

**Table S12.** Atomic Parameters x,y,z and Biso for [(2,4,6-(i-Pr)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)SCH<sub>2</sub>CH=PMes\*]PdMeCl 10a.

E.S.Ds. refer to the last digit printed.

	x	y	z	Biso
Pd1	0.811831(14)	0.826918( 8)	0.172434(17)	1.611( 8)
Cl1	0.73033 ( 6)	0.77091 ( 3)	0.02808 ( 7)	3.06 ( 3)
P1	0.88236 ( 5)	0.87524 ( 3)	0.31837 ( 6)	1.488(23)
S1	0.67155 ( 5)	0.82211 ( 3)	0.27967 ( 6)	1.709(23)
C1	0.9387 ( 3)	0.83103 (12)	0.0922 ( 3)	2.81 (12)
C2	0.80376 (19)	0.88964 (11)	0.41070 (22)	1.89 (10)
C3	0.69406 (20)	0.87208 (13)	0.39005 (24)	2.35 (12)
C4	1.01406 (18)	0.89760 (10)	0.36675 (22)	1.44 ( 9)
C5	1.08683 (18)	0.86492 (10)	0.43508 (23)	1.68 (10)
C6	1.18908 (20)	0.88128 (11)	0.4605 ( 3)	2.12 (11)
C7	1.22253 (19)	0.92698 (11)	0.4235 ( 3)	2.00 (11)
C8	1.14984 (19)	0.95809 (10)	0.35953 (25)	1.91 (10)
C9	1.04559 (18)	0.94550 (10)	0.32809 (22)	1.57 ( 9)
C10	1.06258 (20)	0.81276 (11)	0.4861 ( 3)	1.96 (10)
C11	0.9874 ( 3)	0.81828 (13)	0.5733 ( 3)	3.34 (14)
C12	1.0247 ( 3)	0.77482 (12)	0.3883 ( 3)	3.36 (14)
C13	1.15989 (23)	0.78811 (13)	0.5578 ( 3)	2.92 (13)
C14	1.33620 (20)	0.94286 (12)	0.4516 ( 3)	2.63 (13)
C15	1.4047 ( 3)	0.90445 (18)	0.5187 ( 7)	9.2 ( 4)
C16	1.3755 ( 3)	0.95199 (22)	0.3351 ( 4)	6.14 (25)
C17	1.34385 (24)	0.99193 (15)	0.5182 ( 3)	3.92 (16)
C18	0.97373 (20)	0.98555 (11)	0.25800 (25)	2.06 (10)
C19	1.03451 (25)	1.03060 (13)	0.2211 ( 3)	3.54 (15)
C20	0.9008 ( 3)	1.00743 (13)	0.3354 ( 3)	3.42 (15)
C21	0.91158 (25)	0.96457 (13)	0.1439 ( 3)	2.99 (13)
C22	0.54642 (19)	0.83753 (10)	0.19956 (22)	1.60 ( 9)
C23	0.46545 (19)	0.80514 (11)	0.21664 (23)	1.80 (10)
C24	0.36700 (20)	0.81511 (12)	0.1534 ( 3)	2.21 (11)
C25	0.34836 (20)	0.85507 (12)	0.0752 ( 3)	2.36 (11)
C26	0.42977 (21)	0.88619 (11)	0.06093 (25)	2.26 (11)
C27	0.53008 (20)	0.87847 (11)	0.12147 (23)	1.84 (10)
C28	0.48089 (22)	0.75966 (13)	0.2978 ( 3)	2.84 (12)
C29	0.4911 ( 4)	0.71269 (16)	0.2283 ( 4)	5.91 (24)
C30	0.3946 ( 4)	0.75365 (18)	0.3691 ( 4)	5.42 (22)
C31	0.23922 (24)	0.86465 (13)	0.0092 ( 3)	3.46 (14)
C32	0.2370 ( 3)	0.87336 (21)	-0.1217 ( 4)	6.75 (23)
C33	0.1895 ( 3)	0.90801 (19)	0.0614 ( 3)	4.66 (20)
C34	0.61450 (21)	0.91448 (11)	0.0995 ( 3)	2.22 (11)
C35	0.6286 ( 3)	0.91309 (14)	-0.0296 ( 3)	3.60 (15)
C36	0.5939 ( 3)	0.96841 (13)	0.1378 ( 3)	3.08 (13)
C41	0.7980 ( 4)	0.67892 (18)	0.2674 ( 4)	5.22 (24)
C42	0.7562 ( 3)	0.63172 (17)	0.2230 ( 3)	3.91 (18)
N43	0.7254 ( 4)	0.59468 (18)	0.1872 ( 4)	6.8 ( 3)
H1a	0.927	0.812	0.021	3.7
H1b	0.951	0.866	0.074	3.7
H1c	0.997	0.818	0.144	3.7
H2	0.829	0.909	0.479	2.7
H3a	0.677	0.860	0.463	3.2
H3b	0.650	0.900	0.363	3.2
H6	1.239	0.860	0.506	2.9
H8	1.172	0.990	0.335	2.7

H11a	1.015	0.842	0.633	4.2
H11b	0.922	0.830	0.533	4.2
H11c	0.979	0.786	0.609	4.2
H12a	0.964	0.788	0.340	4.0
H12b	1.077	0.769	0.341	4.0
H12c	1.009	0.743	0.422	4.0
H13a	1.211	0.783	0.508	3.6
H13b	1.187	0.810	0.622	3.6
H13c	1.142	0.756	0.588	3.6
H15a	1.381	0.898	0.592	9.5
H15b	1.402	0.874	0.475	9.5
H15c	1.474	0.917	0.534	9.5
H16a	1.372	0.921	0.291	7.1
H16b	1.333	0.977	0.290	7.1
H16c	1.445	0.964	0.351	7.1
H17a	1.300	1.016	0.473	4.7
H17b	1.322	0.987	0.593	4.7
H17c	1.414	1.004	0.531	4.7
H19a	1.081	1.019	0.172	4.3
H19b	0.988	1.054	0.178	4.3
H19c	1.073	1.047	0.290	4.3
H20a	0.941	1.021	0.406	4.3
H20b	0.860	1.034	0.294	4.3
H20c	0.856	0.981	0.354	4.3
H21a	0.872	0.936	0.162	3.7
H21b	0.866	0.990	0.106	3.7
H21c	0.958	0.954	0.093	3.7
H24	0.311	0.793	0.164	2.9
H26	0.417	0.914	0.007	3.0
H28	0.544	0.764	0.352	3.5
H29a	0.546	0.717	0.184	6.8
H29b	0.506	0.684	0.280	6.8
H29c	0.428	0.707	0.175	6.8
H30a	0.389	0.784	0.414	6.4
H30b	0.331	0.748	0.317	6.4
H30c	0.409	0.725	0.421	6.4
H31	0.199	0.835	0.017	4.0
H32a	0.268	0.845	-0.155	7.1
H32b	0.167	0.877	-0.161	7.1
H32c	0.275	0.903	-0.131	7.1
H33a	0.190	0.902	0.144	5.4
H33b	0.228	0.938	0.052	5.4
H33c	0.120	0.912	0.022	5.4
H34	0.678	0.904	0.146	3.0
H35a	0.642	0.879	-0.051	4.5
H35b	0.567	0.925	-0.078	4.5
H35c	0.686	0.934	-0.040	4.5
H36a	0.586	0.968	0.219	3.8
H36b	0.651	0.990	0.128	3.8
H36c	0.532	0.981	0.090	3.8
H41a	0.787	0.683	0.347	6.1
H41b	0.871	0.680	0.265	6.1
H41c	0.764	0.706	0.219	6.1

Biso is the Mean of the Principal Axes of the Thermal Ellipsoid

**Table S13.**  $u(i,j)$  or  $U$  values\*100 for [(2,4,6-(*i*-Pr)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)SCH<sub>2</sub>CH=PMes\*]PdMeCl 10a .

E.S.Ds. refer to the last digit printed

	u11(U)	u22	u33	u12	u13	u23
Pd1	1.919(10)	2.153(12)	2.004(11)	-0.102( 8)	0.210( 7)	-0.378( 8)
C11	4.87 ( 4)	3.80 ( 5)	2.74 ( 4)	-1.11 ( 4)	0.02 ( 3)	-1.08 ( 3)
P1	1.32 ( 3)	2.26 ( 4)	2.05 ( 3)	-0.160(25)	0.212(23)	-0.34 ( 3)
S1	1.54 ( 3)	2.59 ( 4)	2.21 ( 3)	-0.274(25)	-0.106(22)	0.41 ( 3)
C1	3.81 (16)	3.59 (19)	3.72 (17)	-0.35 (14)	1.89 (14)	-1.17 (14)
C2	1.84 (11)	3.31 (16)	1.94 (13)	-0.07 (11)	0.09 ( 9)	-0.55 (11)
C3	1.78 (12)	5.17 (20)	2.02 (14)	-0.25 (12)	0.43 (10)	-0.59 (13)
C4	1.35 (10)	1.97 (13)	2.15 (12)	-0.09 ( 9)	0.28 ( 9)	-0.45 (10)
C5	1.64 (11)	2.06 (14)	2.62 (13)	0.08 (10)	0.23 (10)	-0.20 (11)
C6	1.74 (12)	2.25 (15)	3.87 (16)	0.08 (11)	-0.12 (11)	-0.29 (12)
C7	1.47 (11)	2.21 (14)	3.84 (16)	-0.16 (10)	0.27 (10)	-0.52 (12)
C8	1.97 (12)	2.00 (14)	3.36 (15)	-0.29 (10)	0.70 (11)	-0.31 (11)
C9	1.77 (11)	2.09 (14)	2.13 (13)	0.07 (10)	0.35 ( 9)	-0.32 (10)
C10	1.92 (12)	2.16 (14)	3.24 (15)	-0.24 (10)	0.14 (11)	0.35 (11)
C11	3.84 (17)	4.15 (21)	5.07 (21)	0.76 (15)	1.79 (16)	1.74 (16)
C12	5.67 (21)	2.09 (16)	4.47 (20)	-0.47 (15)	-0.63 (16)	0.26 (14)
C13	2.83 (15)	3.28 (18)	4.73 (19)	0.28 (13)	-0.10 (13)	1.33 (15)
C14	1.48 (12)	2.80 (17)	5.63 (20)	-0.43 (11)	0.36 (12)	-0.91 (14)
C15	2.05 (18)	4.9 ( 3)	26.0 ( 8)	-0.79 (18)	-3.1 ( 3)	3.8 ( 4)
C16	2.82 (18)	13.4 ( 5)	7.6 ( 3)	-3.18 (23)	2.25 (19)	-5.2 ( 3)
C17	2.59 (15)	5.83 (25)	6.41 (24)	-1.35 (16)	0.61 (15)	-2.97 (20)
C18	2.25 (12)	2.40 (15)	3.15 (15)	0.10 (11)	0.38 (11)	0.34 (12)
C19	3.51 (17)	3.19 (19)	6.44 (24)	-0.17 (14)	-0.01 (16)	1.71 (17)
C20	4.84 (20)	3.23 (19)	5.08 (21)	1.82 (15)	1.30 (16)	0.35 (16)
C21	3.94 (17)	3.71 (19)	3.41 (17)	0.08 (14)	-0.26 (13)	0.82 (14)
C22	1.67 (11)	2.48 (15)	1.80 (12)	-0.21 (10)	-0.04 ( 9)	-0.03 (10)
C23	1.92 (12)	2.71 (15)	2.09 (13)	-0.58 (11)	0.02 (10)	-0.13 (11)
C24	1.84 (12)	3.15 (16)	3.16 (16)	-0.45 (11)	-0.25 (11)	-0.43 (12)
C25	2.14 (13)	3.13 (17)	3.28 (16)	0.23 (12)	-0.68 (11)	-0.55 (13)
C26	2.73 (13)	2.77 (16)	2.76 (14)	0.60 (12)	-0.44 (11)	0.26 (12)
C27	2.18 (12)	2.61 (15)	2.11 (13)	0.25 (11)	0.13 (10)	0.08 (11)
C28	2.67 (14)	3.94 (19)	3.69 (17)	-1.69 (13)	-0.86 (12)	1.28 (14)
C29	11.1 ( 4)	3.89 (25)	7.8 ( 3)	2.9 ( 3)	2.6 ( 3)	1.80 (23)
C30	8.7 ( 3)	5.8 ( 3)	6.9 ( 3)	-1.24 (25)	3.77 (25)	1.90 (24)
C31	2.76 (15)	3.68 (19)	5.87 (22)	0.00 (14)	-1.67 (15)	-0.09 (16)
C32	6.6 ( 3)	11.7 ( 4)	5.5 ( 3)	5.4 ( 3)	-4.18 (21)	-3.9 ( 3)
C33	2.90 (17)	9.4 ( 4)	5.12 (23)	2.19 (19)	-0.01 (15)	-0.51 (22)
C34	2.63 (13)	2.62 (16)	3.13 (15)	0.21 (11)	0.36 (11)	0.89 (12)
C35	5.40 (21)	4.61 (22)	4.23 (20)	0.24 (17)	2.38 (17)	1.17 (16)
C36	4.24 (18)	3.12 (18)	4.26 (19)	-0.55 (14)	0.45 (14)	0.38 (14)
C41	9.4 ( 3)	6.5 ( 3)	4.29 (23)	-0.1 ( 3)	2.42 (23)	-0.22 (21)
C42	7.2 ( 3)	4.9 ( 3)	3.03 (19)	1.79 (21)	1.78 (17)	0.21 (17)
N43	13.5 ( 4)	6.6 ( 3)	6.3 ( 3)	0.5 ( 3)	2.6 ( 3)	-1.14 (23)
H1a	4.7					
H1b	4.7					
H1c	4.7					
H2	3.4					
H3a	4.0					
H3b	4.0					
H6	3.6					
H8	3.4					
H11a	5.4					

H11b	5.4
H11c	5.4
H12a	5.1
H12b	5.1
H12c	5.1
H13a	4.6
H13b	4.6
H13c	4.6
H15a	12.0
H15b	12.0
H15c	12.0
H16a	8.9
H16b	8.9
H16c	8.9
H17a	5.9
H17b	5.9
H17c	5.9
H19a	5.4
H19b	5.4
H19c	5.4
H20a	5.4
H20b	5.4
H20c	5.4
H21a	4.7
H21b	4.7
H21c	4.7
H24	3.7
H26	3.8
H28	4.4
H29a	8.6
H29b	8.6
H29c	8.6
H30a	8.1
H30b	8.1
H30c	8.1
H31	5.1
H32a	8.9
H32b	8.9
H32c	8.9
H33a	6.8
H33b	6.8
H33c	6.8
H34	3.8
H35a	5.7
H35b	5.7
H35c	5.7
H36a	4.9
H36b	4.9
H36c	4.9
H41a	7.8
H41b	7.8
H41c	7.8

Anisotropic Temperature Factors are of the form  

$$\text{Temp} = -2 \cdot \pi^2 \cdot (h^2 \cdot u_{11}^2 \cdot a^2 + \dots + 2 \cdot h \cdot k \cdot u_{12}^2 \cdot a \cdot b + \dots)$$

**Table S14.** Bond Lengths (Å) and Angles (deg) for [(2,4,6-(i-Pr)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)SCH<sub>2</sub>CH=PMes\*]PdMeCl 10a

DISANG -- The NRCVAX Distance and Angle Program

The Space Group is P 21/C                      Centrosymmetric

The Equivalent Positions are:

1)        x        y        z        2)        -x    1/2+y    1/2-z

The Lattice is Primitive. There are no Centering Vectors

Pd(1)-Cl(1)	2.3496(7)	C(14)-C(16)	1.539(6)
Pd(1)-P(1)	2.1920(7)	C(14)-C(17)	1.506(5)
Pd(1)-S(1)	2.3965(7)	C(18)-C(19)	1.538(4)
Pd(1)-C(1)	2.046(3)	C(18)-C(20)	1.533(4)
P(1)-C(2)	1.652(3)	C(18)-C(21)	1.532(4)
P(1)-C(4)	1.8276(24)	C(22)-C(23)	1.409(4)
S(1)-C(3)	1.826(3)	C(22)-C(27)	1.404(4)
S(1)-C(22)	1.7934(25)	C(23)-C(24)	1.400(4)
C(2)-C(3)	1.498(4)	C(23)-C(28)	1.519(4)
C(4)-C(5)	1.426(4)	C(24)-C(25)	1.386(4)
C(4)-C(9)	1.431(4)	C(25)-C(26)	1.385(4)
C(5)-C(6)	1.397(4)	C(25)-C(31)	1.528(4)
C(5)-C(10)	1.557(4)	C(26)-C(27)	1.400(4)
C(6)-C(7)	1.382(4)	C(27)-C(34)	1.519(4)
C(7)-C(8)	1.378(4)	C(28)-C(29)	1.500(6)
C(7)-C(14)	1.535(4)	C(28)-C(30)	1.522(5)
C(8)-C(9)	1.399(3)	C(31)-C(32)	1.523(6)
C(9)-C(18)	1.554(4)	C(31)-C(33)	1.499(6)
C(10)-C(11)	1.535(4)	C(34)-C(35)	1.533(5)
C(10)-C(12)	1.530(4)	C(34)-C(36)	1.534(5)
C(10)-C(13)	1.546(4)	C(41)-C(42)	1.426(7)
C(14)-C(15)	1.487(5)	C(42)-N(43)	1.115(7)

Cl(1)-Pd(1)-P(1)	175.02(3)	C(7)-C(14)-C(16)	108.6(3)
Cl(1)-Pd(1)-S(1)	91.92(3)	C(7)-C(14)-C(17)	108.80(24)
Cl(1)-Pd(1)-C(1)	91.27(9)	C(15)-C(14)-C(16)	107.3(4)
P(1)-Pd(1)-S(1)	84.093(24)	C(15)-C(14)-C(17)	110.1(4)
P(1)-Pd(1)-C(1)	92.58(9)	C(16)-C(14)-C(17)	107.9(3)
S(1)-Pd(1)-C(1)	175.88(10)	C(9)-C(18)-C(19)	112.04(22)
Pd(1)-P(1)-C(2)	113.62(9)	C(9)-C(18)-C(20)	109.97(23)
Pd(1)-P(1)-C(4)	132.81(8)	C(9)-C(18)-C(21)	112.82(24)
C(2)-P(1)-C(4)	113.23(12)	C(19)-C(18)-C(20)	106.0(3)
Pd(1)-S(1)-C(3)	105.91(9)	C(19)-C(18)-C(21)	105.7(3)
Pd(1)-S(1)-C(22)	116.31(9)	C(20)-C(18)-C(21)	110.03(25)
C(3)-S(1)-C(22)	102.68(13)	S(1)-C(22)-C(23)	116.09(20)
P(1)-C(2)-C(3)	121.28(20)	S(1)-C(22)-C(27)	122.25(19)
S(1)-C(3)-C(2)	111.93(19)	C(23)-C(22)-C(27)	121.63(23)
P(1)-C(4)-C(5)	119.02(19)	C(22)-C(23)-C(24)	117.9(3)
P(1)-C(4)-C(9)	120.23(18)	C(22)-C(23)-C(28)	123.04(23)
C(5)-C(4)-C(9)	120.55(21)	C(24)-C(23)-C(28)	119.06(24)
C(4)-C(5)-C(6)	117.41(24)	C(23)-C(24)-C(25)	121.9(3)
C(4)-C(5)-C(10)	125.92(22)	C(24)-C(25)-C(26)	118.56(24)
C(6)-C(5)-C(10)	116.67(23)	C(24)-C(25)-C(31)	119.9(3)
C(5)-C(6)-C(7)	123.64(25)	C(26)-C(25)-C(31)	121.5(3)
C(6)-C(7)-C(8)	117.47(23)	C(25)-C(26)-C(27)	122.5(3)
C(6)-C(7)-C(14)	121.74(25)	C(22)-C(27)-C(26)	117.48(25)
C(8)-C(7)-C(14)	120.8(3)	C(22)-C(27)-C(34)	123.83(22)
C(7)-C(8)-C(9)	123.9(3)	C(26)-C(27)-C(34)	118.69(24)
C(4)-C(9)-C(8)	117.06(23)	C(23)-C(28)-C(29)	110.1(3)
C(4)-C(9)-C(18)	125.82(21)	C(23)-C(28)-C(30)	112.5(3)
C(8)-C(9)-C(18)	117.08(23)	C(29)-C(28)-C(30)	110.3(3)
C(5)-C(10)-C(11)	111.11(24)	C(25)-C(31)-C(32)	112.1(3)
C(5)-C(10)-C(12)	111.52(24)	C(25)-C(31)-C(33)	111.4(3)
C(5)-C(10)-C(13)	111.87(22)	C(32)-C(31)-C(33)	110.3(3)
C(11)-C(10)-C(12)	112.4(3)	C(27)-C(34)-C(35)	111.1(3)
C(11)-C(10)-C(13)	104.97(25)	C(27)-C(34)-C(36)	111.54(24)
C(12)-C(10)-C(13)	104.6(3)	C(35)-C(34)-C(36)	111.0(3)
C(7)-C(14)-C(15)	113.9(3)	C(41)-C(42)-N(43)	178.4(5)

**Table S15.** Torsion angles (deg) for [(2,4,6-(*i*-Pr)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)SCH<sub>2</sub>CH=PMes\*]PdMeCl 10a .

C11	Pd1	P1	C2	-44.74(16)	C11	Pd1	P1	C4	128.00(14)
S1	Pd1	P1	C2	-7.84(16)	S1	Pd1	P1	C4	164.91(14)
C1	Pd1	P1	C2	174.60(23)	C1	Pd1	P1	C4	-12.65(20)
C11	Pd1	S1	C3	-169.03(17)	C11	Pd1	S1	C22	-55.73(14)
P1	Pd1	S1	C3	13.96(15)	P1	Pd1	S1	C22	127.26(15)
C1	Pd1	S1	C3	50.19(22)	C1	Pd1	S1	C22	163.49(21)
Pd1	P1	C2	C3	-2.27(19)	C4	P1	C2	C3	-176.5( 4)
Pd1	P1	C4	C5	-80.7( 3)	Pd1	P1	C4	C9	94.0( 3)
C2	P1	C4	C5	92.0( 3)	C2	P1	C4	C9	-93.2( 3)
Pd1	S1	C3	C2	-18.77(19)	C22	S1	C3	C2	-141.2( 4)
Pd1	S1	C22	C23	135.9( 3)	Pd1	S1	C22	C27	-42.14(22)
C3	S1	C22	C23	-108.9( 3)	C3	S1	C22	C27	73.0( 3)
P1	C2	C3	S1	14.80( 8)	P1	C4	C5	C6	173.8( 5)
P1	C4	C5	C10	-7.31(18)	C9	C4	C5	C6	-1.0( 3)
C9	C4	C5	C10	178.0( 5)	P1	C4	C9	C8	-174.1( 5)
P1	C4	C9	C18	8.08(18)	C5	C4	C9	C8	0.53(25)
C5	C4	C9	C18	-177.2( 5)	C4	C5	C6	C7	0.18(25)
C10	C5	C6	C7	-178.8( 6)	C4	C5	C10	C11	-62.0( 4)
C4	C5	C10	C12	64.2( 4)	C4	C5	C10	C13	-178.9( 5)
C6	C5	C10	C11	117.0( 5)	C6	C5	C10	C12	-116.8( 5)
C6	C5	C10	C13	0.0( 3)	C5	C6	C7	C8	1.0( 3)
C5	C6	C7	C14	-178.8( 6)	C6	C7	C8	C9	-1.6( 3)
C14	C7	C8	C9	178.2( 6)	C6	C7	C14	C15	1.2( 4)
C6	C7	C14	C16	120.8( 6)	C6	C7	C14	C17	-122.0( 6)
C8	C7	C14	C15	-178.6( 7)	C8	C7	C14	C16	-59.0( 4)
C8	C7	C14	C17	58.2( 4)	C7	C8	C9	C4	0.79(25)
C7	C8	C9	C18	178.8( 5)	C4	C9	C18	C19	-174.8( 5)
C4	C9	C18	C20	67.6( 4)	C4	C9	C18	C21	-55.6( 3)
C8	C9	C18	C19	7.5( 3)	C8	C9	C18	C20	-110.1( 5)
C8	C9	C18	C21	126.6( 5)	S1	C22	C23	C24	-178.4( 5)
S1	C22	C23	C28	0.17(20)	C27	C22	C23	C24	-0.3( 3)
C27	C22	C23	C28	178.3( 5)	S1	C22	C27	C26	178.2( 5)
S1	C22	C27	C34	-1.92(19)	C23	C22	C27	C26	0.2( 3)
C23	C22	C27	C34	-179.9( 5)	C22	C23	C24	C25	0.7( 3)
C28	C23	C24	C25	-178.0( 6)	C22	C23	C28	C29	-97.6( 5)
C22	C23	C28	C30	139.0( 6)	C24	C23	C28	C29	80.9( 5)
C24	C23	C28	C30	-42.5( 4)	C23	C24	C25	C26	-0.9( 3)
C23	C24	C25	C31	-179.4( 6)	C24	C25	C26	C27	0.7( 3)
C31	C25	C26	C27	179.3( 6)	C24	C25	C31	C32	-132.8( 6)
C24	C25	C31	C33	103.1( 6)	C26	C25	C31	C32	48.7( 4)
C26	C25	C31	C33	-75.4( 5)	C25	C26	C27	C22	-0.4( 3)
C25	C26	C27	C34	179.7( 6)	C22	C27	C34	C35	118.9( 5)
C22	C27	C34	C36	-116.6( 5)	C26	C27	C34	C35	-61.2( 4)
C26	C27	C34	C36	63.3( 4)					

Table S16. Crystal Data and Structure Refinement for [(2,4,6-(i-Pr)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)SCMe<sub>2</sub>CH=PMes\*]PdMeCl 13.

Space Group and Cell Dimensions      Monoclinic,      P 2<sub>1</sub>/n  
 a 11.9591(5)    b 15.8500(7)    c 23.3435(10)  
 beta 104.795(1)  
 Volume 4278.1(3)A\*\*3

Empirical formula : C40 H65 S Cl Pd P N

Cell dimensions were obtained from 6741 reflections with 2Theta angle in the range 5.00 - 50.00 degrees.

Crystal dimensions : 0.20 X 0.20 X 0.20 mm

FW = 764.84      Z = 4      F(000) = 1622.11

Dcalc 1.188Mg.m-3, mu 0.61mm-1, lambda 0.71073A, 2Theta(max) 50.0

The intensity data were collected on a Bruker SMART diffractometer, using the omega scan mode.

The h,k,l ranges used during structure solution and refinement are :--

Hmin,max -14 13; Kmin,max 0 18; Lmin,max 0 27

No. of reflections measured 36040

No. of unique reflections 7572

No. of reflections with Inet > 2.5sigma(Inet) 6236

Merging R-value on intensities 0.038

Correction was made for absorption using SADABS

Details of the last least squares cycle

110 atoms, 407 parameters Full-matrix on Fo Counter wts (k 0.000300)

The residuals are as follows :--

Significant reflections: 6236 Rf 0.038, Rw 0.050

All reflections: 7572 Rf 0.047, Rw 0.051

Included reflections: 6236 Rf 0.038, Rw 0.050 GoF 1.9215

where Rf = Sum(Fo-Fc)/Sum(Fo),

Rw = Sqrt[Sum(w(Fo-Fc)\*\*2)/Sum(wFo\*\*2)] and

GoF = Sqrt[Sum(w(Fo-Fc)\*\*2)/(No. of reflns - No. of params.)]

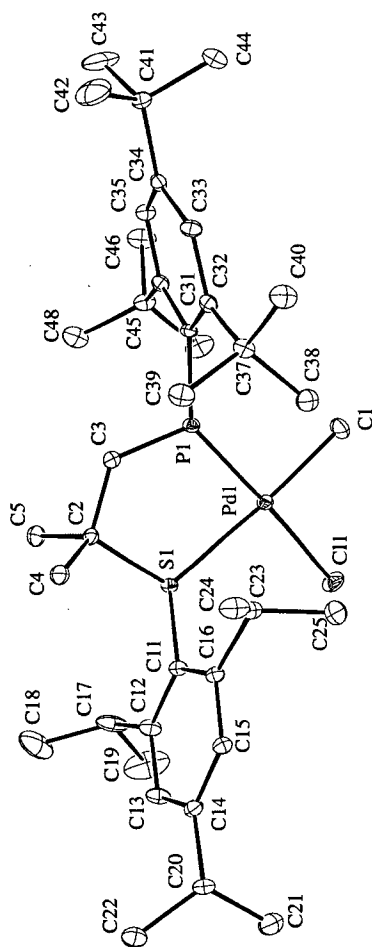
The maximum shift/sigma ratio was 0.001.

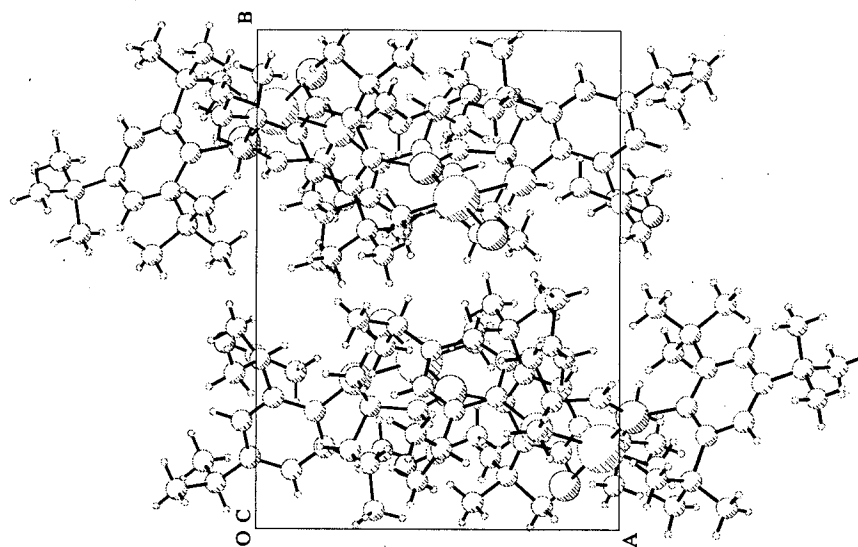
Last D-map: Minimum density -0.650e/A\*\*3, Maximum density 0.720e/A\*\*3.

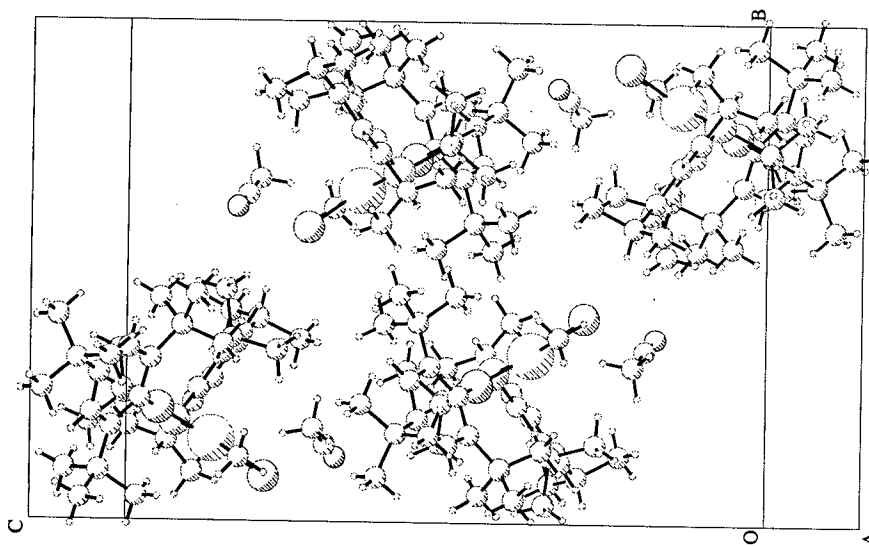
Secondary ext. coeff. 4.3373microns sigma 0.2717

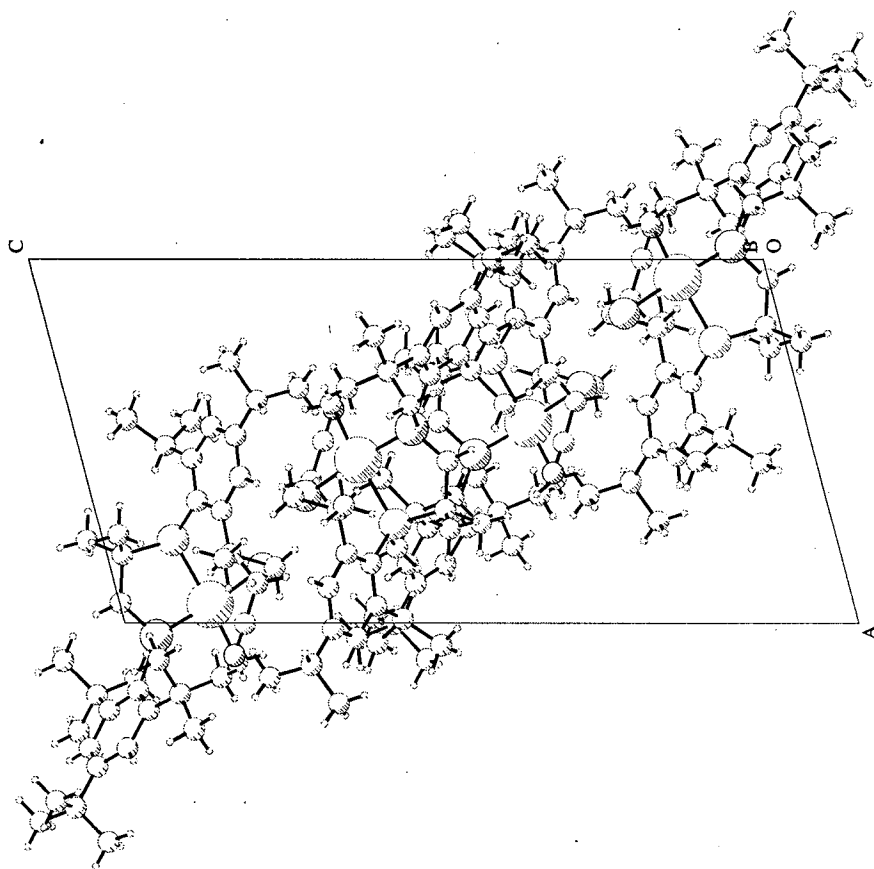


**Figure S6.** Structural View (50% Ellipsoids) and Packing Diagrams of [(2,4,6-(*i*-Pr)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)SCMe<sub>2</sub>CH=PMes\*]PdMeCl 13.









**Table S17.** Atomic Parameters x,y,z and Biso for [(2,4,6-(i-Pr)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)SCMe<sub>2</sub>CH=PMes\*]PdMeCl 13.

E.S.Ds. refer to the last digit printed.

	x	y	z	Biso
Pd1	0.050345 (20)	0.836582 (15)	0.122802 (10)	1.254 (11)
Cl1	0.14915 ( 8)	0.91085 ( 6)	0.20766 ( 4)	2.39 ( 4)
S1	0.22674 ( 6)	0.79946 ( 5)	0.09542 ( 3)	1.19 ( 3)
P1	-0.03566 ( 7)	0.77469 ( 5)	0.03835 ( 4)	1.23 ( 3)
C1	-0.1020 ( 3)	0.8729 ( 3)	0.14008 (16)	2.47 (16)
C2	0.1852 ( 3)	0.74456 (20)	0.02107 (13)	1.25 (12)
C3	0.0547 ( 3)	0.73724 (20)	0.00114 (13)	1.35 (12)
C4	0.2414 ( 3)	0.65780 (21)	0.02265 (15)	1.81 (14)
C5	0.2257 ( 3)	0.80292 (23)	-0.02235 (15)	1.92 (14)
C11	0.3376 ( 3)	0.73507 (20)	0.14262 (13)	1.30 (13)
C12	0.4532 ( 3)	0.76176 (21)	0.15034 (15)	1.74 (13)
C13	0.5400 ( 3)	0.71491 (22)	0.18811 (16)	2.02 (15)
C14	0.5171 ( 3)	0.64310 (21)	0.21820 (14)	1.57 (13)
C15	0.4021 ( 3)	0.61966 (21)	0.20969 (14)	1.48 (13)
C16	0.3110 ( 3)	0.66380 (20)	0.17246 (14)	1.36 (12)
C17	0.4892 ( 3)	0.83815 (24)	0.11892 (20)	2.93 (17)
C18	0.5600 ( 4)	0.8105 ( 3)	0.07584 (25)	4.95 (25)
C19	0.5553 ( 4)	0.9019 ( 3)	0.1625 ( 3)	5.8 ( 3)
C20	0.6121 ( 3)	0.59296 (22)	0.25978 (14)	1.80 (14)
C21	0.6461 ( 3)	0.6352 ( 3)	0.32125 (17)	2.95 (17)
C22	0.7192 ( 3)	0.57930 (25)	0.23620 (16)	2.74 (16)
C23	0.1878 ( 3)	0.63275 (22)	0.16820 (14)	1.67 (13)
C24	0.1750 ( 3)	0.53734 (23)	0.15818 (17)	2.45 (15)
C25	0.1519 ( 3)	0.6576 ( 3)	0.22438 (17)	2.88 (18)
C31	-0.18359 (25)	0.75414 (20)	-0.00577 (13)	1.22 (12)
C32	-0.2380 ( 3)	0.67578 (20)	0.00159 (14)	1.37 (13)
C33	-0.3398 ( 3)	0.65489 (20)	-0.04104 (15)	1.58 (13)
C34	-0.3910 ( 3)	0.70601 (21)	-0.08861 (14)	1.46 (13)
C35	-0.3397 ( 3)	0.78360 (21)	-0.09246 (14)	1.57 (13)
C36	-0.2382 ( 3)	0.81103 (20)	-0.05246 (14)	1.39 (13)
C37	-0.1924 ( 3)	0.60834 (21)	0.05009 (14)	1.60 (14)
C38	-0.1457 ( 3)	0.64579 (22)	0.11241 (15)	2.06 (14)
C39	-0.0980 ( 3)	0.55469 (22)	0.03317 (16)	2.14 (15)
C40	-0.2887 ( 3)	0.54693 (23)	0.05683 (16)	2.39 (15)
C41	-0.5029 ( 3)	0.67711 (22)	-0.13282 (15)	1.73 (13)
C42	-0.4854 ( 4)	0.5898 ( 3)	-0.15667 (20)	4.47 (21)
C43	-0.5416 ( 4)	0.7363 ( 3)	-0.18577 (19)	4.30 (20)
C44	-0.5979 ( 3)	0.6725 ( 3)	-0.10044 (19)	4.03 (23)
C45	-0.1957 ( 3)	0.90040 (21)	-0.06325 (14)	1.73 (13)
C46	-0.2948 ( 3)	0.95508 (23)	-0.10141 (18)	2.65 (17)
C47	-0.1514 ( 3)	0.95146 (23)	-0.00566 (18)	3.00 (18)
C48	-0.1012 ( 3)	0.89643 (24)	-0.09698 (17)	2.74 (17)
N51	0.9127 ( 4)	0.3714 ( 3)	0.13819 (21)	5.87 (23)
C52	0.9982 ( 4)	0.3467 ( 3)	0.16373 (19)	3.48 (20)
C53	1.1090 ( 4)	0.3136 ( 3)	0.19459 (23)	5.11 (24)
H1a	-0.086	0.903	0.177	3.3
H1b	-0.144	0.909	0.109	3.3

H1c	-0.147	0.824	0.143	3.3
H3	0.022	0.710	-0.036	2.1
H4a	0.215	0.622	0.050	2.6
H4b	0.220	0.633	-0.016	2.6
H4c	0.324	0.664	0.035	2.6
H5a	0.190	0.857	-0.023	2.7
H5b	0.308	0.809	-0.010	2.7
H5c	0.204	0.779	-0.061	2.7
H13	0.619	0.732	0.194	2.7
H15	0.385	0.571	0.230	2.2
H17	0.421	0.866	0.096	3.6
H18a	0.515	0.771	0.048	6.0
H18b	0.579	0.858	0.055	6.0
H18c	0.630	0.783	0.098	6.0
H19a	0.510	0.920	0.189	6.0
H19b	0.625	0.875	0.185	6.0
H19c	0.575	0.950	0.142	6.0
H20	0.581	0.538	0.265	2.5
H21a	0.579	0.643	0.336	3.6
H21b	0.701	0.601	0.348	3.6
H21c	0.680	0.689	0.318	3.6
H22a	0.696	0.552	0.198	3.5
H22b	0.753	0.633	0.232	3.5
H22c	0.775	0.545	0.263	3.5
H23	0.137	0.660	0.135	2.4
H24a	0.198	0.522	0.123	3.1
H24b	0.224	0.508	0.192	3.1
H24c	0.096	0.521	0.154	3.1
H25a	0.161	0.718	0.230	3.7
H25b	0.073	0.642	0.221	3.7
H25c	0.200	0.629	0.258	3.7
H33	-0.376	0.602	-0.037	2.3
H35	-0.376	0.821	-0.124	2.3
H38a	-0.205	0.679	0.123	2.8
H38b	-0.122	0.601	0.141	2.8
H38c	-0.080	0.681	0.113	2.8
H39a	-0.036	0.591	0.029	2.9
H39b	-0.069	0.514	0.064	2.9
H39c	-0.131	0.526	-0.004	2.9
H40a	-0.322	0.521	0.019	3.1
H40b	-0.257	0.504	0.085	3.1
H40c	-0.347	0.578	0.070	3.1
H42a	-0.462	0.551	-0.124	4.9
H42b	-0.556	0.570	-0.183	4.9
H42c	-0.427	0.592	-0.178	4.9
H43a	-0.482	0.739	-0.206	4.7
H43b	-0.612	0.716	-0.212	4.7
H43c	-0.555	0.791	-0.172	4.7
H44a	-0.610	0.728	-0.086	4.8
H44b	-0.668	0.653	-0.127	4.8
H44c	-0.576	0.634	-0.068	4.8
H46a	-0.327	0.927	-0.138	3.3
H46b	-0.354	0.963	-0.081	3.3
H46c	-0.265	1.009	-0.109	3.3
H47a	-0.210	0.953	0.016	3.6
H47b	-0.083	0.925	0.019	3.6
H47c	-0.133	1.008	-0.015	3.6

H48a	-0.037	0.863	-0.075	3.5
H48b	-0.133	0.871	-0.135	3.5
H48c	-0.075	0.952	-0.102	3.5
H53a	1.124	0.324	0.236	5.3
H53b	1.110	0.254	0.188	5.3
H53c	1.168	0.340	0.179	5.3

Biso is the Mean of the Principal Axes of the Thermal Ellipsoid.

Table S19.  $u(i,j)$  or U Values\*100 for [(2,4,6-(i-Pr)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)SCMe<sub>2</sub>CH=PMes\*]PdMeCl 13.

E.S.Ds. refer to the last digit printed

	u11(U)	u22	u33	u12	u13	u23
Pd1	1.508(15)	1.619(16)	1.555(15)	-0.019(10)	0.239(10)	-0.308(10)
Cl1	3.40 ( 5)	3.10 ( 5)	2.14 ( 4)	-0.06 ( 4)	-0.12 ( 4)	-1.07 ( 4)
S1	1.37 ( 4)	1.32 ( 4)	1.70 ( 4)	0.00 ( 3)	0.14 ( 3)	-0.03 ( 3)
P1	1.29 ( 4)	1.57 ( 5)	1.71 ( 4)	-0.13 ( 3)	0.18 ( 3)	-0.24 ( 3)
C1	2.30 (19)	4.07 (23)	3.24 (20)	0.45 (17)	1.12 (16)	-1.07 (18)
C2	1.67 (16)	1.54 (17)	1.49 (15)	0.05 (13)	0.31 (12)	-0.19 (13)
C3	1.72 (16)	1.66 (18)	1.68 (16)	-0.11 (13)	0.34 (13)	0.08 (14)
C4	2.38 (18)	2.24 (20)	2.22 (18)	0.11 (14)	0.54 (14)	-0.36 (15)
C5	2.55 (19)	2.75 (20)	2.14 (18)	-0.04 (15)	0.85 (15)	0.36 (15)
C11	1.50 (16)	1.48 (17)	1.77 (16)	0.05 (13)	0.06 (13)	-0.06 (13)
C12	1.80 (17)	1.79 (18)	2.89 (19)	-0.23 (14)	0.33 (14)	0.23 (15)
C13	1.42 (17)	2.49 (21)	3.43 (20)	-0.22 (14)	0.01 (15)	0.25 (16)
C14	2.11 (17)	2.10 (19)	1.57 (16)	0.16 (14)	0.09 (14)	-0.12 (14)
C15	1.89 (17)	1.83 (19)	1.77 (16)	-0.02 (14)	0.20 (13)	0.18 (14)
C16	1.80 (16)	1.45 (17)	1.76 (16)	-0.03 (13)	0.18 (13)	-0.15 (14)
C17	1.60 (18)	2.93 (23)	6.1 ( 3)	-0.29 (16)	0.05 (18)	2.28 (20)
C18	3.8 ( 3)	7.1 ( 4)	8.8 ( 4)	0.85 (24)	3.3 ( 3)	4.3 ( 3)
C19	7.1 ( 4)	3.5 ( 3)	9.1 ( 4)	-2.5 ( 3)	-2.4 ( 3)	1.6 ( 3)
C20	1.74 (17)	2.47 (20)	2.28 (18)	0.25 (14)	-0.14 (14)	0.24 (15)
C21	3.38 (22)	4.7 ( 3)	2.67 (20)	0.99 (19)	-0.04 (17)	-0.22 (19)
C22	3.03 (21)	3.80 (24)	3.35 (21)	1.46 (18)	0.40 (17)	0.50 (18)
C23	1.69 (17)	2.24 (18)	2.23 (17)	-0.33 (14)	0.16 (14)	0.78 (15)
C24	2.50 (19)	2.41 (21)	3.88 (22)	-0.52 (16)	-0.13 (16)	1.11 (17)
C25	2.72 (20)	5.3 ( 3)	3.03 (21)	-0.41 (18)	1.03 (17)	0.44 (19)
C31	1.20 (15)	1.59 (17)	1.77 (16)	0.10 (13)	0.21 (12)	-0.20 (13)
C32	1.60 (16)	1.48 (18)	2.18 (17)	0.06 (13)	0.57 (13)	-0.12 (14)
C33	1.55 (16)	1.68 (18)	2.60 (18)	-0.42 (13)	0.24 (14)	-0.11 (14)
C34	1.58 (16)	2.08 (19)	2.02 (17)	-0.03 (13)	0.68 (13)	-0.40 (14)
C35	1.69 (16)	1.99 (19)	2.06 (17)	-0.03 (13)	0.12 (13)	0.18 (14)
C36	1.66 (16)	1.62 (17)	2.02 (17)	0.19 (13)	0.51 (13)	0.05 (14)
C37	1.90 (17)	1.50 (18)	2.68 (18)	-0.10 (13)	0.57 (14)	0.22 (14)
C38	2.65 (19)	2.56 (21)	2.60 (19)	-0.28 (15)	0.64 (16)	0.53 (15)
C39	2.58 (19)	1.87 (19)	3.51 (20)	0.35 (15)	0.46 (16)	0.38 (16)
C40	2.79 (19)	2.47 (21)	3.66 (21)	-0.51 (16)	0.55 (16)	0.95 (17)
C41	1.84 (17)	2.60 (20)	1.98 (17)	-0.51 (14)	0.16 (14)	-0.45 (15)
C42	4.8 ( 3)	5.5 ( 3)	5.4 ( 3)	-0.22 (23)	-0.97 (22)	-2.91 (25)
C43	3.72 (24)	6.7 ( 3)	4.3 ( 3)	-2.37 (23)	-1.90 (20)	1.53 (24)
C44	1.95 (20)	9.5 ( 4)	3.96 (25)	-1.25 (22)	0.98 (18)	-0.87 (24)
C45	2.02 (18)	1.72 (18)	2.51 (18)	-0.39 (14)	0.00 (14)	0.48 (15)
C46	2.78 (20)	1.75 (20)	4.95 (24)	0.00 (16)	-0.11 (17)	0.61 (17)
C47	4.76 (24)	1.77 (21)	4.15 (23)	-0.65 (18)	-0.16 (19)	-0.30 (18)
C48	3.14 (21)	2.86 (22)	4.49 (24)	-0.08 (17)	1.11 (18)	1.32 (18)
N51	5.1 ( 3)	7.2 ( 3)	8.5 ( 3)	-1.43 (23)	-1.15 (25)	3.4 ( 3)
C52	4.9 ( 3)	3.5 ( 3)	3.90 (25)	-1.63 (20)	-0.51 (21)	0.92 (19)
C53	5.4 ( 3)	4.9 ( 3)	6.9 ( 3)	-1.57 (24)	-2.4 ( 3)	1.8 ( 3)
H1a	4.2					
H1b	4.2					
H1c	4.2					
H3	2.7					
H4a	3.3					
H4b	3.3					



H4c	3.3
H5a	3.5
H5b	3.5
H5c	3.5
H13	3.4
H15	2.8
H17	4.5
H18a	7.6
H18b	7.6
H18c	7.6
H19a	7.6
H19b	7.6
H19c	7.6
H20	3.2
H21a	4.6
H21b	4.6
H21c	4.6
H22a	4.4
H22b	4.4
H22c	4.4
H23	3.1
H24a	3.9
H24b	3.9
H24c	3.9
H25a	4.7
H25b	4.7
H25c	4.7
H33	2.9
H35	2.9
H38a	3.6
H38b	3.6
H38c	3.6
H39a	3.7
H39b	3.7
H39c	3.7
H40a	4.0
H40b	4.0
H40c	4.0
H42a	6.3
H42b	6.3
H42c	6.3
H43a	5.9
H43b	5.9
H43c	5.9
H44a	6.1
H44b	6.1
H44c	6.1
H46a	4.2
H46b	4.2
H46c	4.2
H47a	4.6
H47b	4.6
H47c	4.6
H48a	4.5
H48b	4.5
H48c	4.5
H53a	6.8

H53b 6.8  
H53c 6.8

Anisotropic Temperature Factors are of the form  
Temp =  $-2 \cdot \pi^2 (h^2 u_{11}^2 a^2 + \dots + 2 h k u_{12}^2 a^2 b^2 + \dots)$

**Table S20.** Bond Lengths (Å) and Angles (deg) for [(2,4,6-(*i*-Pr)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)SCMe<sub>2</sub>CH=PMes\*]PdMeCl 13.

DISANG -- The NRCVAX Distance and Angle Program

The Space Group is P 21/N                      Centrosymmetric  
The Equivalent Positions are:

1)        x            y            z        2) 1/2-x   1/2+y   1/2-z

The Lattice is Primitive. There are no Centering Vectors

Pd(1)-Cl(1)	2.3475(8)	C(20)-C(22)	1.532(5)
Pd(1)-S(1)	2.4277(8)	C(23)-C(24)	1.532(5)
Pd(1)-P(1)	2.2071(8)	C(23)-C(25)	1.532(5)
Pd(1)-C(1)	2.047(3)	C(31)-C(32)	1.433(4)
S(1)-C(2)	1.891(3)	C(31)-C(36)	1.436(4)
S(1)-C(11)	1.808(3)	C(32)-C(33)	1.401(4)
P(1)-C(3)	1.659(3)	C(32)-C(37)	1.551(5)
P(1)-C(31)	1.835(3)	C(33)-C(34)	1.385(5)
C(2)-C(3)	1.515(4)	C(34)-C(35)	1.388(5)
C(2)-C(4)	1.527(5)	C(34)-C(41)	1.537(4)
C(2)-C(5)	1.539(5)	C(35)-C(36)	1.398(4)
C(11)-C(12)	1.412(4)	C(36)-C(45)	1.547(5)
C(11)-C(16)	1.406(4)	C(37)-C(38)	1.538(5)
C(12)-C(13)	1.393(5)	C(37)-C(39)	1.543(5)
C(12)-C(17)	1.534(5)	C(37)-C(40)	1.547(5)
C(13)-C(14)	1.401(5)	C(41)-C(42)	1.527(6)
C(14)-C(15)	1.389(4)	C(41)-C(43)	1.527(5)
C(14)-C(20)	1.517(4)	C(41)-C(44)	1.518(5)
C(15)-C(16)	1.396(4)	C(45)-C(46)	1.553(5)
C(16)-C(23)	1.531(4)	C(45)-C(47)	1.542(5)
C(17)-C(18)	1.534(7)	C(45)-C(48)	1.535(5)
C(17)-C(19)	1.507(6)	N(51)-C(52)	1.114(6)
C(20)-C(21)	1.541(5)	C(52)-C(53)	1.437(7)
Cl(1)-Pd(1)-S(1)	93.43(3)	C(21)-C(20)-C(22)	110.5(3)
Cl(1)-Pd(1)-P(1)	174.87(3)	C(16)-C(23)-C(24)	112.6(3)
Cl(1)-Pd(1)-C(1)	88.52(10)	C(16)-C(23)-C(25)	109.7(3)
S(1)-Pd(1)-P(1)	83.98(3)	C(24)-C(23)-C(25)	110.2(3)
S(1)-Pd(1)-C(1)	175.68(11)	P(1)-C(31)-C(32)	119.26(22)
P(1)-Pd(1)-C(1)	93.78(10)	P(1)-C(31)-C(36)	120.05(23)
Pd(1)-S(1)-C(2)	108.10(10)	C(32)-C(31)-C(36)	120.2(3)
Pd(1)-S(1)-C(11)	121.86(11)	C(31)-C(32)-C(33)	117.3(3)
C(2)-S(1)-C(11)	106.24(14)	C(31)-C(32)-C(37)	126.8(3)
Pd(1)-P(1)-C(3)	114.17(11)	C(33)-C(32)-C(37)	115.8(3)
Pd(1)-P(1)-C(31)	137.99(10)	C(32)-C(33)-C(34)	123.9(3)
C(3)-P(1)-C(31)	107.81(14)	C(33)-C(34)-C(35)	117.3(3)
S(1)-C(2)-C(3)	109.02(20)	C(33)-C(34)-C(41)	119.7(3)
S(1)-C(2)-C(4)	112.42(21)	C(35)-C(34)-C(41)	123.0(3)
S(1)-C(2)-C(5)	105.94(21)	C(34)-C(35)-C(36)	123.7(3)
C(3)-C(2)-C(4)	110.5(3)	C(31)-C(36)-C(35)	117.4(3)
C(3)-C(2)-C(5)	108.49(25)	C(31)-C(36)-C(45)	126.4(3)
C(4)-C(2)-C(5)	110.3(3)	C(35)-C(36)-C(45)	116.2(3)
P(1)-C(3)-C(2)	124.69(23)	C(32)-C(37)-C(38)	113.5(3)
S(1)-C(11)-C(12)	116.77(24)	C(32)-C(37)-C(39)	109.7(3)
S(1)-C(11)-C(16)	122.11(23)	C(32)-C(37)-C(40)	112.1(3)

C(12)-C(11)-C(16)	121.1(3)	C(38)-C(37)-C(39)	110.0(3)
C(11)-C(12)-C(13)	117.9(3)	C(38)-C(37)-C(40)	104.3(3)
C(11)-C(12)-C(17)	124.1(3)	C(39)-C(37)-C(40)	107.0(3)
C(13)-C(12)-C(17)	117.9(3)	C(34)-C(41)-C(42)	109.8(3)
C(12)-C(13)-C(14)	122.8(3)	C(34)-C(41)-C(43)	113.1(3)
C(13)-C(14)-C(15)	117.3(3)	C(34)-C(41)-C(44)	108.3(3)
C(13)-C(14)-C(20)	122.4(3)	C(42)-C(41)-C(43)	107.7(3)
C(15)-C(14)-C(20)	120.3(3)	C(42)-C(41)-C(44)	109.2(3)
C(14)-C(15)-C(16)	122.8(3)	C(43)-C(41)-C(44)	108.8(3)
C(11)-C(16)-C(15)	118.1(3)	C(36)-C(45)-C(46)	111.7(3)
C(11)-C(16)-C(23)	124.2(3)	C(36)-C(45)-C(47)	113.1(3)
C(15)-C(16)-C(23)	117.7(3)	C(36)-C(45)-C(48)	111.2(3)
C(12)-C(17)-C(18)	110.9(3)	C(46)-C(45)-C(47)	104.4(3)
C(12)-C(17)-C(19)	111.7(4)	C(46)-C(45)-C(48)	106.4(3)
C(18)-C(17)-C(19)	110.7(4)	C(47)-C(45)-C(48)	109.5(3)
C(14)-C(20)-C(21)	110.2(3)	N(51)-C(52)-C(53)	177.8(6)
C(14)-C(20)-C(22)	113.7(3)		

**Table S21.** Torsion Angles (deg) for [(2,4,6-(*i*-Pr)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)SCMe<sub>2</sub>CH-PMes\*]PdMeCl 13.

C11	Pd1	S1	C2	-174.48(17)	C11	Pd1	S1	C11	62.18(16)
P1	Pd1	S1	C2	1.08(15)	P1	Pd1	S1	C11	-122.26(17)
C1	Pd1	S1	C2	-57.81(23)	C1	Pd1	S1	C11	178.86(24)
C11	Pd1	P1	C3	59.56(18)	C11	Pd1	P1	C31	-118.09(17)
S1	Pd1	P1	C3	-0.28(17)	S1	Pd1	P1	C31	-177.93(17)
C1	Pd1	P1	C3	176.0( 3)	C1	Pd1	P1	C31	-1.63(23)
Pd1	S1	C2	C3	-1.75(20)	Pd1	S1	C2	C4	-124.7( 3)
Pd1	S1	C2	C5	114.8( 3)	C11	S1	C2	C3	130.6( 4)
C11	S1	C2	C4	7.7( 3)	C11	S1	C2	C5	-112.8( 4)
Pd1	S1	C11	C12	-135.8( 4)	Pd1	S1	C11	C16	41.51(25)
C2	S1	C11	C12	100.0( 4)	C2	S1	C11	C16	-82.7( 3)
Pd1	P1	C3	C2	-0.93(19)	C31	P1	C3	C2	177.4( 4)
Pd1	P1	C31	C32	-93.7( 3)	Pd1	P1	C31	C36	94.4( 3)
C3	P1	C31	C32	88.6( 4)	C3	P1	C31	C36	-83.3( 4)
S1	C2	C3	P1	1.81( 7)	C4	C2	C3	P1	125.9( 5)
C5	C2	C3	P1	-113.1( 5)	S1	C11	C12	C13	177.8( 6)
S1	C11	C12	C17	-3.31(24)	C16	C11	C12	C13	0.5( 3)
C16	C11	C12	C17	179.3( 6)	S1	C11	C16	C15	-177.7( 6)
S1	C11	C16	C23	0.47(21)	C12	C11	C16	C15	-0.5( 3)
C12	C11	C16	C23	177.7( 6)	C11	C12	C13	C14	0.1( 3)
C17	C12	C13	C14	-178.8( 7)	C11	C12	C17	C18	-114.1( 7)
C11	C12	C17	C19	121.9( 7)	C13	C12	C17	C18	64.8( 5)
C13	C12	C17	C19	-59.2( 5)	C12	C13	C14	C15	-0.7( 3)
C12	C13	C14	C20	-179.3( 7)	C13	C14	C15	C16	0.7( 3)
C20	C14	C15	C16	179.4( 6)	C13	C14	C20	C21	82.1( 5)
C13	C14	C20	C22	-42.6( 4)	C15	C14	C20	C21	-96.5( 5)
C15	C14	C20	C22	138.9( 6)	C14	C15	C16	C11	-0.2( 3)
C14	C15	C16	C23	-178.4( 6)	C11	C16	C23	C24	133.8( 6)
C11	C16	C23	C25	-103.1( 5)	C15	C16	C23	C24	-48.1( 4)
C15	C16	C23	C25	75.0( 5)	P1	C31	C32	C33	-166.8( 5)
P1	C31	C32	C37	9.35(20)	C36	C31	C32	C33	5.1( 3)
C36	C31	C32	C37	-178.7( 6)	P1	C31	C36	C35	166.7( 5)
P1	C31	C36	C45	-13.24(21)	C32	C31	C36	C35	-5.2( 3)
C32	C31	C36	C45	174.9( 6)	C31	C32	C33	C34	-1.3( 3)
C37	C32	C33	C34	-177.9( 6)	C31	C32	C37	C38	44.2( 4)
C31	C32	C37	C39	-79.4( 5)	C31	C32	C37	C40	162.0( 6)
C33	C32	C37	C38	-139.6( 6)	C33	C32	C37	C39	96.8( 5)
C33	C32	C37	C40	-21.8( 3)	C32	C33	C34	C35	-2.4( 3)
C32	C33	C34	C41	-179.9( 6)	C33	C34	C35	C36	2.3( 3)
C41	C34	C35	C36	179.7( 6)	C33	C34	C41	C42	-54.1( 4)
C33	C34	C41	C43	-174.4( 7)	C33	C34	C41	C44	65.0( 5)
C35	C34	C41	C42	128.5( 6)	C35	C34	C41	C43	8.3( 3)
C35	C34	C41	C44	-112.4( 6)	C34	C35	C36	C31	1.5( 3)
C34	C35	C36	C45	-178.6( 6)	C31	C36	C45	C46	-159.1( 6)
C31	C36	C45	C47	-41.6( 4)	C31	C36	C45	C48	82.2( 5)
C35	C36	C45	C46	21.0( 3)	C35	C36	C45	C47	138.5( 6)
C35	C36	C45	C48	-97.7( 5)					