-643	7130	24
H(38)	5061	4171	6280	20
H(39A)	5771	4162	6991	35
H(39B)	6025	3150	6771	35
H(39C)	5002	3251	7101	35
H(40A)	3327	4295	6903	38
H(40B)	3106	4617	6415	38
H(40C)	4043	5160	6707	38
H(41)	2334	3371	6056	24
H(42A)	1809	2262	5474	50
H(42B)	1926	1780	5939	50
H(42C)	2930	1663	5603	50
H(43A)	3769	3294	5324	43
H(43B)	3708	4208	5633	43
H(43C)	2604	3886	5356	43
H(44)	9035	639	5972	19
H(45A)	9462	1982	6408	39
H(45B)	8478	1352	6617	39
H(45C)	8159	2324	6370	39
H(46A)	8420	2396	5550	46
H(46B)	8776	1441	5302	46
H(46C)	9693	1987	5602	46
H(47)	6959	521	5145	22
H(48A)	8161	-1032	5551	36
H(48B)	8767	-145	5323	36
H(48C)	8017	-883	5042	36
H(49A)	5857	-883	5100	38
H(49B)	5265	-160	5426	38
H(49C)	5990	-1050	5608	38
H(50A)	5666	3471	5581	27
H(50B)	6595	2774	5378	27
H(50C)	6868	3303	5825	27

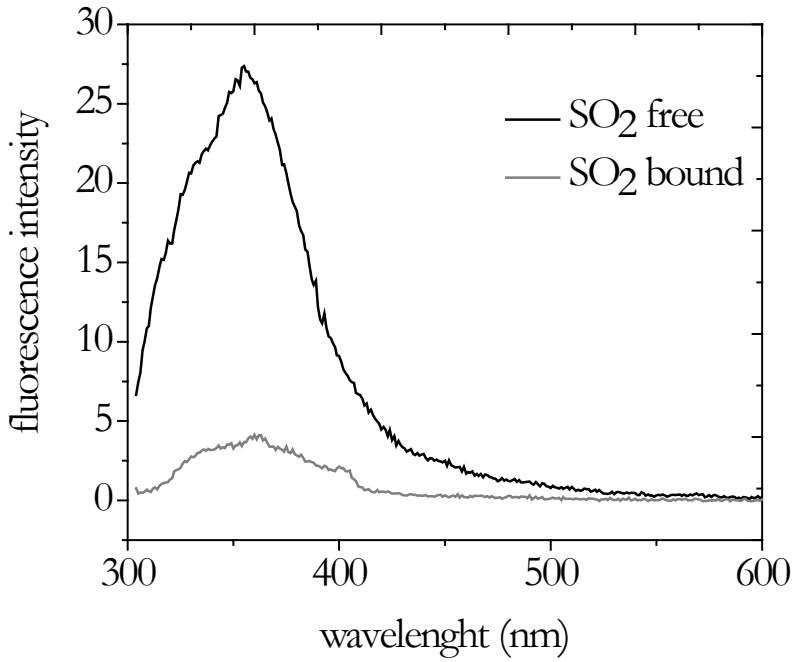

Figure S3. Emission spectrum of **1** in the SO_2 free form (black trace) and in the SO_2 bound form (grey trace). **1** concentration = 1 μM; [SO_2] = 90 mM. All time traces were measured at room temperature and in benzene.

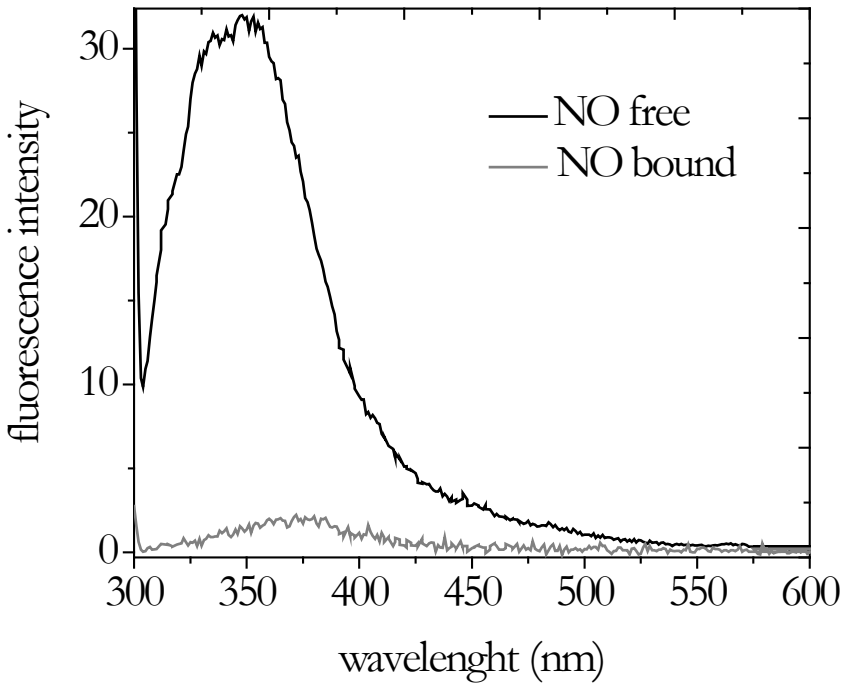

Figure S4. Emission spectrum of **1** in the NO free form (black trace) and in the NO bound form (grey trace). **1** concentration = 1 μM; [NO] = 230 μM. All time traces were measured at room temperature and in benzene.

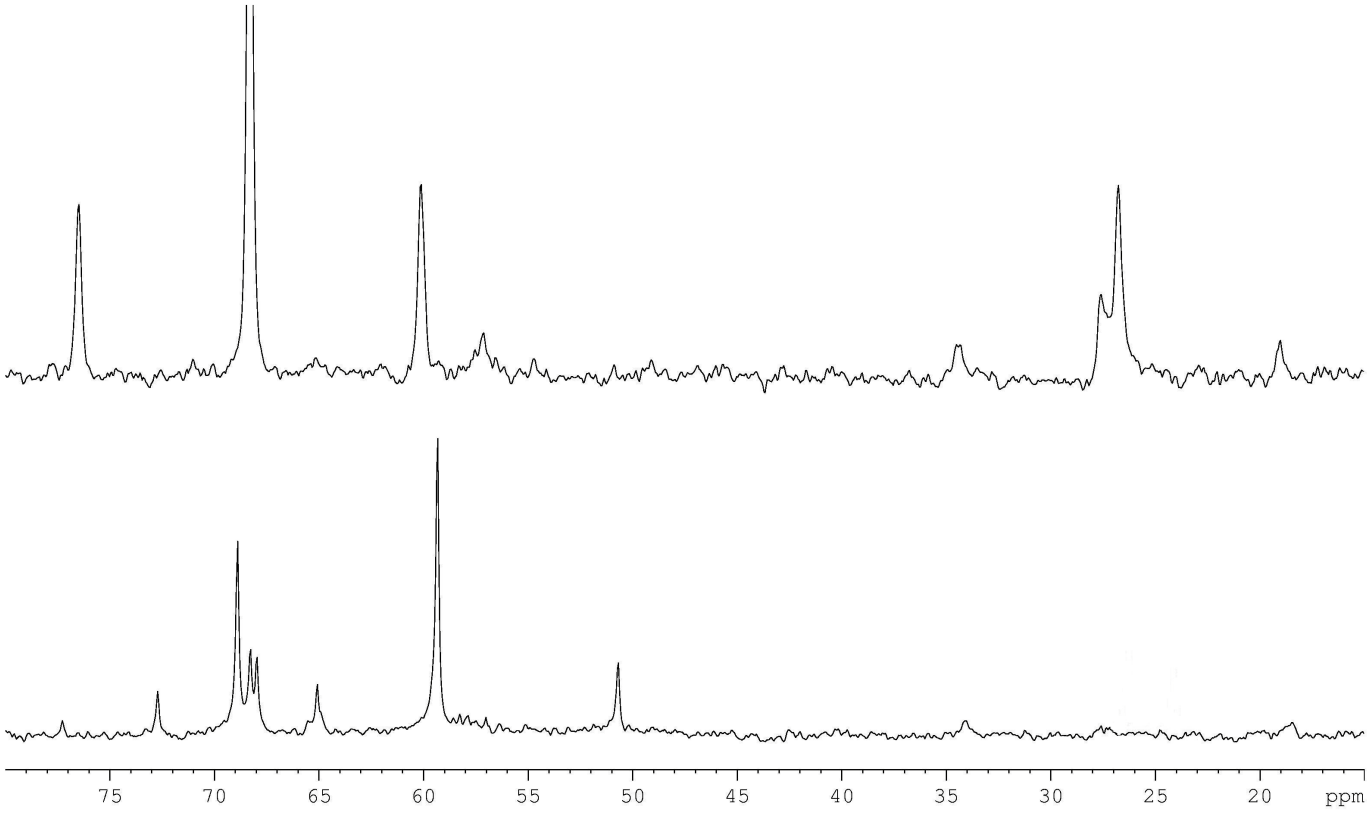

Figure S5. ^{31}P-NMR of **1** in the NO free form (lower spectrum) and in the NO bound form. The spectra were measured at room temperature, C_6D_6. [NO] = 300 µM.