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Supplementary Material

Synthesis and Structure of a Novel Substituted Benzothiazolyl-*N*-phenyl-2-pyridinecarbothioamide; Kinetics of Formation and Electrochemistry of Two of its Palladium Pincer Complexes

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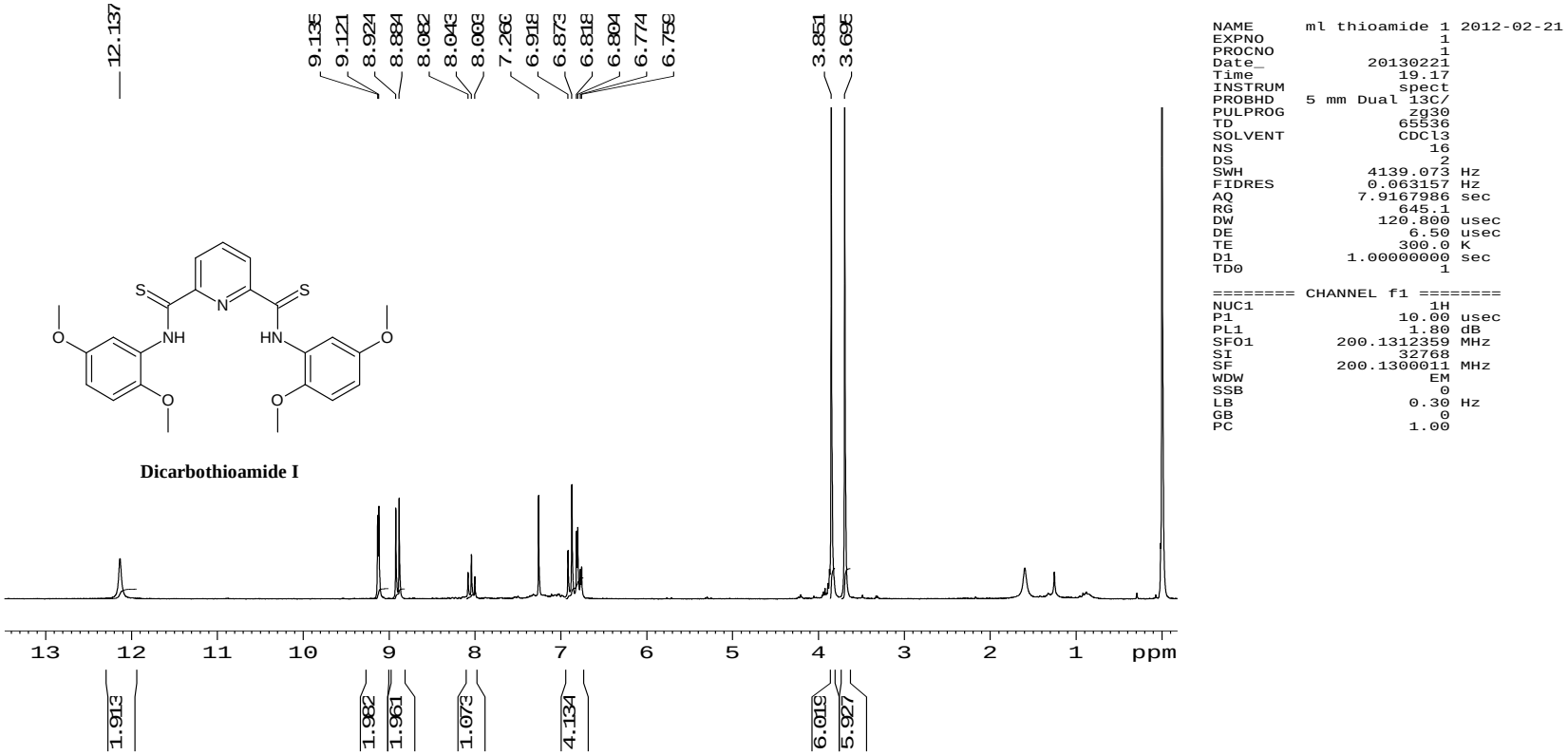
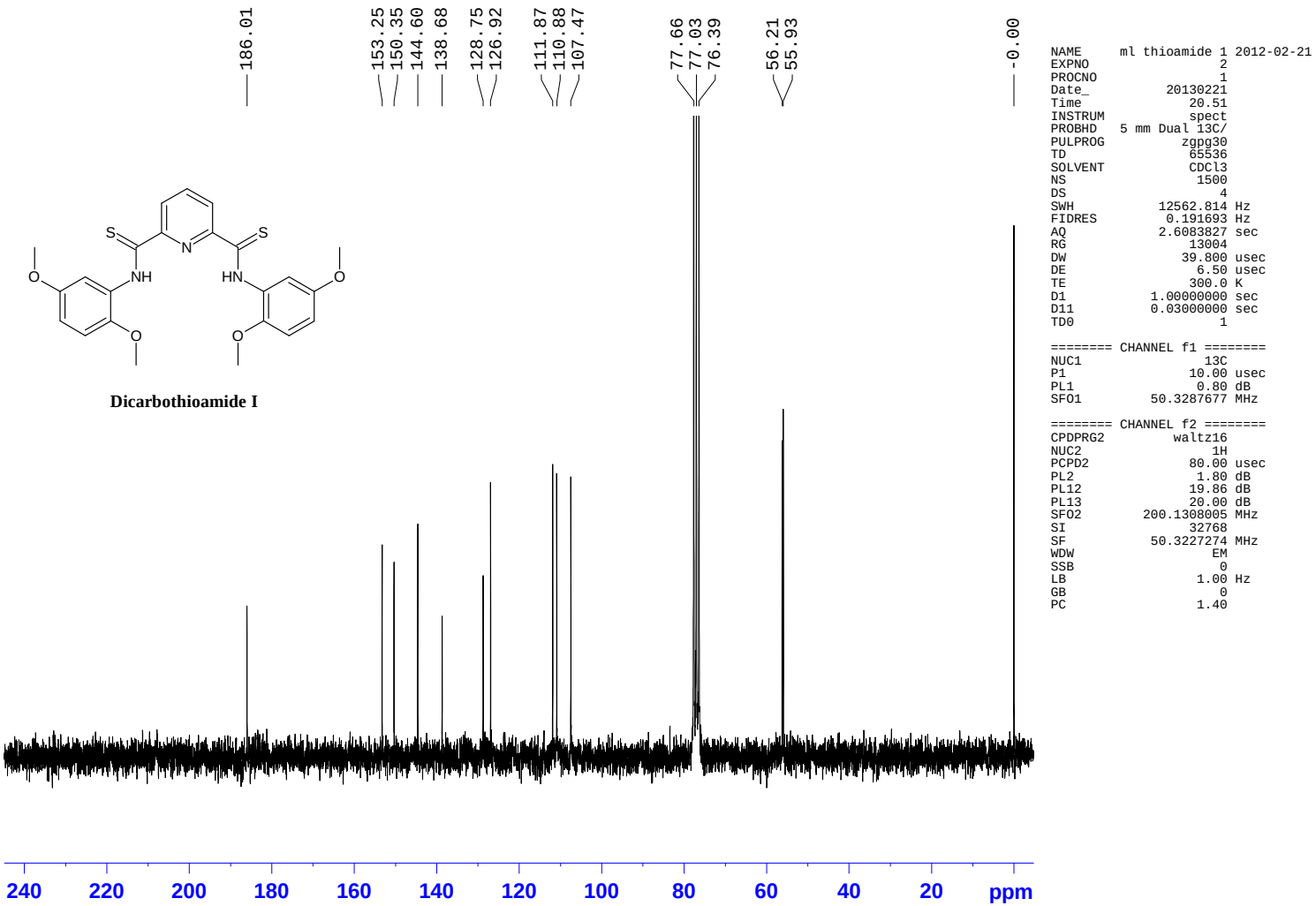


Figure S1: ^{1}HNMR of bis-*N*-(2,5-dimethoxyphenyl)pyridine-2,6-dicarbothioamide (dicarbothioamide I)

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SOLVENT            CDCl3
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DS                     4
SWH           12562.814 Hz
FIDRES         0.191693 Hz
AQ            2.6083827 sec
RG                 13004
DW                39.800 usec
DE                 6.50 usec
TE                300.0 K
D1           1.00000000 sec
D11          0.03000000 sec
TD0                    1

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PL1                0.80 dB
SFO1         50.3287677 MHz

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NUC2                 1H
PCPD2             80.00 usec
PL2                1.80 dB
PL12              19.86 dB
PL13              20.00 dB
SFO2        200.1308005 MHz
SI                 32768
SF           50.3227274 MHz
WDW                  EM
SSB                    0
LB                  1.00 Hz
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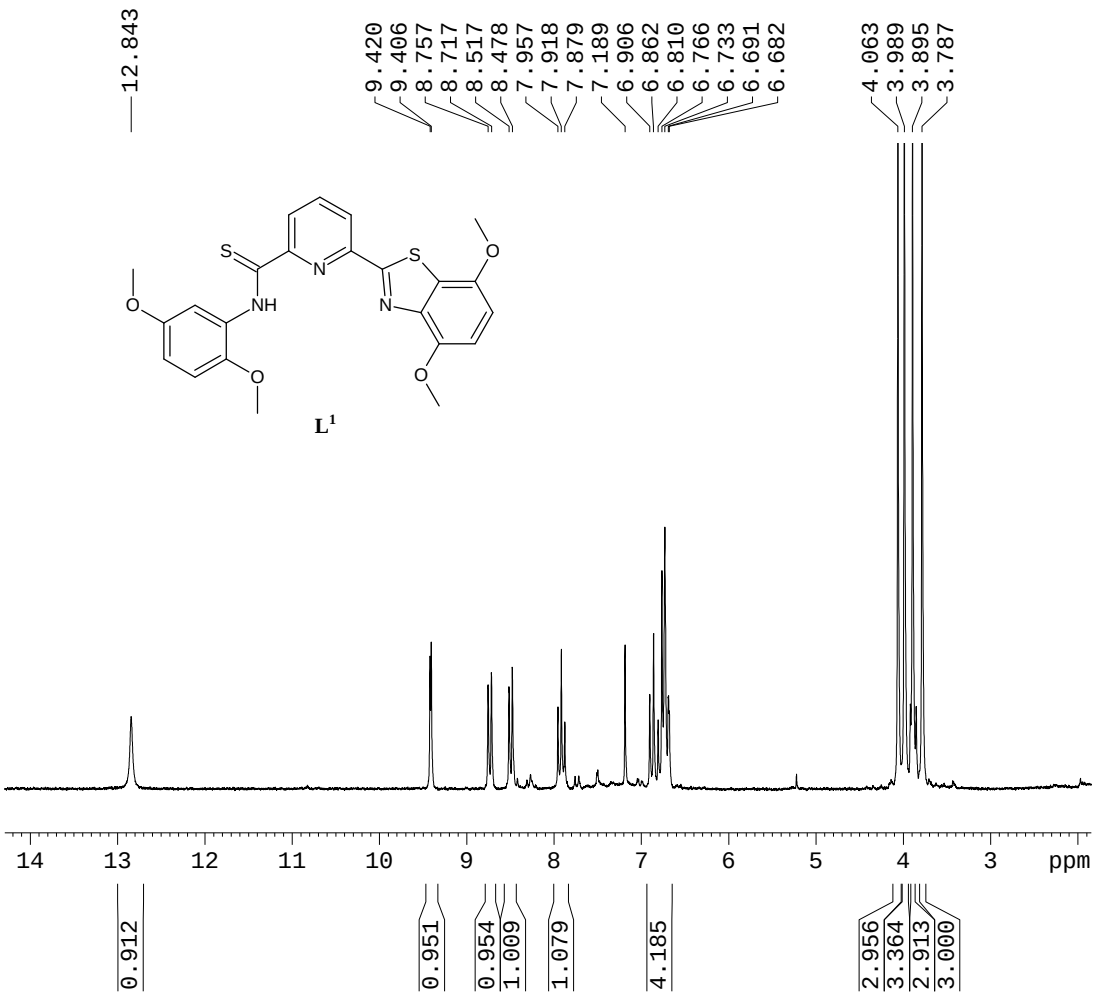
Figure S2: ^{13}CNMR of bis-*N*-(2,5-dimethoxyphenyl)pyridine-2,6-dicarbothioamide (dicarbothioamide I)

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D1           1.00000000 sec
TD0                    1

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PL1                1.80 dB
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SI                32768
SF          200.1300151 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 1.00
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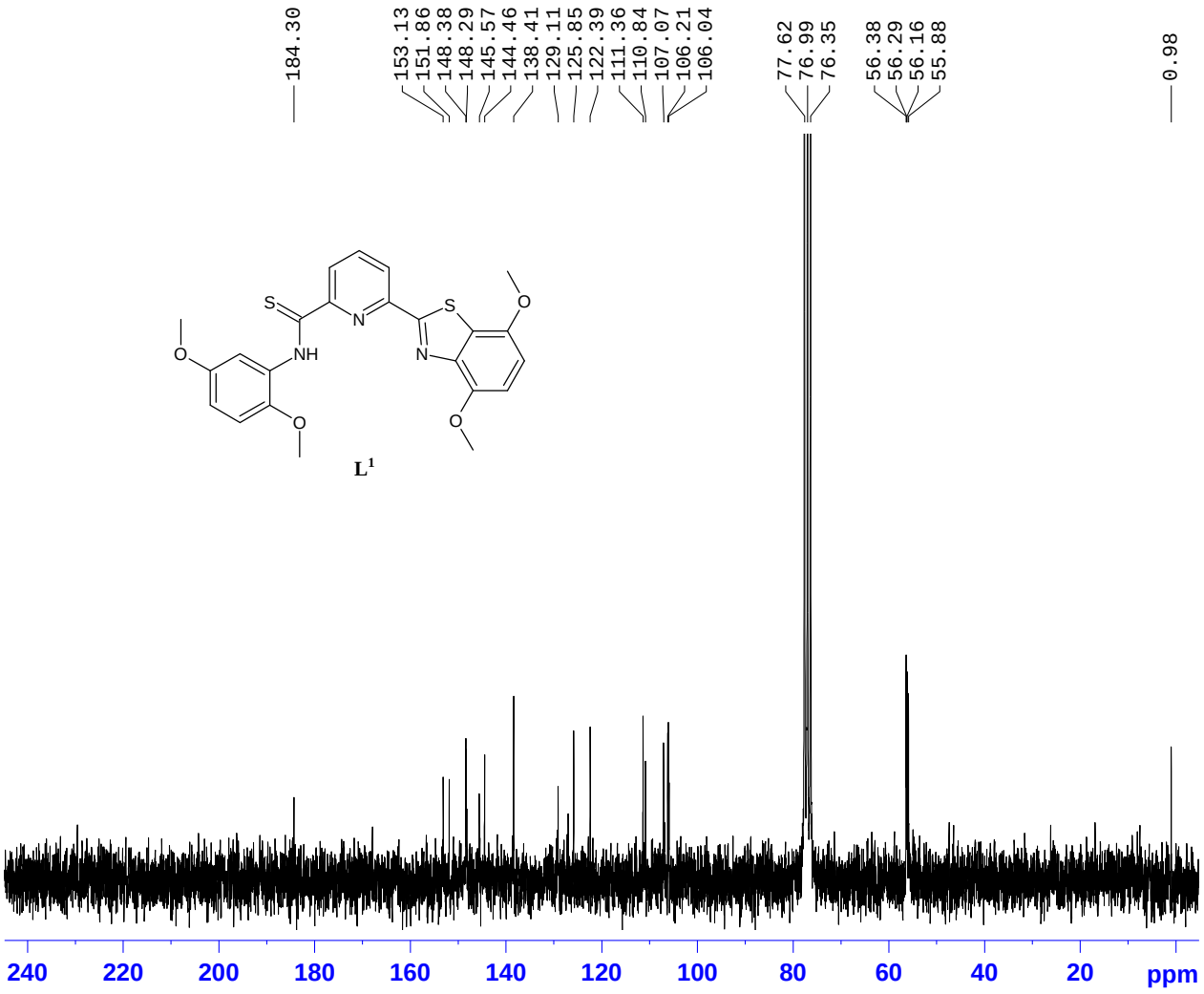
Figure S3: ^{1}HNMR of 6-(4,7-dimethoxy-2-benzothiazolyl)-*N*-(2,5-dimethoxyphenyl)-2-pyridinecarbothioamide (L^{1}).

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TD                 65536
SOLVENT            CDCl3
NS                  1196
DS                     4
SWH            12562.814 Hz
FIDRES          0.191693 Hz
AQ             2.6083827 sec
RG                 16384
DW                39.800 usec
DE                 6.50 usec
TE                300.0 K
D1           1.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
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PL1                0.80 dB
SFO1         50.3287677 MHz

======== CHANNEL f2 ========
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NUC2                  1H
PCPD2             80.00 usec
PL2                1.80 dB
PL12              19.86 dB
PL13              20.00 dB
SFO2        200.1308005 MHz
SI                 32768
SF           50.3227290 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
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Figure S4: ^{13}CNMR of 6-(4,7-dimethoxy-2-benzothiazolyl)-*N*-(2,5-dimethoxyphenyl)-2-pyridinecarbothioamide (L^1)

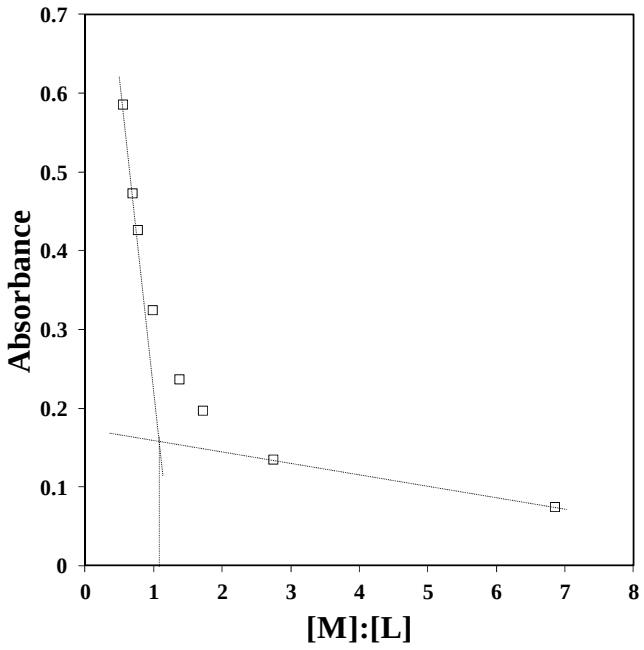

Figure S5: Mole ratio plot of $Pd(OAc)_2$:**L**^{1} at 340 nm.

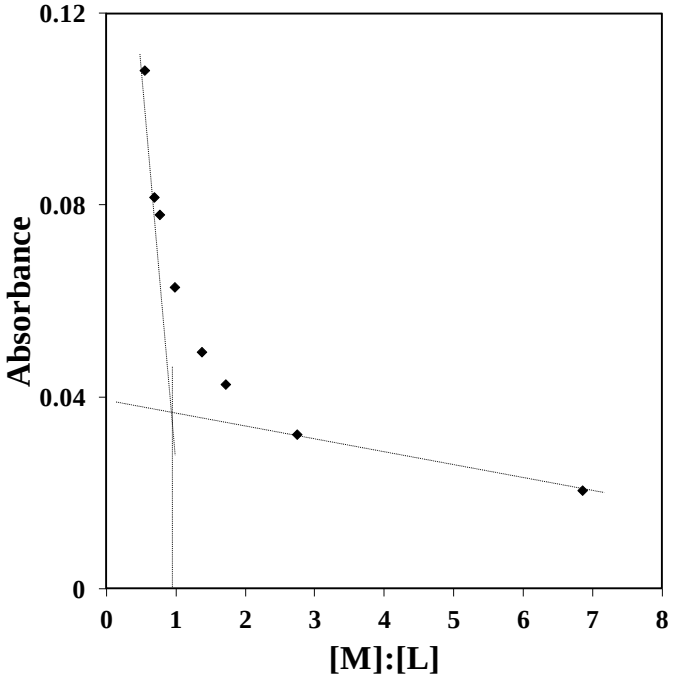

Figure S6: Mole ratio plot of $PdCl_2(CH_3CN)_2$:**L**^{1} at 340 nm.

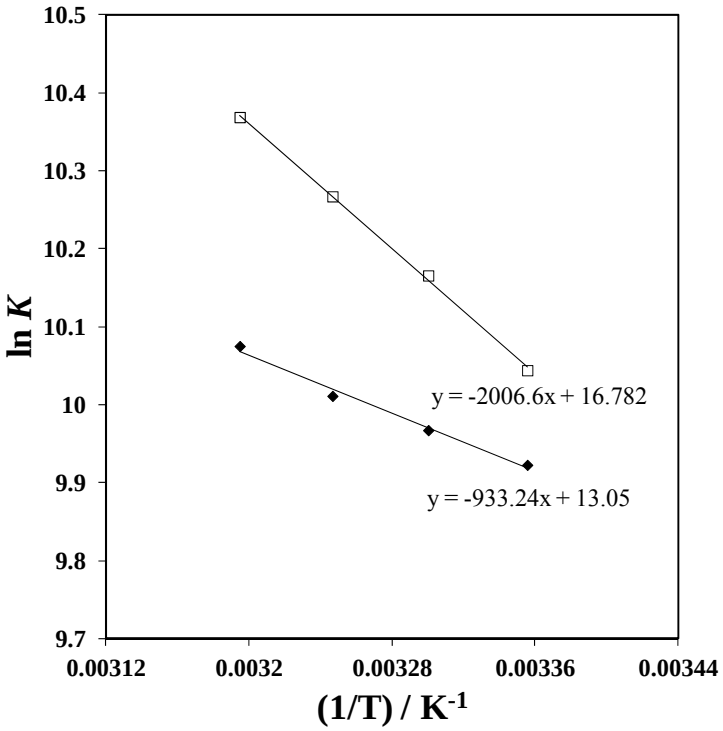

Figure S7: A plot of ln *K* against 1/T for the formation of $PdClL^1$ (♦) and $Pd(OAc)L^1$ (□) in acetonitrile.

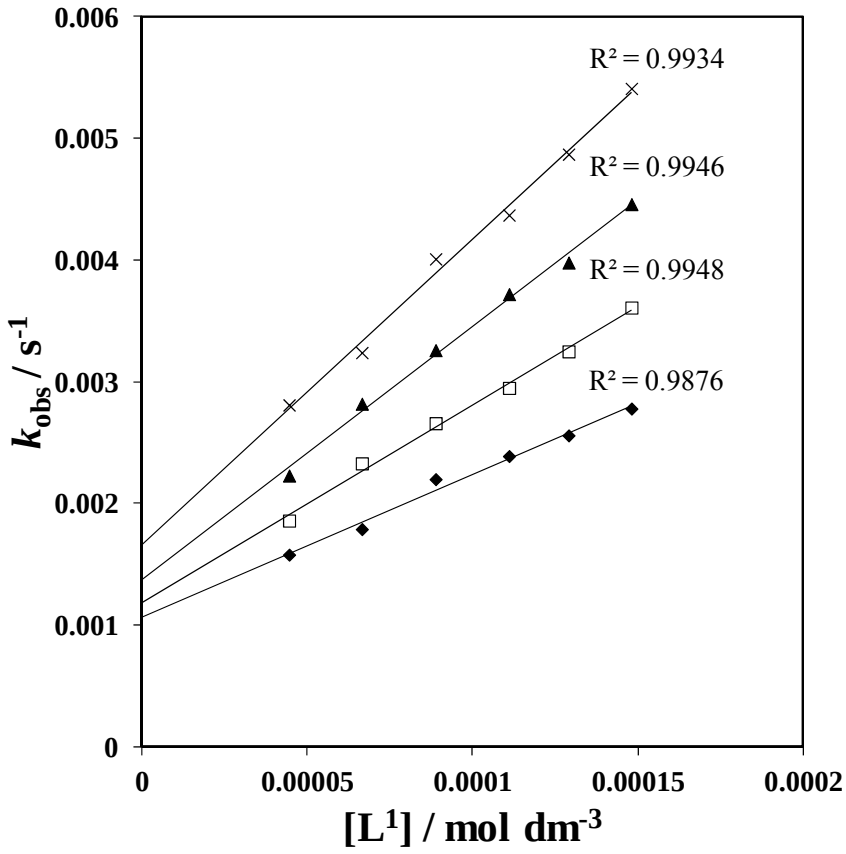

Figure S8: Plots of k_{obs} against [**L**^{1}]; [Pd(OAc)$_2$] = 3.9 μmol dm^{-3} (♦ : 298 K; □ : 303 K; ▲ : 308 K; × : 313 K)

Table S1: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for Dicarbothioamide 1. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	7793(2)	5632(1)	1993(1)	13(1)
C(2)	6651(2)	6148(1)	1459(1)	16(1)
C(3)	7005(2)	6413(1)	796(1)	19(1)
C(4)	8495(2)	6170(1)	693(1)	17(1)
C(5)	9569(2)	5644(1)	1249(1)	14(1)
C(6)	7486(2)	5323(1)	2726(1)	14(1)
C(7)	8867(2)	4338(1)	3837(1)	13(1)
C(8)	10503(2)	4224(1)	4285(1)	14(1)
C(9)	10831(2)	3827(1)	4997(1)	16(1)
C(10)	9551(2)	3544(1)	5276(1)	17(1)
C(11)	7946(2)	3649(1)	4826(1)	15(1)
C(12)	7598(2)	4036(1)	4101(1)	15(1)
C(13)	11182(2)	5324(1)	1155(1)	14(1)
C(14)	13200(2)	4085(1)	1737(1)	14(1)
C(15)	13392(2)	3407(1)	2308(1)	14(1)
C(16)	14729(2)	2840(1)	2476(1)	17(1)
C(17)	15906(2)	2920(1)	2083(1)	16(1)
C(18)	15700(2)	3568(1)	1516(1)	15(1)
C(19)	14349(2)	4152(1)	1338(1)	14(1)
C(20)	13324(2)	4404(1)	4372(1)	21(1)
C(21)	6880(2)	3116(1)	5818(1)	25(1)
C(22)	12132(2)	2613(1)	3131(1)	22(1)
C(23)	18219(2)	3171(1)	1288(1)	20(1)
N(1)	9221(2)	5373(1)	1886(1)	13(1)
N(2)	8652(2)	4754(1)	3119(1)	14(1)
N(3)	11799(2)	4627(1)	1627(1)	14(1)
O(1)	11645(2)	4549(1)	3957(1)	17(1)
O(2)	6593(2)	3396(1)	5042(1)	20(1)
O(3)	12154(2)	3376(1)	2651(1)	19(1)
O(4)	16754(2)	3700(1)	1084(1)	19(1)
S(1)	5886(1)	5695(1)	2984(1)	17(1)
S(2)	11985(1)	5809(1)	530(1)	18(1)

Table S2: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) For **L**[1]. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	8052(2)	4315(1)	6298(1)	12(1)
C(2)	8069(2)	5140(1)	5966(1)	15(1)
C(3)	7138(2)	5533(1)	5638(1)	16(1)
C(4)	6226(2)	5087(1)	5655(1)	15(1)
C(5)	6280(2)	4275(1)	6010(1)	13(1)
C(6)	9030(2)	3851(1)	6664(1)	13(1)
C(7)	9457(2)	2402(1)	7331(1)	13(1)
C(8)	10521(2)	2371(1)	7471(1)	15(1)
C(9)	11068(2)	1673(1)	7864(1)	15(1)
C(10)	10545(2)	1009(2)	8107(1)	18(1)
C(11)	9471(2)	1033(2)	7963(1)	19(1)
C(12)	8921(2)	1719(1)	7579(1)	15(1)
C(13)	12717(2)	1067(2)	8396(1)	22(1)
C(14)	7289(2)	1129(2)	7635(1)	24(1)
C(15)	5336(2)	3808(1)	6068(1)	13(1)
C(16)	4093(2)	2754(1)	6314(1)	14(1)
C(17)	3460(2)	2090(1)	6497(1)	17(1)
C(18)	2414(2)	2272(2)	6340(1)	19(1)
C(19)	1998(2)	3100(2)	6012(1)	18(1)
C(20)	2616(2)	3760(2)	5834(1)	16(1)
C(21)	3689(2)	3580(1)	5987(1)	14(1)
C(22)	1199(2)	4736(2)	5322(1)	22(1)
C(23)	3326(2)	645(2)	7010(1)	27(1)
C(24)	7181(2)	2113(1)	5310(1)	13(1)
C(25)	7222(2)	2945(1)	4986(1)	14(1)
C(26)	6309(2)	3325(1)	4636(1)	16(1)
C(27)	5384(2)	2872(1)	4624(1)	16(1)
C(28)	5408(2)	2078(1)	4987(1)	13(1)
C(29)	8147(2)	1636(1)	5680(1)	13(1)
C(30)	8533(2)	201(1)	6360(1)	15(1)
C(31)	9598(2)	179(1)	6532(1)	16(1)
C(32)	10113(2)	-546(2)	6916(1)	17(1)

C(33)	9564(2)	-1235(2)	7125(1)	20(1)
C(34)	8492(2)	-1211(2)	6952(1)	22(1)
C(36)	11731(2)	-1215(2)	7449(1)	23(1)
C(37)	6305(2)	-1141(2)	6550(1)	30(1)
C(38)	4446(2)	1645(1)	5041(1)	14(1)
C(39)	3153(2)	676(2)	5298(1)	17(1)
C(40)	2486(2)	49(2)	5484(1)	20(1)
C(41)	1454(2)	271(2)	5317(1)	24(1)
C(42)	1074(2)	1077(2)	4960(1)	24(1)
C(43)	1717(2)	1680(2)	4762(1)	20(1)
C(44)	2784(2)	1475(2)	4937(1)	17(1)
C(45)	2292(2)	-1376(2)	6011(1)	31(1)
C(46)	329(2)	2602(2)	4173(1)	31(1)
C(35)	7967(2)	-505(2)	6575(1)	18(1)
N(1)	7170(1)	3889(1)	6324(1)	12(1)
N(2)	8824(1)	3065(1)	6944(1)	13(1)
N(3)	4417(1)	4173(1)	5848(1)	14(1)
N(4)	6289(1)	1693(1)	5320(1)	13(1)
N(5)	7921(1)	884(1)	5978(1)	15(1)
N(6)	3540(1)	2018(1)	4793(1)	16(1)
O(1)	12120(1)	1720(1)	7972(1)	20(1)
O(2)	7869(1)	1810(1)	7405(1)	20(1)
O(3)	3965(1)	1330(1)	6823(1)	23(1)
O(4)	2288(1)	4599(1)	5524(1)	18(1)
O(5)	11172(1)	-499(1)	7053(1)	21(1)
O(6)	6914(1)	-410(1)	6377(1)	24(1)
O(7)	2957(1)	-719(1)	5822(1)	24(1)
O(8)	1413(1)	2480(1)	4414(1)	25(1)
S(1)	10170(1)	4331(1)	6695(1)	20(1)
S(2)	5418(1)	2723(1)	6455(1)	14(1)
S(3)	9306(1)	2043(1)	5679(1)	16(1)
S(4)	4477(1)	615(1)	5470(1)	16(1)

Table S3: Bond lengths [Å] and angles [°] for Dicarbothioamide 1.

C(1)-N(1)	1.349(2)
C(1)-C(2)	1.390(2)
C(1)-C(6)	1.513(2)
C(2)-C(3)	1.392(3)
C(3)-C(4)	1.390(3)
C(4)-C(5)	1.392(3)
C(5)-N(1)	1.348(2)
C(5)-C(13)	1.516(2)
C(6)-N(2)	1.341(2)
C(6)-S(1)	1.6664(17)
C(7)-C(12)	1.385(2)
C(7)-C(8)	1.411(2)
C(7)-N(2)	1.414(2)
C(8)-O(1)	1.374(2)
C(8)-C(9)	1.382(2)
C(9)-C(10)	1.402(2)
C(10)-C(11)	1.389(3)
C(11)-O(2)	1.380(2)
C(11)-C(12)	1.397(2)
C(13)-N(3)	1.348(2)
C(13)-S(2)	1.6593(17)
C(14)-C(19)	1.390(2)
C(14)-N(3)	1.406(2)
C(14)-C(15)	1.423(2)
C(15)-C(16)	1.377(3)
C(15)-O(3)	1.381(2)
C(16)-C(17)	1.403(2)
C(17)-C(18)	1.386(2)
C(18)-O(4)	1.376(2)
C(18)-C(19)	1.402(2)
C(20)-O(1)	1.433(2)
C(21)-O(2)	1.432(2)
C(22)-O(3)	1.433(2)
C(23)-O(4)	1.431(2)

N(1)-C(1)-C(2)	122.25(16)
N(1)-C(1)-C(6)	116.29(15)
C(2)-C(1)-C(6)	121.45(15)
C(1)-C(2)-C(3)	118.76(16)
C(4)-C(3)-C(2)	119.23(17)
C(3)-C(4)-C(5)	118.69(16)
N(1)-C(5)-C(4)	122.32(16)
N(1)-C(5)-C(13)	116.40(15)
C(4)-C(5)-C(13)	121.26(15)
N(2)-C(6)-C(1)	111.78(14)
N(2)-C(6)-S(1)	126.70(13)
C(1)-C(6)-S(1)	121.50(13)
C(12)-C(7)-C(8)	120.31(15)
C(12)-C(7)-N(2)	124.20(16)
C(8)-C(7)-N(2)	115.49(15)
O(1)-C(8)-C(9)	125.85(15)
O(1)-C(8)-C(7)	114.58(15)
C(9)-C(8)-C(7)	119.56(15)
C(8)-C(9)-C(10)	120.38(16)
C(11)-C(10)-C(9)	119.55(16)
O(2)-C(11)-C(10)	124.58(15)
O(2)-C(11)-C(12)	114.78(15)
C(10)-C(11)-C(12)	120.64(16)
C(7)-C(12)-C(11)	119.52(16)
N(3)-C(13)-C(5)	111.31(14)
N(3)-C(13)-S(2)	127.48(14)
C(5)-C(13)-S(2)	121.22(13)
C(19)-C(14)-N(3)	126.11(15)
C(19)-C(14)-C(15)	119.31(15)
N(3)-C(14)-C(15)	114.57(15)
C(16)-C(15)-O(3)	125.22(15)
C(16)-C(15)-C(14)	120.06(15)
O(3)-C(15)-C(14)	114.71(15)
C(15)-C(16)-C(17)	120.56(16)
C(18)-C(17)-C(16)	119.35(16)

O(4)-C(18)-C(17)	124.62(15)
O(4)-C(18)-C(19)	114.47(15)
C(17)-C(18)-C(19)	120.92(15)
C(14)-C(19)-C(18)	119.77(15)
C(5)-N(1)-C(1)	118.71(15)
C(6)-N(2)-C(7)	130.24(15)
C(13)-N(3)-C(14)	133.07(15)
C(8)-O(1)-C(20)	116.56(14)
C(11)-O(2)-C(21)	116.54(14)
C(15)-O(3)-C(22)	117.01(14)
C(18)-O(4)-C(23)	116.37(13)

Table S4: Bond lengths [Å] and angles [°] for $\mathbf{L^1}$.

C(1)-N(1)	1.348(2)
C(1)-C(2)	1.392(3)
C(1)-C(6)	1.510(3)
C(2)-C(3)	1.394(3)
C(3)-C(4)	1.389(3)
C(4)-C(5)	1.395(3)
C(5)-N(1)	1.339(3)
C(5)-C(15)	1.472(3)
C(6)-N(2)	1.343(2)
C(6)-S(1)	1.660(2)
C(7)-C(8)	1.385(3)
C(7)-N(2)	1.410(2)
C(7)-C(12)	1.418(3)
C(8)-C(9)	1.405(3)
C(9)-O(1)	1.375(2)
C(9)-C(10)	1.383(3)
C(10)-C(11)	1.397(3)
C(11)-C(12)	1.383(3)
C(12)-O(2)	1.373(2)
C(13)-O(1)	1.429(2)
C(14)-O(2)	1.430(2)
C(15)-N(3)	1.307(3)
C(15)-S(2)	1.747(2)
C(16)-C(21)	1.402(3)
C(16)-C(17)	1.405(3)
C(16)-S(2)	1.730(2)
C(17)-O(3)	1.368(3)
C(17)-C(18)	1.382(3)
C(18)-C(19)	1.408(3)
C(19)-C(20)	1.383(3)
C(20)-O(4)	1.377(2)
C(20)-C(21)	1.416(3)
C(21)-N(3)	1.391(3)
C(22)-O(4)	1.428(2)

C(23)-O(3)	1.436(3)
C(24)-N(4)	1.345(2)
C(24)-C(25)	1.394(3)
C(24)-C(29)	1.509(3)
C(25)-C(26)	1.388(3)
C(26)-C(27)	1.390(3)
C(27)-C(28)	1.395(3)
C(28)-N(4)	1.345(3)
C(28)-C(38)	1.471(3)
C(29)-N(5)	1.343(2)
C(29)-S(3)	1.666(2)
C(30)-C(31)	1.384(3)
C(30)-N(5)	1.410(3)
C(30)-C(35)	1.422(3)
C(31)-C(32)	1.405(3)
C(32)-O(5)	1.378(3)
C(32)-C(33)	1.385(3)
C(33)-C(34)	1.392(3)
C(34)-C(35)	1.383(3)
C(36)-O(5)	1.431(2)
C(37)-O(6)	1.434(2)
C(38)-N(6)	1.308(3)
C(38)-S(4)	1.747(2)
C(39)-C(44)	1.403(3)
C(39)-C(40)	1.410(3)
C(39)-S(4)	1.723(2)
C(40)-C(41)	1.374(3)
C(40)-O(7)	1.376(3)
C(41)-C(42)	1.409(3)
C(42)-C(43)	1.381(3)
C(43)-O(8)	1.375(3)
C(43)-C(44)	1.415(3)
C(44)-N(6)	1.387(3)
C(45)-O(7)	1.437(2)
C(46)-O(8)	1.428(3)
C(35)-O(6)	1.376(3)

N(1)-C(1)-C(2)	122.61(18)
N(1)-C(1)-C(6)	115.56(16)
C(2)-C(1)-C(6)	121.82(17)
C(1)-C(2)-C(3)	118.94(18)
C(4)-C(3)-C(2)	118.72(18)
C(3)-C(4)-C(5)	118.55(18)
N(1)-C(5)-C(4)	123.21(18)
N(1)-C(5)-C(15)	116.03(17)
C(4)-C(5)-C(15)	120.74(18)
N(2)-C(6)-C(1)	111.21(17)
N(2)-C(6)-S(1)	128.18(15)
C(1)-C(6)-S(1)	120.60(14)
C(8)-C(7)-N(2)	125.27(17)
C(8)-C(7)-C(12)	119.87(17)
N(2)-C(7)-C(12)	114.86(18)
C(7)-C(8)-C(9)	119.93(18)
O(1)-C(9)-C(10)	125.30(18)
O(1)-C(9)-C(8)	114.50(17)
C(10)-C(9)-C(8)	120.21(19)
C(9)-C(10)-C(11)	119.96(18)
C(12)-C(11)-C(10)	120.60(19)
O(2)-C(12)-C(11)	125.63(18)
O(2)-C(12)-C(7)	114.92(17)
C(11)-C(12)-C(7)	119.45(19)
N(3)-C(15)-C(5)	123.10(18)
N(3)-C(15)-S(2)	117.05(15)
C(5)-C(15)-S(2)	119.85(15)
C(21)-C(16)-C(17)	121.82(19)
C(21)-C(16)-S(2)	110.36(15)
C(17)-C(16)-S(2)	127.80(16)
O(3)-C(17)-C(18)	127.08(18)
O(3)-C(17)-C(16)	115.18(18)
C(18)-C(17)-C(16)	117.74(19)
C(17)-C(18)-C(19)	121.07(19)
C(20)-C(19)-C(18)	121.55(19)

O(4)-C(20)-C(19)	125.90(19)
O(4)-C(20)-C(21)	115.97(17)
C(19)-C(20)-C(21)	118.12(19)
N(3)-C(21)-C(16)	114.87(18)
N(3)-C(21)-C(20)	125.42(18)
C(16)-C(21)-C(20)	119.70(18)
N(4)-C(24)-C(25)	122.63(18)
N(4)-C(24)-C(29)	115.77(17)
C(25)-C(24)-C(29)	121.59(17)
C(26)-C(25)-C(24)	118.77(18)
C(25)-C(26)-C(27)	119.13(18)
C(26)-C(27)-C(28)	118.34(19)
N(4)-C(28)-C(27)	122.91(18)
N(4)-C(28)-C(38)	116.47(17)
C(27)-C(28)-C(38)	120.57(18)
N(5)-C(29)-C(24)	111.23(17)
N(5)-C(29)-S(3)	127.93(16)
C(24)-C(29)-S(3)	120.84(14)
C(31)-C(30)-N(5)	125.49(18)
C(31)-C(30)-C(35)	119.93(18)
N(5)-C(30)-C(35)	114.58(18)
C(30)-C(31)-C(32)	119.62(18)
O(5)-C(32)-C(33)	124.95(18)
O(5)-C(32)-C(31)	114.46(17)
C(33)-C(32)-C(31)	120.6(2)
C(32)-C(33)-C(34)	119.70(19)
C(35)-C(34)-C(33)	120.85(19)
N(6)-C(38)-C(28)	122.71(18)
N(6)-C(38)-S(4)	116.80(15)
C(28)-C(38)-S(4)	120.45(15)
C(44)-C(39)-C(40)	121.9(2)
C(44)-C(39)-S(4)	110.56(15)
C(40)-C(39)-S(4)	127.58(18)
C(41)-C(40)-O(7)	127.27(19)
C(41)-C(40)-C(39)	117.5(2)
O(7)-C(40)-C(39)	115.22(19)

C(40)-C(41)-C(42)	121.22(19)
C(43)-C(42)-C(41)	121.8(2)
O(8)-C(43)-C(42)	125.6(2)
O(8)-C(43)-C(44)	116.50(18)
C(42)-C(43)-C(44)	117.9(2)
N(6)-C(44)-C(39)	114.72(19)
N(6)-C(44)-C(43)	125.56(19)
C(39)-C(44)-C(43)	119.70(19)
O(6)-C(35)-C(34)	125.85(19)
O(6)-C(35)-C(30)	114.84(18)
C(34)-C(35)-C(30)	119.3(2)
C(5)-N(1)-C(1)	117.95(16)
C(6)-N(2)-C(7)	132.79(18)
C(15)-N(3)-C(21)	109.55(17)
C(28)-N(4)-C(24)	118.03(17)
C(29)-N(5)-C(30)	133.08(19)
C(38)-N(6)-C(44)	109.71(17)
C(9)-O(1)-C(13)	116.89(16)
C(12)-O(2)-C(14)	117.24(16)
C(17)-O(3)-C(23)	115.69(18)
C(20)-O(4)-C(22)	116.14(16)
C(32)-O(5)-C(36)	116.56(16)
C(35)-O(6)-C(37)	117.18(17)
C(40)-O(7)-C(45)	116.34(19)
C(43)-O(8)-C(46)	116.12(18)
C(16)-S(2)-C(15)	88.17(9)
C(39)-S(4)-C(38)	88.21(10)

Table S5: Anisotropic displacement parameters ($Å^2$x 10^3)for Dicarbothioamide 1. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	14(1)	10(1)	15(1)	-2(1)	3(1)	-1(1)
C(2)	16(1)	13(1)	21(1)	-1(1)	5(1)	2(1)
C(3)	20(1)	15(1)	19(1)	4(1)	1(1)	4(1)
C(4)	22(1)	15(1)	15(1)	2(1)	6(1)	1(1)
C(5)	18(1)	11(1)	13(1)	-1(1)	4(1)	-1(1)
C(6)	13(1)	12(1)	15(1)	-1(1)	2(1)	-2(1)
C(7)	15(1)	12(1)	12(1)	-1(1)	2(1)	2(1)
C(8)	12(1)	14(1)	17(1)	-2(1)	5(1)	1(1)
C(9)	13(1)	17(1)	16(1)	-1(1)	2(1)	2(1)
C(10)	19(1)	15(1)	15(1)	2(1)	3(1)	3(1)
C(11)	15(1)	13(1)	19(1)	2(1)	7(1)	1(1)
C(12)	11(1)	15(1)	17(1)	-1(1)	2(1)	1(1)
C(13)	17(1)	11(1)	13(1)	-2(1)	2(1)	-1(1)
C(14)	15(1)	10(1)	14(1)	-1(1)	3(1)	0(1)
C(15)	17(1)	14(1)	13(1)	-1(1)	6(1)	-2(1)
C(16)	22(1)	14(1)	14(1)	2(1)	4(1)	0(1)
C(17)	15(1)	14(1)	19(1)	0(1)	3(1)	3(1)
C(18)	15(1)	15(1)	15(1)	-3(1)	6(1)	-2(1)
C(19)	16(1)	11(1)	14(1)	1(1)	4(1)	0(1)
C(20)	10(1)	30(1)	23(1)	-3(1)	3(1)	1(1)
C(21)	24(1)	28(1)	24(1)	12(1)	11(1)	3(1)
C(22)	28(1)	17(1)	24(1)	4(1)	13(1)	-3(1)
C(23)	17(1)	20(1)	25(1)	3(1)	9(1)	4(1)
N(1)	14(1)	11(1)	14(1)	-1(1)	4(1)	-1(1)
N(2)	11(1)	18(1)	14(1)	2(1)	4(1)	1(1)
N(3)	15(1)	14(1)	16(1)	2(1)	7(1)	1(1)
O(1)	9(1)	24(1)	19(1)	1(1)	4(1)	1(1)
O(2)	15(1)	26(1)	22(1)	9(1)	7(1)	0(1)
O(3)	22(1)	18(1)	21(1)	6(1)	12(1)	2(1)
O(4)	16(1)	20(1)	23(1)	5(1)	10(1)	5(1)
S(1)	15(1)	19(1)	18(1)	1(1)	6(1)	5(1)
S(2)	20(1)	17(1)	17(1)	4(1)	8(1)	1(1)

Table S6: Anisotropic displacement parameters ($Å^2$x 10^3)for **L**^{1}. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

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

C(33)	27(1)	18(1)	16(1)	5(1)	7(1)	1(1)
C(34)	30(1)	20(1)	19(1)	4(1)	10(1)	-7(1)
C(36)	26(1)	23(1)	21(1)	6(1)	6(1)	8(1)
C(37)	25(1)	36(1)	27(1)	10(1)	5(1)	-18(1)
C(38)	16(1)	13(1)	16(1)	-4(1)	9(1)	-2(1)
C(39)	18(1)	17(1)	21(1)	-8(1)	12(1)	-7(1)
C(40)	24(1)	17(1)	23(1)	-8(1)	15(1)	-9(1)
C(41)	22(1)	27(1)	30(1)	-14(1)	18(1)	-16(1)
C(42)	15(1)	29(1)	31(1)	-14(1)	12(1)	-10(1)
C(43)	16(1)	21(1)	24(1)	-10(1)	8(1)	-5(1)
C(44)	15(1)	19(1)	19(1)	-8(1)	8(1)	-7(1)
C(45)	45(2)	23(1)	36(1)	-7(1)	29(1)	-18(1)
C(46)	12(1)	34(1)	43(1)	-10(1)	2(1)	-3(1)
C(35)	20(1)	19(1)	16(1)	1(1)	6(1)	-6(1)
N(1)	11(1)	13(1)	11(1)	-1(1)	3(1)	0(1)
N(2)	10(1)	16(1)	14(1)	1(1)	3(1)	-1(1)
N(3)	11(1)	17(1)	14(1)	-3(1)	4(1)	-2(1)
N(4)	14(1)	13(1)	14(1)	-2(1)	8(1)	-2(1)
N(5)	13(1)	17(1)	16(1)	2(1)	5(1)	-3(1)
N(6)	13(1)	16(1)	19(1)	-4(1)	7(1)	-4(1)
O(1)	14(1)	22(1)	21(1)	6(1)	1(1)	3(1)
O(2)	15(1)	21(1)	24(1)	7(1)	9(1)	-2(1)
O(3)	25(1)	21(1)	26(1)	6(1)	12(1)	-3(1)
O(4)	10(1)	23(1)	22(1)	2(1)	3(1)	2(1)
O(5)	19(1)	24(1)	21(1)	10(1)	8(1)	7(1)
O(6)	19(1)	27(1)	26(1)	9(1)	5(1)	-10(1)
O(7)	32(1)	19(1)	29(1)	-3(1)	20(1)	-11(1)
O(8)	12(1)	28(1)	34(1)	-2(1)	4(1)	-2(1)
S(1)	12(1)	21(1)	25(1)	6(1)	3(1)	-2(1)
S(2)	13(1)	16(1)	14(1)	1(1)	5(1)	0(1)
S(3)	13(1)	19(1)	18(1)	2(1)	6(1)	-3(1)
S(4)	17(1)	13(1)	20(1)	-1(1)	11(1)	-3(1)

Table S7: Pseudo-first-order rate constants for the formation of $PdClL^1$ and $Pd(OAc)L^1$ from PdX_2, where X = Cl or OAc, and $\mathbf{L^1}$ in acetonitrile, $[PdCl_2(CH_3CN)_2]$ = 3.7 μmol dm^{-3}, $[Pd(OAc)_2]$ = 3.9 μmol dm^{-3}.

10^5 $[L^1]$ / M	10^3 k_{obs}							
	298 K		303 K		308 K		313 K	
	Cl	OAc	Cl	OAc	Cl	OAc	Cl	OAc
4.45	1.14	1.58	1.46	1.86	1.73	2.23	1.98	2.81
6.65	1.22	1.79	1.67	2.33	1.99	2.82	2.30	3.24
8.88	1.45	2.20	1.94	2.66	2.24	3.26	2.67	4.01
11.1	1.53	2.39	2.14	2.95	2.59	3.72	2.96	4.37
12.9	1.77	2.56	2.32	3.25	2.83	3.98	3.30	4.87
14.8	1.89	2.78	2.50	3.61	3.00	4.46	3.55	5.41

NB: Cl and OAc represents the species formed from $PdCl_2(CH_3CN)_2$ and $Pd(OAc)_2$ (i.e. the formation of $PdClL^1$ and $Pd(OAc)L^1$) respectively.

Table S8: Standard enthalpy and entropy values deduced from the kinetic data for the formation of $PdClL^1$ and $Pd(OAc)L^1$ in acetonitrile.

		ln (k_1/(k_2 [I]))		ln K	
T/K	10^4 T^{-1}/K^{-1}	$PdClL^1$	$Pd(OAc)L^1$	$PdClL^1$	$Pd(OAc)L^1$
298	33.56	9.19	9.30	9.92	10.0
303	33.00	9.21	9.52	9.97	10.2
308	32.47	9.31	9.62	10.0	10.3
313	31.95	9.38	9.62	10.1	10.4
	$\Delta_f H$ /kJ mol^{-1}	10 ± 2	8 ± 4	8 ± 1	17 ± 4
	$\Delta_f S^0$ /J K^{-1} mol^{-1}	110 ± 6	107 ± 14	108 ± 10	140 ± 20

Table S9. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for PdClL[1]. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	4916(1)	773(1)	1959(1)	37(1)
S(2)	3109(2)	283(1)	-2354(1)	45(1)
S(1)	6309(2)	1242(1)	3064(1)	49(1)
Cl(1)	4109(2)	608(1)	4223(1)	63(1)
O(3)	2899(5)	-105(1)	2773(4)	59(1)
O(4)	845(5)	-371(1)	-2885(4)	56(1)
N(3)	3765(5)	381(1)	382(4)	36(1)
O(2)	6213(6)	2227(1)	2901(5)	71(1)
N(1)	5650(5)	998(1)	108(4)	37(1)
N(2)	8152(6)	1729(1)	1575(5)	48(1)
O(1)	11910(6)	1975(2)	5456(6)	87(2)
C(12)	7594(7)	2169(2)	3597(7)	55(1)
C(5)	5063(6)	851(1)	-1141(5)	39(1)
C(15)	4033(6)	519(1)	-934(5)	39(1)
C(20)	1242(6)	-333(2)	-1450(6)	44(1)
C(21)	2286(6)	-29(2)	-1125(5)	40(1)
C(19)	723(6)	-549(2)	-309(6)	49(1)
C(8)	10016(7)	1836(2)	3520(6)	53(1)
C(1)	6632(6)	1305(1)	95(5)	39(1)
C(16)	2787(6)	57(1)	296(5)	37(1)
C(11)	8072(9)	2353(2)	4879(8)	71(2)
C(9)	10503(8)	2025(2)	4795(7)	63(2)
C(7)	8583(7)	1905(2)	2933(6)	49(1)
C(4)	5443(6)	1010(2)	-2471(6)	46(1)
C(23)	2197(9)	-274(2)	4017(6)	66(2)
C(3)	6457(7)	1322(2)	-2500(6)	49(1)
C(18)	1243(6)	-475(2)	1115(6)	48(1)
C(2)	7057(6)	1472(2)	-1207(6)	46(1)
C(10)	9503(9)	2279(2)	5466(8)	73(2)
C(6)	7148(6)	1455(1)	1541(6)	40(1)
C(22)	-177(8)	-688(2)	-3250(7)	66(2)
C(13)	12850(10)	1675(3)	4929(11)	107(3)

C(17)	2271(6)	-179(2)	1443(6)	41(1)
C(14)	5195(10)	2498(3)	3499(12)	105(3)
Cl(2)	3012(3)	1810(1)	489(4)	143(1)
Cl(3)	1268(4)	1345(1)	-1593(4)	145(1)
C(24)	1477(11)	1804(3)	-772(13)	119(4)

Table S10. Bond lengths [Å] and angles [°] for PdClL[1].

Pd(1)-N(1)	1.994(4)
Pd(1)-N(3)	2.198(4)
Pd(1)-S(1)	2.2387(14)
Pd(1)-Cl(1)	2.2917(14)
S(2)-C(15)	1.721(5)
S(2)-C(21)	1.723(5)
S(1)-C(6)	1.759(5)
O(3)-C(17)	1.355(6)
O(3)-C(23)	1.435(7)
O(4)-C(20)	1.367(6)
O(4)-C(22)	1.435(7)
N(3)-C(15)	1.328(6)
N(3)-C(16)	1.395(6)
O(2)-C(12)	1.373(8)
O(2)-C(14)	1.404(8)
N(1)-C(5)	1.347(6)
N(1)-C(1)	1.353(6)
N(2)-C(6)	1.281(6)
N(2)-C(7)	1.431(7)
O(1)-C(9)	1.376(8)
O(1)-C(13)	1.407(9)
C(12)-C(11)	1.393(9)
C(12)-C(7)	1.399(8)
C(5)-C(4)	1.388(7)
C(5)-C(15)	1.461(7)
C(20)-C(19)	1.371(7)
C(20)-C(21)	1.409(7)

C(21)-C(16)	1.403(7)
C(19)-C(18)	1.403(8)
C(8)-C(7)	1.378(8)
C(8)-C(9)	1.397(8)
C(1)-C(2)	1.386(7)
C(1)-C(6)	1.488(7)
C(16)-C(17)	1.411(7)
C(11)-C(10)	1.379(10)
C(9)-C(10)	1.388(9)
C(4)-C(3)	1.385(7)
C(3)-C(2)	1.388(7)
C(18)-C(17)	1.379(7)
Cl(2)-C(24)	1.759(11)
Cl(3)-C(24)	1.740(11)

N(1)-Pd(1)-N(3)	79.55(15)
N(1)-Pd(1)-S(1)	86.08(12)
N(3)-Pd(1)-S(1)	165.63(11)
N(1)-Pd(1)-Cl(1)	171.36(12)
N(3)-Pd(1)-Cl(1)	107.92(11)
S(1)-Pd(1)-Cl(1)	86.40(5)
C(15)-S(2)-C(21)	89.0(2)
C(6)-S(1)-Pd(1)	99.47(17)
C(17)-O(3)-C(23)	118.5(5)
C(20)-O(4)-C(22)	116.1(5)
C(15)-N(3)-C(16)	110.4(4)
C(15)-N(3)-Pd(1)	107.6(3)
C(16)-N(3)-Pd(1)	141.8(3)
C(12)-O(2)-C(14)	118.3(6)
C(5)-N(1)-C(1)	120.6(4)
C(5)-N(1)-Pd(1)	117.7(3)
C(1)-N(1)-Pd(1)	121.6(3)
C(6)-N(2)-C(7)	119.4(5)
C(9)-O(1)-C(13)	117.7(6)
O(2)-C(12)-C(11)	125.2(6)
O(2)-C(12)-C(7)	116.1(5)

C(11)-C(12)-C(7)	118.7(6)
N(1)-C(5)-C(4)	121.1(5)
N(1)-C(5)-C(15)	113.5(4)
C(4)-C(5)-C(15)	125.3(4)
N(3)-C(15)-C(5)	121.1(4)
N(3)-C(15)-S(2)	116.1(4)
C(5)-C(15)-S(2)	122.8(4)
O(4)-C(20)-C(19)	127.7(5)
O(4)-C(20)-C(21)	115.1(5)
C(19)-C(20)-C(21)	117.1(5)
C(16)-C(21)-C(20)	122.6(5)
C(16)-C(21)-S(2)	111.1(4)
C(20)-C(21)-S(2)	126.3(4)
C(20)-C(19)-C(18)	121.0(5)
C(7)-C(8)-C(9)	120.7(6)
N(1)-C(1)-C(2)	120.4(5)
N(1)-C(1)-C(6)	115.8(4)
C(2)-C(1)-C(6)	123.7(5)
N(3)-C(16)-C(21)	113.3(4)
N(3)-C(16)-C(17)	127.8(4)
C(21)-C(16)-C(17)	118.9(5)
C(10)-C(11)-C(12)	120.3(6)
O(1)-C(9)-C(10)	116.8(6)
O(1)-C(9)-C(8)	124.7(6)
C(10)-C(9)-C(8)	118.5(6)
C(8)-C(7)-C(12)	120.6(5)
C(8)-C(7)-N(2)	119.5(5)
C(12)-C(7)-N(2)	119.8(6)
C(3)-C(4)-C(5)	118.9(5)
C(4)-C(3)-C(2)	119.5(5)
C(17)-C(18)-C(19)	122.2(5)
C(1)-C(2)-C(3)	119.4(5)
C(11)-C(10)-C(9)	121.2(6)
N(2)-C(6)-C(1)	117.6(5)
N(2)-C(6)-S(1)	125.6(4)
C(1)-C(6)-S(1)	116.8(4)

O(3)-C(17)-C(18)	125.6(5)
O(3)-C(17)-C(16)	116.3(4)
C(18)-C(17)-C(16)	118.0(5)
Cl(3)-C(24)-Cl(2)	111.7(5)

Table S11. Anisotropic displacement parameters ($Å^2$x 10^3)for PdClL[1]. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd(1)	44(1)	42(1)	26(1)	-2(1)	1(1)	-3(1)
S(2)	55(1)	50(1)	30(1)	-1(1)	-1(1)	-9(1)
S(1)	61(1)	56(1)	31(1)	-7(1)	2(1)	-16(1)
Cl(1)	79(1)	84(1)	26(1)	-1(1)	3(1)	-31(1)
O(3)	81(3)	63(3)	31(2)	3(2)	2(2)	-17(2)
O(4)	65(3)	58(2)	45(2)	-2(2)	-9(2)	-18(2)
N(3)	41(2)	37(2)	32(2)	-3(2)	-2(2)	1(2)
O(2)	72(3)	62(3)	79(3)	-17(2)	4(3)	10(2)
N(1)	40(2)	36(2)	34(2)	-4(2)	2(2)	-3(2)
N(2)	61(3)	46(2)	38(2)	-7(2)	5(2)	-9(2)
O(1)	89(4)	87(4)	84(4)	-25(3)	-29(3)	4(3)
C(12)	64(4)	41(3)	59(4)	-9(3)	10(3)	-7(3)
C(5)	47(3)	42(3)	29(2)	-3(2)	1(2)	1(2)
C(15)	48(3)	38(3)	32(2)	-3(2)	2(2)	0(2)
C(20)	46(3)	44(3)	43(3)	-4(2)	0(2)	0(2)
C(21)	40(3)	42(3)	38(3)	-1(2)	3(2)	-1(2)
C(19)	47(3)	42(3)	57(3)	3(2)	5(3)	-5(2)
C(8)	63(4)	47(3)	49(3)	-9(2)	3(3)	-4(3)
C(1)	47(3)	38(3)	31(2)	-3(2)	3(2)	1(2)
C(16)	38(3)	36(2)	37(3)	-4(2)	3(2)	3(2)
C(11)	92(5)	52(4)	70(5)	-22(3)	12(4)	-3(4)
C(9)	78(5)	52(3)	59(4)	-11(3)	-9(3)	-2(3)
C(7)	69(4)	37(3)	40(3)	-7(2)	6(3)	-14(3)
C(4)	56(3)	52(3)	30(2)	-1(2)	-1(2)	-8(3)
C(23)	95(5)	66(4)	37(3)	7(3)	12(3)	-10(4)
C(3)	63(4)	51(3)	32(3)	6(2)	9(2)	-4(3)
C(18)	53(3)	46(3)	46(3)	4(2)	8(3)	0(3)
C(2)	53(3)	44(3)	40(3)	2(2)	7(2)	-3(2)
C(10)	97(6)	62(4)	59(4)	-26(3)	-7(4)	-6(4)
C(6)	46(3)	36(3)	39(3)	-5(2)	2(2)	-2(2)
C(22)	66(4)	68(4)	62(4)	-11(3)	-12(3)	-23(3)
C(13)	84(6)	114(7)	122(8)	-26(6)	-33(6)	24(5)

C(17)	43(3)	41(3)	38(3)	2(2)	9(2)	2(2)
C(14)	74(5)	93(6)	148(9)	-46(6)	12(6)	6(5)
Cl(2)	96(2)	196(3)	138(3)	24(2)	19(2)	13(2)
Cl(3)	131(2)	98(2)	207(4)	3(2)	56(2)	-22(2)
C(24)	84(6)	97(7)	176(11)	29(7)	15(7)	13(5)