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Calculations and Data for Visible Spectroscopic Studies

If we express the general equation for the oxidative addition reaction of tin reagents to platinum(II) as

$$\text{Pt(II)} + \text{Sn} \rightleftharpoons \text{Pt(IV)} \tag{1}$$

then the equilibrium expression is

$$K = \frac{[\text{Pt(IV)}]}{[\text{Pt(II)}][\text{Sn}]} \tag{2}$$

If both the Pt(II) and Pt(IV) complexes absorb at a given wavelength but the tin complex does not, then

$$A = \varepsilon_{\text{Pt(II)}}[\text{Pt(II)}] + \varepsilon_{\text{Pt(IV)}}[\text{Pt(IV)}]. \tag{3}$$

However,

$$[\text{Pt(II)}] = [\text{Pt(II)}]_i - [\text{Pt(IV)}], \tag{4}$$

and so Equation 3 can be expressed as

$$A = \varepsilon_{\text{Pt(II)}}([\text{Pt(II)}]_i - [\text{Pt(IV)}]) + \varepsilon_{\text{Pt(IV)}}[\text{Pt(IV)}]. \tag{5}$$

If we define

$$A_0 = \varepsilon_{\text{Pt(II)}}[\text{Pt(II)}]_i \tag{6}$$

$$\Delta\varepsilon = \varepsilon_{\text{Pt(II)}} - \varepsilon_{\text{Pt(IV)}} \tag{7}$$

$$\Delta A = A_0 - A \tag{8}$$

and solve Equation 5 for [Pt(IV)], we get:

$$[\text{Pt(IV)}] = \frac{\Delta A}{\Delta\varepsilon}. \tag{9}$$

Substituting Equations 4 and 9 into Equation 2 and rearranging, we get

$$\boxed{\frac{\Delta A}{[\text{Sn}]} = K\cdot\Delta\varepsilon\cdot[\text{Pt}]_{tot} - K\cdot\Delta A} \tag{10}$$

and a plot of $\frac{\Delta A}{[\text{Sn}]}$ *vs* ΔA has a slope of $-K$ and an intercept of $K\cdot\Delta\varepsilon\cdot[\text{Pt}]_{tot}$.

We have thus determined the equilibrium constant of the oxidative addition reaction through the use of a Scatchard plot. It can be shown that the most accurate data are obtained for $0.2 < S < 0.8$, where

$$\text{Fraction of saturation} = S = \frac{[\text{Pt(IV)}]}{[\text{Pt(II)}]_i} \qquad (11)$$

For the oxidative addition of Me_3SnI to Pt(II) we need to use Equation 10 since both Pt(II) and Pt(IV) complexes absorb at λ_{max} of Pt(II). This is not the case for the oxidative addition reactions of Me_3SnCl and Me_3SnBr. If $\varepsilon_{Pt(IV)} = 0$, then Equation 10 can be reduced to:

$$\boxed{\frac{1}{[\text{Sn}]} = K\frac{A}{\Delta A}} \qquad (12)$$

and a plot of $\frac{1}{[\text{Sn}]}$ *vs* $\frac{A}{\Delta A}$ has a slope of K.

If K is small, then large excesses of tin reagent are required and $[\text{Sn}] \approx [\text{Sn}]_i$. This is the case for Me_3SnX (X = Cl, Br) additions to Pt(II).

Errors in direct measurements:

∂ mass Sn reagent = ∂m_{Sn} = 0.5 mg

∂ volume of Sn stock solutions = ∂V_{stock} = 0.05 mL

∂ absorbance = ∂A = 0.0002

∂ volume of Sn titrant (single addition) = ∂V_{Sn} = 0.5 μL

∂ volume of Pt(II) soln. in cell = ∂V_{Pt} = 0.0009 mL

For titrations of Pt(II) with Me_3SnX (X = Cl, Br), calculations were carried out as follows:

$$[Sn]_{stock} = (m_{Sn}/MW_{Sn})/V_{stock} \quad (13)$$

$$\partial[Sn]_{stock} = [(\partial m_{Sn}/m_{Sn})^2 + (\partial V_{stock}/V_{stock})^2]^{1/2}.[Sn]_{stock} \quad (14)$$

$$V_{tot} = V_{Pt} + V_{Sn} \quad (15)$$

$$\partial V_{tot} = \{(\partial V_{Pt})^2 + (\partial V_{Sn})^2\}^{1/2} \quad (16)$$

$$[Sn]_{eq} = ([Sn]_{stock}\cdot V_{Sn})/V_{tot} \quad (17)$$

$$\partial[Sn]_{eq} = \{(\partial[Sn]_{stock}/[Sn]_{stock})^2+(\partial V_{Sn}/V_{Sn})^2+(\partial V_{tot}/V_{tot})^2\}^{1/2}.[Sn]_{eq} \quad (18)$$

$$A_{0\ corr} = (V_{Pt}/V_{tot})(A_0 - A_{tol}) \quad (19)$$

$$\partial A_{0\ corr} = \{(\partial V_{tot}/V_{tot})^2+(\partial V_{Pt}/V_{Pt})^2+(0.0003/[A_0 - A_{tol}])^2\}^{1/2}.A_{0\ corr} \quad (20)$$

$$A_{corr} = A - A_{tol} \quad (21)$$

$$\partial A_{corr} = [(\partial A/A)^2 + (\partial A_{tol}/A_{tol})^2]^{1/2} = 0.0003 \quad (22)$$

$$\Delta A = A_{0\ corr} - A_{corr} \quad (23)$$

$$\partial\Delta A = [\partial A_{0\ corr}^2 + \partial A_{corr}^2]^{1/2} = [0.0003^2 + \partial A_{corr}^2]^{1/2} \quad (24)$$

For titrations involving Me_3SnI, the following equations were different to those used for Me_3SnX (X = Cl, Br):

$$\Delta\varepsilon = \varepsilon_{Pt(II)} - \varepsilon_{Pt(IV)} \quad (25)$$

$$\partial\Delta\varepsilon = [\partial\varepsilon_{Pt(II)}^2 - \varepsilon_{Pt(IV)}^2]^{1/2} \quad (26)$$

$$[Sn]_{tot} = ([Sn]_{stock} \cdot V_{Sn})/V_{tot} \quad (27)$$

$$\partial[Sn]_{tot} = \{\partial[Sn]_{stock}/[Sn]_{stock})^2 + (\partial V_{Sn}/V_{Sn})^2 + (\partial V_{tot}/V_{tot})^2)\}^{1/2} \cdot [Sn]_{tot} \quad (28)$$

$$[Sn]_{eq} = [Sn]_{tot} - \Delta A/\Delta\varepsilon \quad (29)$$

$$\partial[Sn]_{eq} = \{\partial[Sn]_{tot}^2 + [\{(\partial\Delta A/\Delta A)^2 + (\partial\Delta\varepsilon/\Delta\varepsilon)^2\}^{1/2} \cdot \Delta A/\Delta\varepsilon]^2\}^{1/2} \quad (30)$$

$$\partial(\Delta A/[Sn]_{eq}) = \{(\partial\Delta A/\Delta A)^2 + (\partial[Sn]_{eq}/[Sn]_{eq})^2\} \cdot \Delta A/[Sn]_{eq} \quad (31)$$

Titration of $[PtMe_2(bipy)]$ with Me_3SnCl at 25°C

MW Me_3SnCl = 199.27 g/mol
V_{Pt} = 3.000 ± 0.009 mol·L^{-1}

Mass Me_3SnCl = 203.2 ± 0.5 mg
A_{tol} = 0.0694 ± 0.0002

V_{stock} = 10.00 ± 0.05 mL
$[Me_3SnCl]_i$ = 0.1020 ± 0.0008

V_{Sn} (μL)	$[Me_3SnCl]$x10^3 (mol·L^{-1})	$[Me_3SnCl]^{-1}$ (L·mol^{-1})	$A_{0\ corr}$ (± 0.0003)	A_{uncorr} (± 0.0002)	A_{corr} (± 0.0003)	A /ΔA
0	–	–	0.8774	0.9468	0.8774	–
25.0 ± 0.5	0.843 ± 0.02	1190 ± 26	0.8701	0.8545	0.7851	9.231 ± 0.05
50.0 ± 0.7	1.672 ± 0.03	598 ± 9.7	0.8630	0.7603	0.6909	4.014 ± 0.01
75.0 ± 0.9	2.487 ± 0.04	402 ± 5.7	0.8560	0.6683	0.5989	2.329 ± 0.004
100.0 ± 1.0	3.289 ± 0.04	304 ± 3.9	0.8491	0.5784	0.5090	1.497 ± 0.002
125.0 ± 1.1	4.079 ± 0.05	245 ± 2.9	0.8423	0.4898	0.4204	0.996 ± 0.001
150.0 ± 1.2	4.856 ± 0.06	206 ± 2.4	0.8356	0.4018	0.3324	0.6605 ± 0.0008
175.0 ± 1.3	5.621 ± 0.06	178 ± 2.0	0.8290	0.3193	0.2499	0.4315 ± 0.0006
200.0 ± 1.4	6.373 ± 0.07	157 ± 1.7	0.8226	0.2377	0.1683	0.2572 ± 0.0005
225.0 ± 1.5	7.114 ± 0.07	141 ± 1.5	0.8162	0.1631	0.0937	0.1297 ± 0.0004
250.0 ± 1.6	7.844 ± 0.08	127 ± 1.3	0.8099	0.1096	0.0402	0.0522 ± 0.0004

Titration of [$PtMe_2$(bipy-^{t}bu$_2$)] with Me_3SnCl at 25°C

MW Me_3SnCl = 199.27 g/mol
V_{Pt} = 3.000 ± 0.009 mol·L^{-1}

Mass Me_3SnCl = 230.2 ± 0.5 mg
A_{tol} = 0.0692 ± 0.0002

V_{stock} = 10.00 ± 0.05 mL
$[Me_3SnCl]_i$ = 0.1155 ± 0.0009

V_{Sn} (μL)	$[Me_3SnCl]$ x 10^3 (mol·L^{-1})	$[Me_3SnCl]^{-1}$ (L·mol^{-1})	$A_{0\,corr}$ (± 0.0003)	A_{uncorr} (± 0.0002)	A_{corr} (± 0.0003)	A/ΔA
0	–	–	2.1274	2.1966	2.1274	–
25.0 ± 0.5	0.955 ± 0.021	1047 ± 23	2.1098	2.0843	2.0151	21.3 ± 1.4
50.0 ± 0.7	1.894 ± 0.031	528.0 ± 8.6	2.0925	1.9700	1.9008	9.91 ± 0.32
75.0 ± 0.9	2.818 ± 0.040	354.9 ± 5.0	2.0755	1.8550	1.7858	6.16 ± 0.13
100.0 ± 1.0	3.727 ± 0.048	268.3 ± 3.4	2.0588	1.7396	1.6704	4.30 ± 0.07
150.0 ± 1.2	5.501 ± 0.063	181.8 ± 2.1	2.0261	1.5195	1.4503	2.519 ± 0.026
200.0 ± 1.4	7.220 ± 0.077	138.5 ± 1.5	1.9944	1.3050	1.2358	1.629 ± 0.012
250.0 ± 1.6	8.886 ± 0.090	112.5 ± 1.1	1.9638	1.1041	1.0349	1.114 ± 0.007
300.0 ± 1.7	10.50 ± 0.10	95.22 ± 0.93	1.9340	0.9096	0.8404	0.7685 ± 0.0037
400.0 ± 2.0	13.59 ± 0.13	73.58 ± 0.69	1.8771	0.5546	0.4854	0.3488 ± 0.0013
500.0 ± 2.2	16.50 ± 0.15	60.59 ± 0.55	1.8235	0.2381	0.1689	0.1021 ± 0.0004
600.0 ± 2.4	19.25 ± 0.17	51.94 ± 0.46	1.7728	0.0858	0.0166	0.0095 ± 0.0002

Titration of [$PtMe_2$(py-*n*-pr)] with Me_3SnCl at 25°C

MW Me_3SnCl = 199.27 g/mol
V_{Pt} = 3.000 ± 0.009 mol·L^{-1}

Mass Me_3SnCl = 203.2 ± 0.5 mg
A_{tol} = 0.0723 ± 0.0002

V_{stock} = 10.00 ± 0.05 mL
$[Me_3SnCl]_i$ = 0.1020 ± 0.0008

V_{Sn} (μL)	$[Me_3SnCl]$ x 10^3 (mol·L^{-1})	$[Me_3SnCl]^{-1}$ (L·mol^{-1})	$A_{0\,corr}$ (± 0.0003)	A_{uncorr} (± 0.0002)	A_{corr} (± 0.0003)	A/ΔA
0	–	–	0.9596	1.0316	0.9596	–
25.0 ± 0.5	0.843 ± 0.018	1187 ± 26	0.9517	0.9239	0.8516	8.51 ± 0.24
50.0 ± 0.7	1.672 ± 0.027	598.2 ± 9.7	0.9439	0.8138	0.7415	3.664 ± 0.051
75.0 ± 0.9	2.487 ± 0.035	402.1 ± 5.7	0.9362	0.7057	0.6334	2.092 ± 0.019
100.0 ± 1.0	3.289 ± 0.042	304.0 ± 3.9	0.9286	0.6001	0.5278	1.3167 ± 0.0089
125.0 ± 1.1	4.079 ± 0.049	245.2 ± 2.9	0.9212	0.4990	0.4267	0.8629 ± 0.0047
150.0 ± 1.2	4.856 ± 0.056	205.9 ± 2.4	0.9139	0.3970	0.3247	0.5511 ± 0.0025
175.0 ± 1.3	5.621 ± 0.062	177.9 ± 2.0	0.9067	0.3011	0.2288	0.3375 ± 0.0014
200.0 ± 1.4	6.373 ± 0.068	156.9 ± 1.7	0.8996	0.2098	0.1375	0.1804 ± 0.0007
225.0 ± 1.5	7.114 ± 0.074	140.6 ± 1.5	0.8927	0.1375	0.0652	0.0788 ± 0.0004
250.0 ± 1.6	7.844 ± 0.080	127.5 ± 1.3	0.8858	0.1057	0.0334	0.0392 ± 0.0004

Titration of $[PtMe_2(pean\text{-}me_2)]$ with Me_3SnCl at 25°C

MW Me_3SnCl = 199.27 g/mol
V_{Pt} = 3.000 ± 0.009 mol·L^{-1}

Mass Me_3SnCl = 207.1 ± 0.5 mg
A_{tol} = 0.0741 ± 0.0002

V_{stock} = 10.00 ± 0.05 mL
$[Me_3SnCl]_i$ = 0.1040 ± 0.0008

V_{Sn} (μL)	$[Me_3SnCl]$ x 10^3 (mol·L^{-1})	$[Me_3SnCl]^{-1}$ (L·mol^{-1})	$A_{0\,corr}$ (± 0.0003)	A_{uncorr} (± 0.0002)	A_{corr} (± 0.0003)	A/ΔA
0	–	–	1.4465	1.5206	1.4465	–
50.0 ± 0.7	1.704 ± 0.022	586.9 ± 7.5	1.4228	1.2936	1.2195	6.00 ± 0.12
100.0 ± 1.0	3.353 ± 0.036	298.3 ± 3.2	1.3998	1.0692	0.9951	2.459 ± 0.025
150.0 ± 1.2	4.949 ± 0.049	202.1 ± 2.0	1.3776	0.8496	0.7755	1.288 ± 0.0085
200.0 ± 1.4	6.469 ± 0.061	154.0 ± 1.5	1.3561	0.6420	0.5679	0.7205 ± 0.0035
250.0 ± 1.6	7.995 ± 0.073	125.1 ± 1.1	1.3352	0.4431	0.3690	0.3819 ± 0.0015
300.0 + 1.7	9.448 ± 0.085	105.8 ± 0.9	1.3150	0.2606	0.1865	0.1653 ± 0.0006
350.0 ± 1.8	10.86 ± 0.10	92.1 ± 0.8	1.2954	0.1198	0.0457	0.0366 ± 0.0003

Titration of $[PtMe_2(bipy)]$ with Me_3SnBr at 25°C

MW Me_3SnBr = 243.7 g/mol Mass Me_3SnBr = 218.2 ± 0.5 mg V_{stock} = 10.00 ± 0.05 mL

V_{Pt} = 3.000 ± 0.009 mL A_{tol} = 0.0817 ± 0.0002 $[Me_3SnBr]_{stock}$ = 0.08954 ± 0.0007 mol·L^{-1}

V_{Sn} (μL)	$[Me_3SnBr]\times10^3$ (mol·L^{-1})	$[Me_3SnBr]^{-1}$ (L·mol^{-1})	$A_{0\,corr}$ (± 0.0003)	A_{uncorr} (± 0.0002)	A_{corr} (± 0.0003)	A/ΔA
0	–	–	0.7746	0.8563	0.7746	–
25.0 ± 0.5	0.7400 ± 0.02	1351 ± 29	0.7682	0.7742	0.6925	9.15 ± 0.28
50.0 ± 0.7	1.468 ± 0.02	681.0 ± 11	0.7619	0.7035	0.6218	4.438 ± 0.072
75.0 ± 0.9	2.184 ± 0.03	457.9 ± 6.4	0.7557	0.6404	0.5587	2.836 ± 0.032
100.0 ± 1.0	2.888 ± 0.04	346.2 ± 4.4	0.7496	0.5874	0.5057	2.073 ± 0.019
150.0 ± 1.2	4.264 ± 0.05	234.5 ± 2.7	0.7377	0.5003	0.4186	1.3118 ± 0.0089
200.0 ± 1.4	5.596 ± 0.06	178.7 ± 1.9	0.7262	0.4343	0.3526	0.9438 ± 0.0053
250.0 ± 1.6	6.887 ± 0.07	145.2 ± 1.5	0.7150	0.3798	0.2981	0.7150 ± 0.0036
300.0 ± 1.7	8.140 ± 0.08	122.9 ± 1.2	0.7042	0.338	0.2563	0.5722 ± 0.0026
400.0 ± 2.0	10.53 ± 0.09	94.93 ± 0.89	0.6835	0.2737	0.1920	0.3907 ± 0.0016
500.0 ± 2.2	12.79 ± 0.11	78.18 ± 0.71	0.6639	0.2300	0.1483	0.2876 ± 0.0012
600.0 ± 2.4	14.92 ± 0.13	67.01 ± 0.59	0.6455	0.1954	0.1137	0.2138 ± 0.0009
700.0 ± 2.6	16.94 ± 0.15	59.03 ± 0.51	0.6281	0.1700	0.0883	0.1636 ± 0.0007

Titration of $[PtMe_2(bipy\text{-}^tbu_2)]$ with Me_3SnBr at 25°C

MW Me_3SnBr = 243.70 g/mol Mass Me_3SnBr = 230.2 ± 0.5 mg V_{stock} = 10.00 ± 0.05 mL

V_{Pt} = 3.000 ± 0.009 mL A_{tol} = 0.0750 ± 0.0002 $[Me_3SnBr]_{stock}$ = 0.09446 ± 0.0007 mol·L^{-1}

V_{Sn} (μL)	$[Me_3SnBr] \times 10^3$ (mol·L^{-1})	$[Me_3SnBr]^{-1}$ (L·mol^{-1})	$A_{0\,corr}$ (± 0.0003)	A_{uncorr} (± 0.0002)	A_{corr} (± 0.0003)	A/ΔA
0	–	–	2.1216	2.1966	2.1216	–
25.0 ± 0.5	0.781 ± 0.017	1281 ± 28	2.1041	1.9610	1.8860	8.65 ± 0.25
50.0 ± 0.7	1.549 ± 0.025	646 ± 10	2.0868	1.7607	1.6857	4.203 ± 0.065
75.0 ± 0.9	2.304 ± 0.032	434.0 ± 6.1	2.0699	1.5870	1.5120	2.710 ± 0.030
100.0 ± 1.0	3.047 ± 0.039	328.2 ± 4.2	2.0532	1.4412	1.3662	1.988 ± 0.017
150.0 ± 1.2	4.498 ± 0.051	222.3 ± 2.5	2.0206	1.2083	1.1333	1.2773 ± 0.0084
200.0 ± 1.4	5.904 ± 0.063	169.4 ± 1.8	1.9890	1.0353	0.9603	0.9335 ± 0.0052
250.0 ± 1.6	7.266 ± 0.074	137.6 ± 1.4	1.9584	0.8976	0.8226	0.7242 ± 0.0036
300.0 ± 1.7	8.587 ± 0.084	116.5 ± 1.1	1.9287	0.7902	0.7152	0.5894 ± 0.0026
400.0 ± 2.0	11.11 ± 0.10	89.98 ± 0.84	1.8720	0.6224	0.5474	0.4133 ± 0.0016
500.0 ± 2.2	13.49 ± 0.12	74.11 ± 0.67	1.8185	0.5170	0.4420	0.3211 ± 0.0012
700.0 ± 2.6	17.87 ± 0.16	55.96 ± 0.49	1.7202	0.3753	0.3003	0.2115 ± 0.0007
900.0 ± 3.0	21.80 ± 0.18	45.87 ± 0.39	1.6320	0.2913	0.2163	0.1528 ± 0.0005

Titration of $[PtMe_2(py\text{-}n\text{-}pr)]$ with Me_3SnBr at 25°C

MW Me_3SnBr = 243.70 g/mol Mass Me_3SnBr = 218.2 ± 0.5 mg V_{stock} = 10.00 ± 0.05 mL

V_{Pt} = 3.000 ± 0.009 mL A_{tol} = 0.0736 ± 0.0002 $[Me_3SnBr]_{stock}$ = 0.08954 ± 0.0007 mol·L^{-1}

V_{Sn} (μL)	$[Me_3SnBr] \times 10^3$ (mol·L^{-1})	$[Me_3SnBr]^{-1}$ (L·mol^{-1})	$A_{0\,corr}$ (± 0.0003)	A_{uncorr} (± 0.0002)	A_{corr} (± 0.0003)	A/ΔA
0	–	–	0.9551	1.0290	0.9551	–
25.0 ± 0.5	0.740 ± 0.016	1351 ± 29	0.9475	0.9600	0.8864	14.51 ± 0.67
50.0 ± 0.7	1.468 ± 0.024	681 ± 11	0.9397	0.8965	0.8229	7.04 ± 0.17
75.0 ± 0.9	2.184 ± 0.031	457.9 ± 6.4	0.9321	0.8361	0.7625	4.496 ± 0.073
100.0 ± 1.0	2.888 ± 0.037	346.2 ± 4.4	0.9246	0.7852	0.7116	3.341 ± 0.042
150.0 ± 1.2	4.264 ± 0.049	234.5 ± 2.7	0.9099	0.6955	0.6219	2.159 ± 0.020
200.0 ± 1.4	5.596 ± 0.060	178.7 ± 1.9	0.8957	0.6273	0.5537	1.619 ± 0.012
250.0 ± 1.6	6.887 ± 0.070	145.2 ± 1.5	0.8819	0.5587	0.4851	1.2225 ± 0.0077
300.0 ± 1.7	8.140 ± 0.080	122.9 ± 1.2	0.8685	0.5074	0.4338	0.9978 ± 0.0056
400.0 ± 2.0	10.53 ± 0.10	94.93 ± 0.89	0.8430	0.4200	0.3464	0.6975 ± 0.0033
500.0 ± 2.2	12.79 ± 0.12	78.18 ± 0.71	0.8189	0.3555	0.2819	0.5249 ± 0.0022
600.0 ± 2.4	14.92 ± 0.13	67.01 ± 0.59	0.7962	0.3021	0.2285	0.4025 ± 0.0016
700.0 ± 2.6	16.94 ± 0.15	59.03 ± 0.51	0.7746	0.2620	0.1884	0.3214 ± 0.0012

Titration of [$PtMe_2$(paen-me_2)] with Me_3SnBr at 25°C

MW Me_3SnBr = 243.70 g/mol Mass Me_3SnBr = 207.2 ± 0.5 mg V_{stock} = 10.00 ± 0.05 mL

V_{Pt} = 3.000 ± 0.009 mL A_{tol} = 0.0750 ± 0.0002 $[Me_3SnBr]_{stock}$ = 0.08502 ± 0.0007 mol·L^{-1}

V_{Sn} (μL)	$[Me_3SnBr] \times 10^3$ (mol·L^{-1})	$[Me_3SnBr]^{-1}$ (L·mol^{-1})	$A_{0\,corr}$ (± 0.0003)	A_{uncorr} (± 0.0002)	A_{corr} (± 0.0003)	A/ΔA
0	–	–	1.4322	1.5072	1.4322	–
25.0 ± 0.5	0.703 ± 0.015	1423 ± 31	1.4204	1.3575	1.2825	9.30 ± 0.29
50.0 ± 0.7	1.394 ± 0.023	718 ± 12	1.4087	1.2301	1.1551	4.554 ± 0.075
75.0 ± 0.9	2.074 ± 0.029	482.2 ± 6.8	1.3973	1.1465	1.0715	3.289 ± 0.042
100.0 ± 1.0	2.743 ± 0.035	364.6 ± 4.7	1.3860	1.0521	0.9771	2.390 ± 0.024
125.0 ± 1.1	3.401 ± 0.041	294.0 ± 3.5	1.3749	0.9736	0.8986	1.887 ± 0.016
150.0 ± 1.2	4.049 ± 0.046	247.0 ± 2.8	1.3640	0.9040	0.8290	1.550 ± 0.011
175.0 ± 1.3	4.686 ± 0.052	213.4 ± 2.3	1.3533	0.8424	0.7674	1.3099 ± 0.0087
200.0 ± 1.4	5.314 ± 0.057	188.2 ± 2.0	1.3427	0.7865	0.7115	1.1272 ± 0.0069
250.0 ± 1.6	6.540 ± 0.067	152.9 ± 1.6	1.3220	0.6954	0.6204	0.8842 ± 0.0047
300.0 ± 1.7	7.729 ± 0.076	129.4 ± 1.3	1.3020	0.6240	0.5490	0.7291 ± 0.0035
350.0 ± 1.9	8.883 ± 0.085	112.6 ± 1.1	1.2826	0.5627	0.4877	0.6138 ± 0.0028
400.0 ± 2.0	10.00 ± 0.094	99.97 ± 0.94	1.2637	0.5130	0.4380	0.5305 ± 0.0022
450.0 ± 2.1	11.09 ± 0.10	90.17 ± 0.83	1.2454	0.4708	0.3958	0.4659 ± 0.0019
500.0 ± 2.2	12.15 ± 0.11	82.33 ± 0.75	1.2276	0.4336	0.3586	0.4127 ± 0.0016
600.0 ± 2.4	14.17 ± 0.13	70.57 ± 0.63	1.1935	0.3720	0.2970	0.3313 ± 0.0011
700.0 ± 2.6	16.09 ± 0.14	62.17 ± 0.54	1.1612	0.3313	0.2563	0.2832 ± 0.0010
800.0 ± 2.8	17.90 ± 0.15	55.87 ± 0.48	1.1307	0.2929	0.2179	0.2387 ± 0.0008
900.0 ± 3.0	19.62 ± 0.17	50.97 ± 0.44	1.1017	0.2673	0.1923	0.2115 ± 0.0007

Titration of $[PtMe_2(bipy)]$ with Me_3SnI at 25°C

MW Me_3SnI = 290.72 g/mol

A_{tol} = 0.0692 ± 0.0002

$\varepsilon_{Pt(II)}$ = 3721 ± 24 $L \cdot mol^{-1} \cdot cm^{-1}$

Mass Me_3SnI = 63.6 ± 0.5 mg

V_{Pt} = 3.000 ± 0.009 mL

$\varepsilon_{Pt(IV)}$ = 1450 ± 10 $L \cdot mol^{-1} \cdot cm^{-1}$

V_{stock} = 50.00 ± 0.05 mL

$[Me_3SnI]_i$ = (4.376 ± 0.035) x 10^{-3} $mol \cdot L^{-1}$

$\Delta\varepsilon$ = 2271 ± 26 $L \cdot mol^{-1} \cdot cm^{-1}$

V_{Sn} (μL)	$[Me_3SnI]_{eq}$ x 10^4 ($mol \cdot L^{-1}$)	$A_{0\ corr}$ (± 0.0003)	A_{uncorr} (± 0.0002)	A_{corr} (± 0.0003)	ΔA (± 0.002)	$\Delta A/[Me_3SnI]_{eq}$ ($L \cdot mol^{-1}$)
0	–	0.7457	0.8149	0.7457	–	–
50.0 ± 0.7	0.098 ± 0.019	0.7334	0.6620	0.5928	0.1406	14355 ± 2700
75.0 ± 0.9	0.169 ± 0.023	0.7275	0.5927	0.5235	0.2040	12066 ± 1600
100.0 ± 1.0	0.263 ± 0.026	0.7216	0.5300	0.4608	0.2608	9913 ± 990
125.0 ± 1.1	0.370 ± 0.029	0.7159	0.4715	0.4023	0.3135	8480 ± 680
150.0 ± 1.2	0.505 ± 0.033	0.7101	0.4208	0.3516	0.3586	7100 ± 460
175.0 ± 1.3	0.688 ± 0.036	0.7046	0.3822	0.3130	0.3916	5690 ± 300
200.0 ± 1.4	0.888 ± 0.038	0.6991	0.3488	0.2796	0.4195	4724 ± 210
225.0 ± 1.5	1.110 ± 0.041	0.6937	0.3216	0.2524	0.4413	3975 ± 150
250.0 ± 1.6	1.352 ± 0.043	0.6884	0.3000	0.2308	0.4575	3384 ± 110
275.0 ± 1.7	1.597 ± 0.046	0.6831	0.2805	0.2113	0.4718	2953 ± 86
300.0 ± 1.7	1.860 ± 0.048	0.6779	0.2660	0.1968	0.4811	2587 ± 68
325.0 ± 1.8	2.120 ± 0.049	0.6728	0.2519	0.1827	0.4901	2312 ± 56
350.0 ± 1.9	2.388 ± 0.052	0.6678	0.2410	0.1718	0.4960	2077 ± 47
375.0 ± 1.9	2.655 ± 0.054	0.6628	0.2308	0.1616	0.5012	1888 ± 40
400.0 ± 2.0	2.927 ± 0.056	0.6580	0.2226	0.1534	0.5046	1724 ± 34

Titration of $[PtMe_2(bipy\text{-}^tbu_2)]$ with Me_3SnI at 25°C

MW Me_3SnI = 290.72 g/mol

A_{tol} = 0.0692 ± 0.0002

$\varepsilon_{Pt(II)}$ = 3463 ± 8 $L \cdot mol^{-1} \cdot cm^{-1}$

Mass Me_3SnI = 53.0 ± 0.5 mg

V_{Pt} = 3.000 ± 0.009 mL

$\varepsilon_{Pt(IV)}$ = 17.5 ± 10 $L \cdot mol^{-1} \cdot cm^{-1}$

V_{stock} = 50.00 ± 0.05 mL

$[Me_3SnI]_i$ = (3.647 ± 0.035) x 10^{-3} $mol \cdot L^{-1}$

$\Delta\varepsilon$ = 3446 ± 13 $L \cdot mol^{-1} \cdot cm^{-1}$

V_{Sn} (μL)	$[Me_3SnI]_{eq}$ x 10^4 ($mol \cdot L^{-1}$)	$A_{0\ corr}$ (± 0.0003)	A_{uncorr} (± 0.0002)	A_{corr} (± 0.0003)	ΔA (± 0.006)	$\Delta A/[Me_3SnI]_{eq}$ ($L \cdot mol^{-1}$)
0	–	2.1278	2.197	2.1278	–	–
150.0 ± 1.2	1.737 ± 0.021	2.0265	1.5460	1.4768	0.5497	38900 ± 7800
200.0 ± 1.4	2.279 ± 0.027	1.9948	1.3530	1.2838	0.7110	33000 ± 5000
250.0 ± 1.6	2.805 ± 0.032	1.9641	1.1773	1.1081	0.8560	26700 ± 3100
300.0 ± 1.7	3.315 ± 0.037	1.9344	1.0226	0.9534	0.9810	20900 ± 1900
350.0 ± 1.9	3.810 ± 0.042	1.9055	0.8878	0.8186	1.0869	16600 ± 1200
400.0 ± 2.0	4.291 ± 0.046	1.8775	0.7754	0.7062	1.1713	13140 ± 740
500.0 ± 2.2	5.210 ± 0.055	1.8238	0.5984	0.5292	1.2946	8910 ± 360
600.0 ± 2.4	6.078 ± 0.063	1.7732	0.4835	0.4143	1.3589	6370 ± 200
700.0 ± 2.6	6.900 ± 0.070	1.7252	0.4064	0.3372	1.3880	4830 ± 120

Titration of [$PtMe_2$(py-*n*-pr)] with Me_3SnI at 25°C

MW Me_3SnI = 290.72 g/mol
A_{tol} = 0.0739 ± 0.0002
$\varepsilon_{Pt(II)}$ = 4407 ± 10 L·mol^{-1}·cm^{-1}

Mass Me_3SnI = 63.6 ± 0.5 mg
V_{Pt} = 3.000 ± 0.009 mL
$\varepsilon_{Pt(IV)}$ = 1085 ± 10 L·mol^{-1}·cm^{-1}

V_{stock} = 50.00 ± 0.05 mL
$[Me_3SnI]_i$ = (4.376 ± 0.035) x 10^{-3} mol·L^{-1}
$\Delta\varepsilon$ = 3322 ± 14 L·mol^{-1}·cm^{-1}

V_{Sn} (μL)	$[Me_3SnI]_{eq}$ x 10^4 (mol·L^{-1})	$A_{0\ corr}$ (± 0.0003)	A_{uncorr} (± 0.0002)	A_{corr} (± 0.0003)	ΔA (± 0.002)	$\Delta A/[Me_3SnI]_{eq}$ (L·mol^{-1})
0	–	0.9561	1.0300	0.9561	–	–
50.0 ± 0.7	0.717 ± 0.012	0.9404	0.8467	0.7728	0.1676	7880 ± 560
75.0 ± 0.9	1.067 ± 0.015	0.9328	0.7672	0.6933	0.2395	6910 ± 360
100.0 ± 1.0	1.412 ± 0.018	0.9253	0.6980	0.6241	0.3012	5960 ± 240
125.0 ± 1.1	1.751 ± 0.021	0.9179	0.6408	0.5669	0.3510	5060 ± 170
150.0 ± 1.2	2.084 ± 0.024	0.9106	0.5864	0.5125	0.3981	4490 ± 130
200.0 ± 1.4	2.735 ± 0.029	0.8963	0.5020	0.4281	0.4682	3532 ± 84
250.0 ± 1.6	3.366 ± 0.034	0.8826	0.4394	0.3655	0.5171	2857 ± 58
300.0 ± 1.7	3.980 ± 0.039	0.8692	0.3916	0.3177	0.5515	2379 ± 43
350.0 ± 1.9	4.572 ± 0.044	0.8562	0.3576	0.2837	0.5725	2110 ± 33
400.0 ± 2.0	5.149 ± 0.048	0.8436	0.3292	0.2553	0.5883	1741 ± 26
450.0 ± 2.1	5.708 ± 0.053	0.8314	0.3072	0.2333	0.5981	1531 ± 22

Titration of $[PtMe_2(paen\text{-}me_2)]$ with Me_3SnI at 25°C

MW Me_3SnI = 290.72 g/mol

A_{tol} = 0.0795 ± 0.0002

$\varepsilon_{Pt(II)}$ = 4133 ± 10 $L \cdot mol^{-1} \cdot cm^{-1}$

Mass Me_3SnI = 64.5 ± 0.5 mg

V_{Pt} = 3.000 ± 0.009 mL

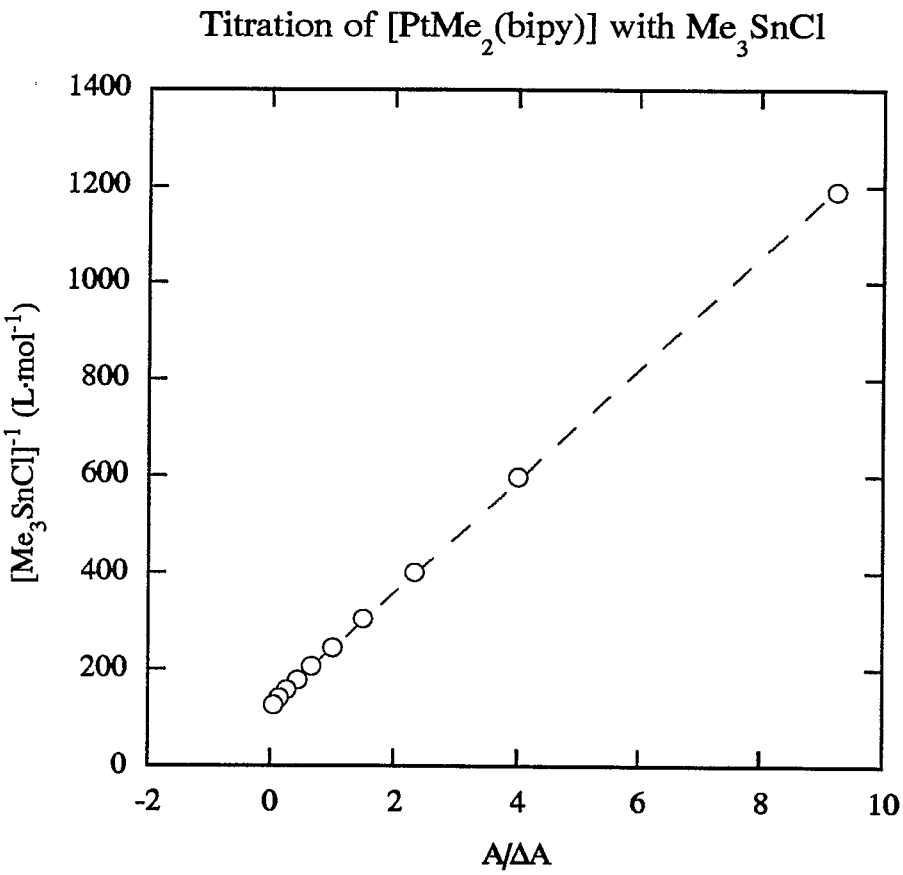
$\varepsilon_{Pt(IV)}$ = 1028 ± 10 $L \cdot mol^{-1} \cdot cm^{-1}$

V_{stock} = 50.00 ± 0.05 mL

$[Me_3SnI]_i$ = (4.438 ± 0.035) x 10^{-3} $mol \cdot L^{-1}$

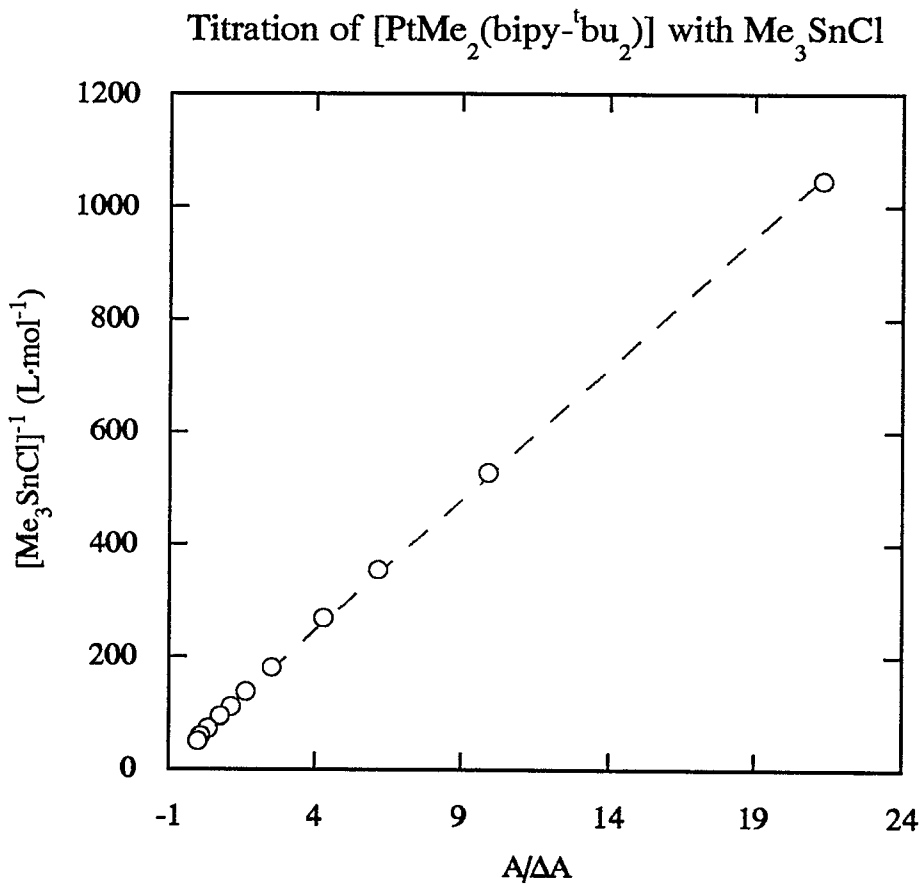
$\Delta\varepsilon$ = 3105 ± 14 $L \cdot mol^{-1} \cdot cm^{-1}$

V_{Sn} (μL)	$[Me_3SnI]_{eq}$ x 10^4 ($mol \cdot L^{-1}$)	$A_{0\ corr}$ (± 0.0003)	A_{uncorr} (± 0.0002)	A_{corr} (± 0.0003)	ΔA (± 0.002)	$\Delta A/[Me_3SnI]_{eq}$ ($L \cdot mol^{-1}$)
0	–	1.3076	1.3871	1.3076	–	–
75.0 ± 0.9	1.082 ± 0.015	1.2757	1.0563	0.9768	0.2989	24900 ± 4200
100.0 ± 1.0	1.432 ± 0.015	1.2654	0.9566	0.8771	0.3883	21400 ± 2700
150.0 ± 1.2	2.114 ± 0.018	1.2453	0.7822	0.7027	0.5426	14800 ± 1100
200.0 ± 1.4	2.774 ± 0.021	1.2259	0.645	0.5655	0.6604	10200 ± 520
250.0 ± 1.6	3.414 ± 0.024	1.2070	0.5422	0.4627	0.7443	7320 ± 270
300.0 ± 1.7	4.035 ± 0.029	1.1887	0.4669	0.3874	0.8013	5510 ± 160
350.0 ± 1.9	4.637 ± 0.034	1.1710	0.4128	0.3333	0.8377	4320 ± 110
400.0 ± 2.0	5.222 ± 0.039	1.1538	0.3687	0.2892	0.8646	3550 ± 76
450.0 ± 2.1	5.789 ± 0.044	1.1370	0.339	0.2595	0.8775	2960 ± 56
500.0 ± 2.2	6.340 ± 0.048	1.1208	0.3162	0.2367	0.8841	2530 ± 43



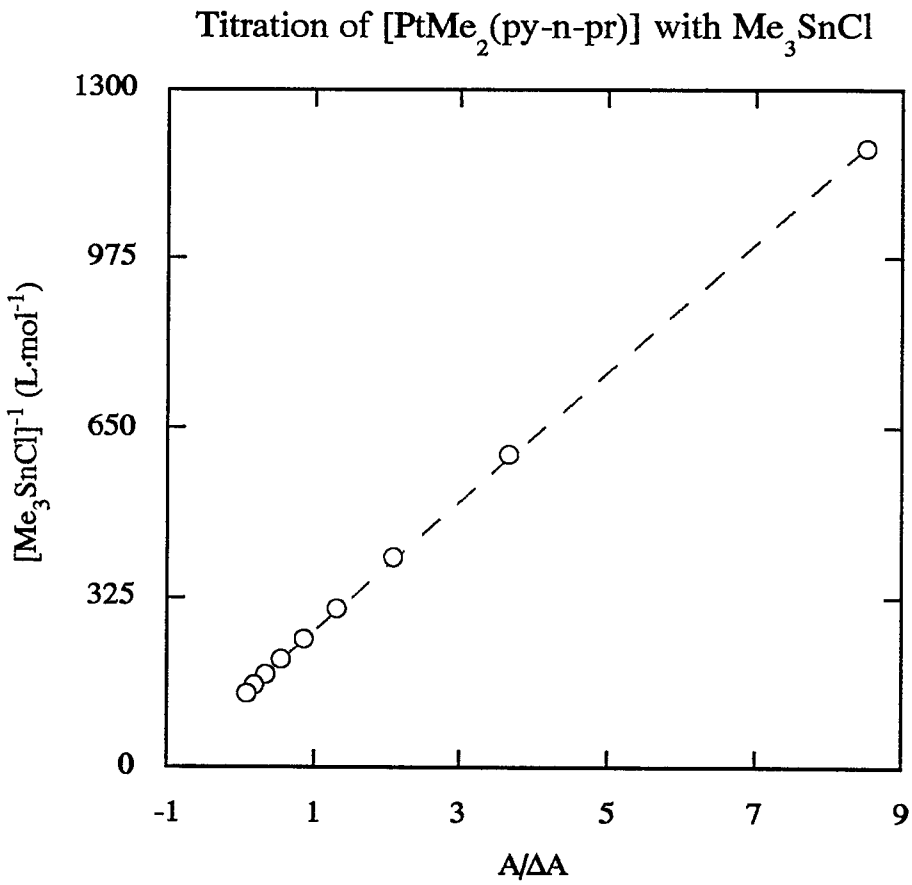
Regression Analysis

slope = 115.1(6) L/mol = K_{eq}	r^2 = 0.9998
intercept = 129(2)	se_y = 4.8
F = 42129	ss_{reg} = 957923
df = 8	ss_{resid} = 181.9



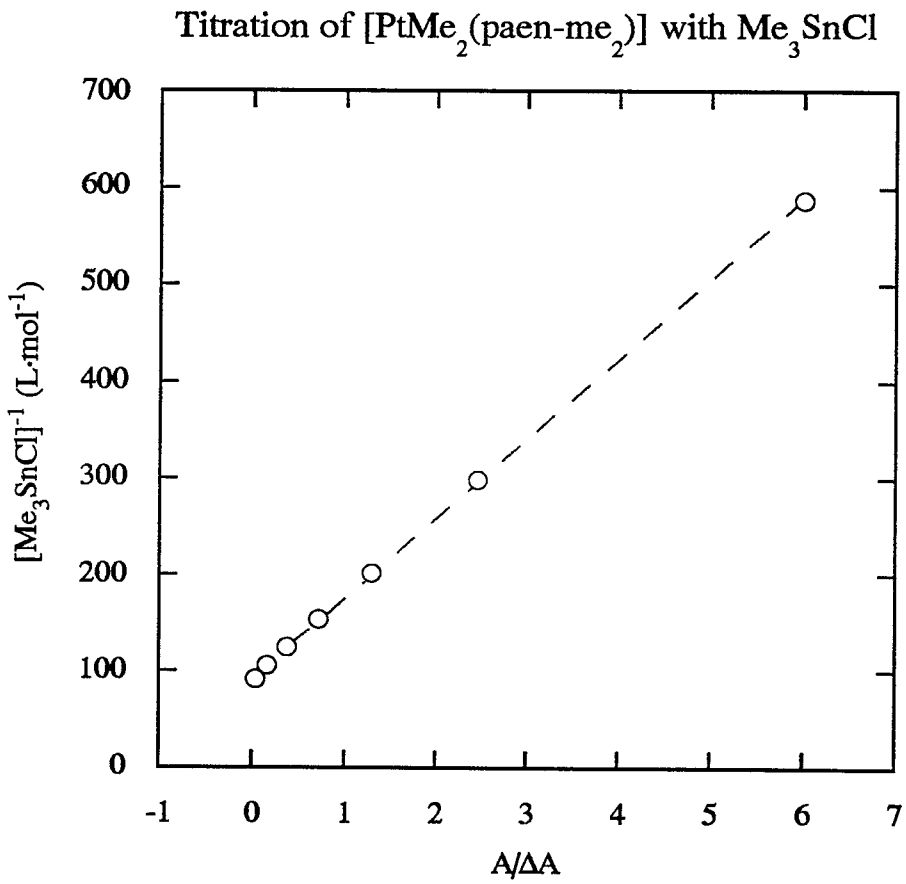
Regression Analysis

slope = 46.5(2) L/mol = $\mathbf{K_{eq}}$	r^2 = 0.9997
intercept = 61(6)	se_y = 5.65
F = 27814	ss_{reg} = 887999
df = 9	ss_{resid} = 287.3



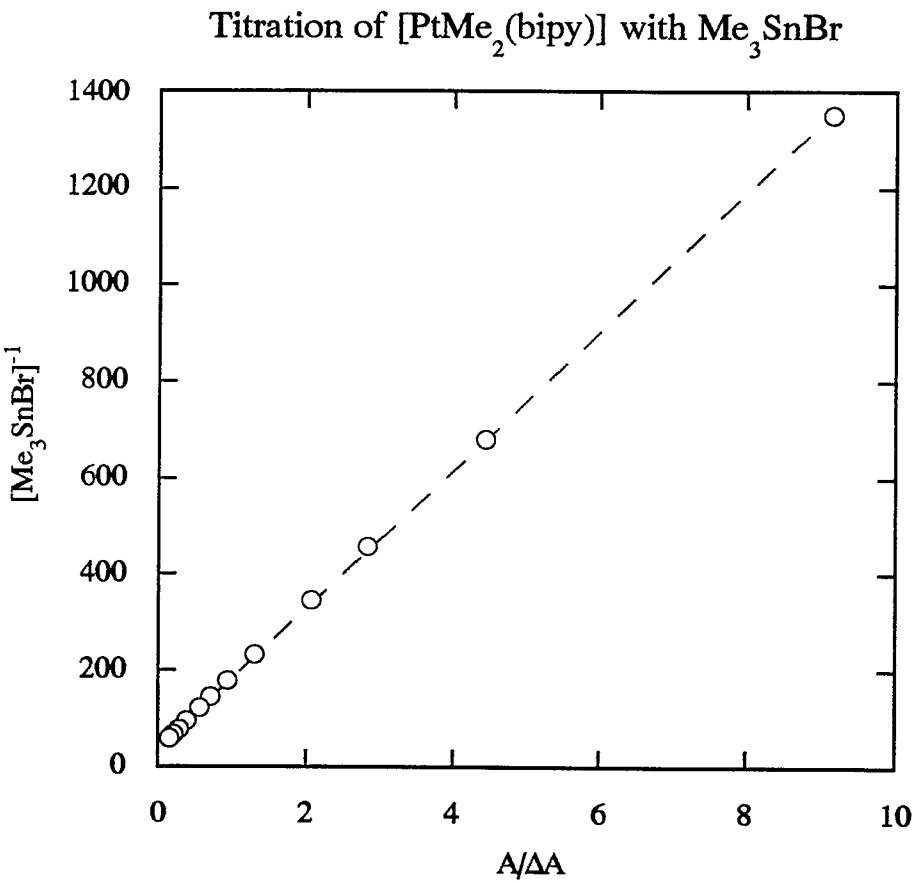
Regression Analysis

slope = 123.8(6) L/mol = K_{eq}	r^2 = 0.9992
intercept = 138(2)	se_y = 4.92
F = 37251	ss_{reg} = 900721
df = 7	ss_{resid} = 169



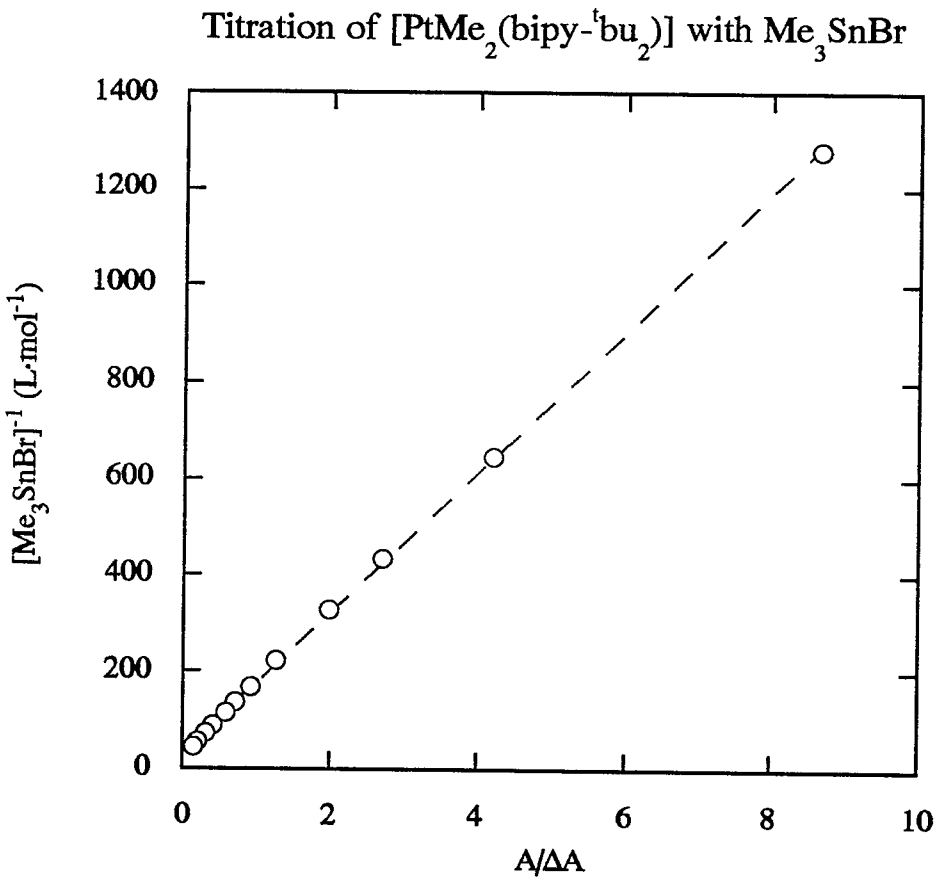
Regression Analysis

slope = 82.6(5) L/mol = K_{eq}	r^2 = 0.9998
intercept = 93(1)	se_y = 2.56
F = 27985	ss_{reg} = 183739
df = 5	ss_{resid} = 32.8



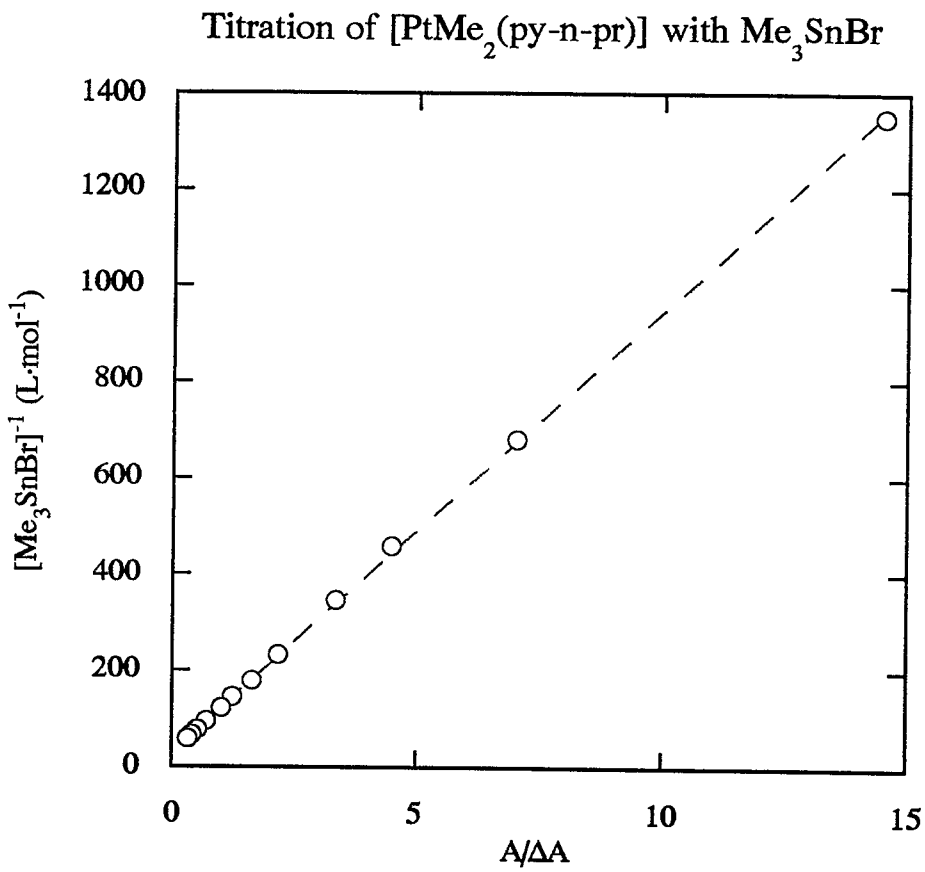
Regression Analysis

slope = 143.8(6) L/mol = K_{eq}	r^2 = 0.9998
intercept = 41(2)	se_y = 5.17
F = 58105	ss_{reg} = 1551658
df = 10	ss_{resid} = 267



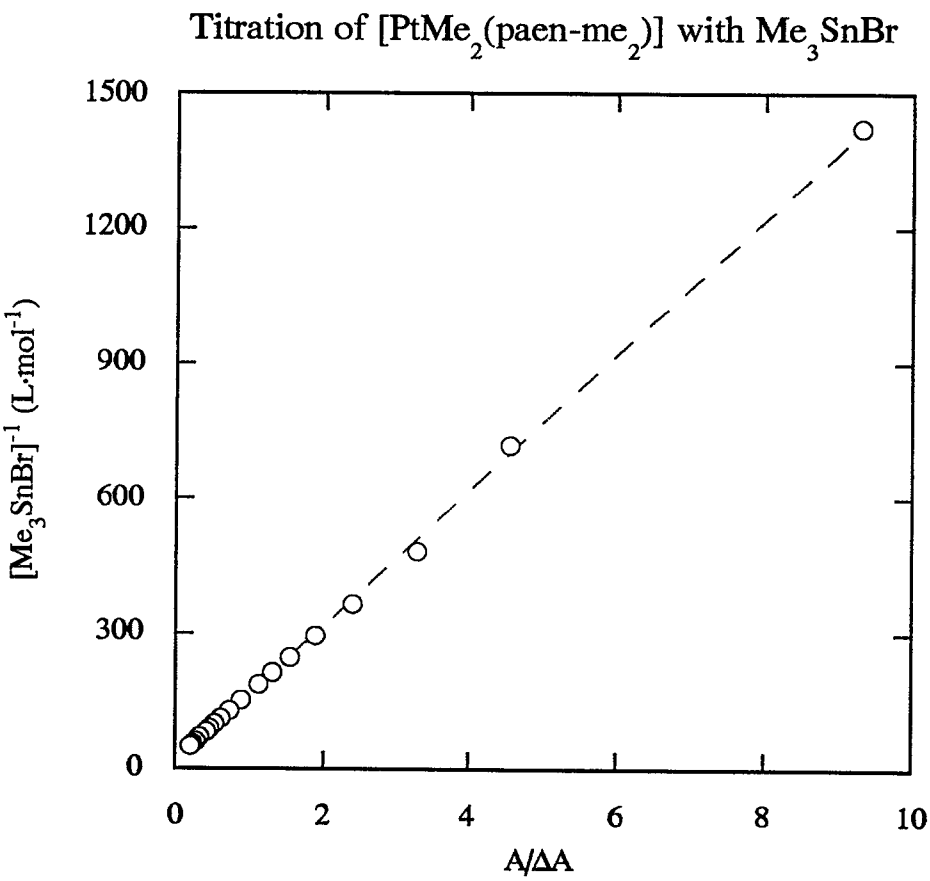
Regression Analysis

slope = 145.2(7) L/mol = K_{eq}	r^2 = 0.9998
intercept = 32(2)	se_y = 5.94
F = 39686	ss_{reg} = 1402674
df = 10	ss_{resid} = 353



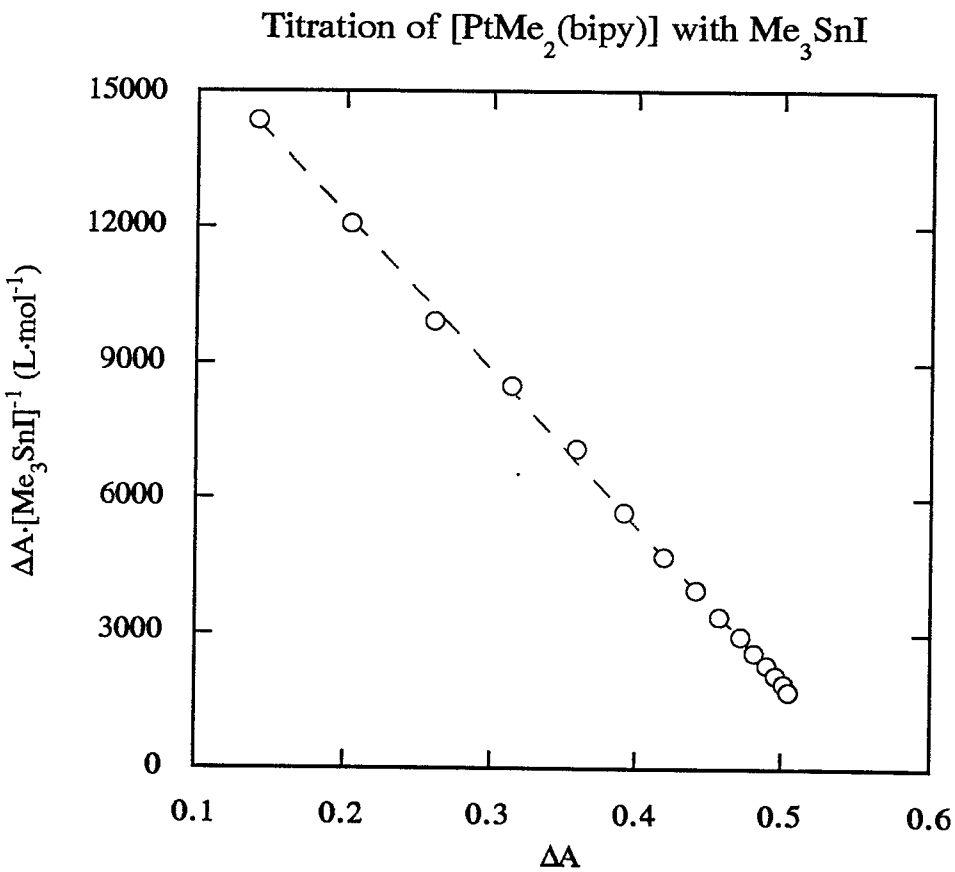
Regression Analysis

slope = 91.3(5) L/mol = K_{eq}	r^2 = 0.9998
intercept = 34(2)	se_y = 6.16
F = 40824	ss_{reg} = 1551545
df = 10	ss_{resid} = 380



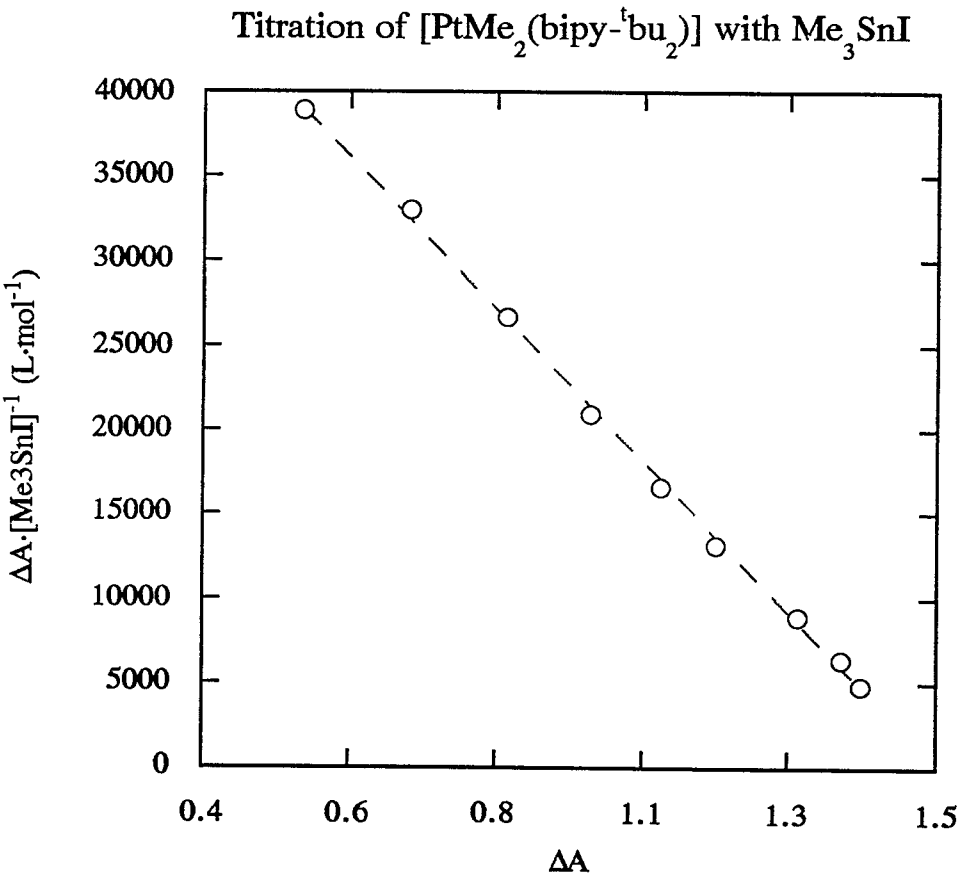
Regression Analysis

slope = 151(1) L/mol = K_{eq}	r^2 = 0.9992
intercept = 16(4)	se_y = 10.4
F = 16151	ss_{reg} = 1762605
df = 13	ss_{resid} = 1419



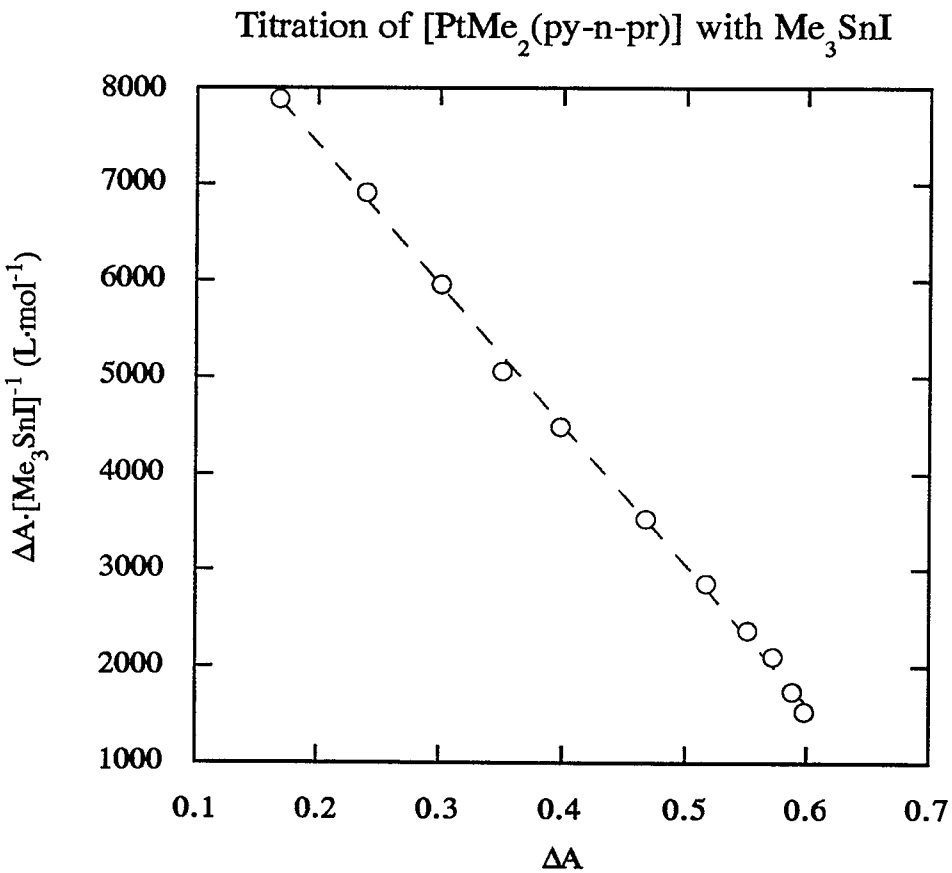
Regression Analysis

slope = -34360(269) L/mol = $-K_{eq}$	r^2 = 0.9992
intercept = 19137(110)	se_y = 117
F = 16247	ss_{reg} = 2.24 x 10^8
df = 13	ss_{resid} = 1.79 x 10^5



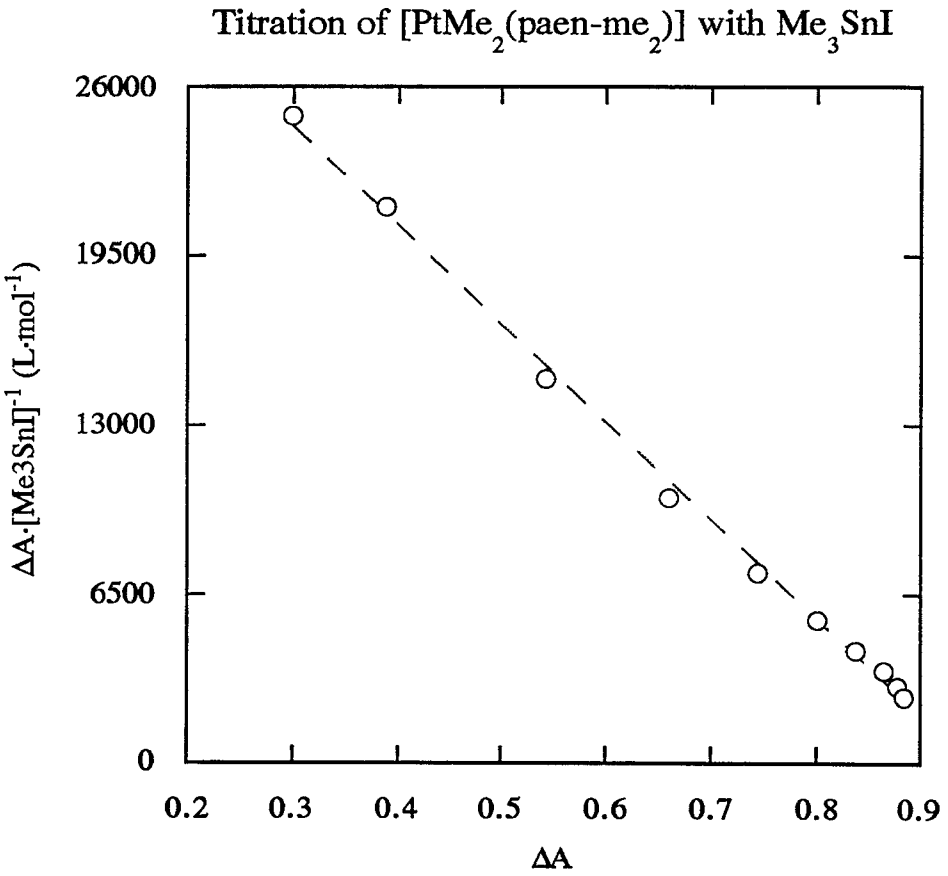
Regression Analysis

slope = -40808(513) L/mol = $-K_{eq}$	r^2 = 0.9989
intercept = 61421(554)	se_y = 427
F = 6311	ss_{reg} = 1.15 x 10^9
df = 7	ss_{resid} = 1.28 x 10^6



Regression Analysis

slope = -14554(159) L/mol = $-K_{eq}$	r^2 = 0.9989
intercept = 10320(72)	se_y = 75.6
F = 8382	ss_{reg} = 4.80 x 10^7
df = 9	ss_{resid} = 5.15 x 10^5



Regression Analysis

slope = -37821(646) L/mol = $-K_{eq}$	r^2 = 0.9977
intercept = 35857(464)	se_y = 412
F = 3428	ss_{reg} = 5.82 x 10^8
df = 8	ss_{resid} = 1.36 x 10^6

Calculations and Data for VT ^{1}H-NMR Spectroscopic Studies

Thermodynamics

The oxidative addition of an alkylhalotin reagent to a Pt(II) complex is represented by Equation 32, where 'Sn' denotes the tin complex, 'Pt' denotes the platinum(II) complex, and 'PtSn' denotes the oxidative addition product.

$$\mathrm{Pt} + \mathrm{Sn} \rightleftharpoons \mathrm{PtSn} \qquad (32)$$

The expression for the equilibrium constant, K_{eq}, is thus given by Equation 33.

$$K_{eq} = \frac{[\mathrm{PtSn}]}{[\mathrm{Pt}][\mathrm{Sn}]} \qquad (33)$$

In our VT-NMR studies we generally observe only one averaged methyl platinum signal, due to the rapid equilibrium and the small chemical shift difference between the Me-Pt(II) and Me-Pt(IV) signals. The Me-Pt coupling constant, ^2J(PtH), is also averaged. With careful measurement of the respective coupling constants of the pure platinum(II) starting material (J_{Pt}) and platinum(IV) oxidative addition product (J_{PtSn}), the mole fractions of each of the species can be determined from the magnitude of the averaged coupling constant by use of Equations 34 and 35. These mole fractions can directly replace [Pt] and [PtSn] in the equilibrium expression, Equation 33. Solutions used in our studies are

$$\chi_{Pt} = \frac{J_{ave} - J_{PtSn}}{J_{Pt} - J_{PtSn}} \qquad (34)$$

$$\chi_{PtSn} = \frac{J_{Pt} - J_{ave}}{J_{Pt} - J_{PtSn}} \tag{35}$$

either prepared by dissolution of platinum(IV) complex of known Pt:Sn ratio, or by the addition of a known number of equivalents of tin reagent to a solution of platinum(II) complex. In either case, the total tin concentration $[Sn]_{tot}$ relative to the total platinum concentration $[Pt]_{tot}$ is known. This relationship can be expressed as in Equation 36.

$$[Sn]_{tot} = n[Pt]_{tot} \qquad (36).$$

We can now derive an expression for [Sn] in terms of χ_{PtSn} (Equation 37) and this can be inserted into the equilibrium expression to give Equation 38. The quantity in brackets can be shown to be the proportion of tin species in the form of free tin complex (p_{Sn}).

$$[Sn] = \left(1 - \frac{\chi_{PtSn}}{n}\right)[Sn]_{tot} \qquad (37)$$

$$K_{eq} = \frac{\chi_{PtSn}}{\chi_{Pt}\left(1 - \frac{\chi_{PtSn}}{n}\right)[Sn]_{tot}} = \frac{\chi_{PtSn}}{\chi_{Pt}\ p_{Sn}\,[Sn]_{tot}} \qquad (38)$$

The reversible oxidative addition of Me_3GeCl to $[PtMe_2(bipy\text{-}^tbu_2)]$ is much slower than the corresponding Me_3SnCl oxidative addition. As a result, the VT-NMR spectra do not show an averaged Me-Pt signal, but instead show separate Me-Pt signals for the platinum(II) and platinum(IV) complexes. Since an averaged ^2J(PtMe) is not available, peak integrals can be used to monitor relative concentrations. It is convenient to monitor the integrals of the resonances corresponding to free Me_3GeCl and the Me_3Ge-Pt(IV) group since there are no other resonances close to either signal. The mole fractions of free Me_3GeCl, χ_{Ge}, and complexed Me_3GeCl, χ_{PtGe},

are thus readily obtained from the integrals of each signal relative to the total integral area of both signals. Since the Pt:Ge ratio in the solution used was 1:1, the [Pt] is simply equal to $\chi_{Ge}[Pt]_{tot}$, and the final equilibrium expression is that given in Equation 39.

$$K_{eq} = \frac{\chi_{PtGe}}{\chi_{Ge}^{2}\,[Pt]_{tot}} \qquad (39)$$

Using the methods above we can obtain a series of equilibrium constants at different temperatures for the oxidative addition reaction. Standard thermodynamic relationships can then be used to determine ΔG, ΔH°, and ΔS° for the reaction. ΔG can be obtained directly from the equilibrium constant according to Equation 40, where R and T have their usual meanings of the ideal gas constant and temperature (K), respectively.

$$\Delta G = -R\,T \ln K_{eq} \qquad (40).$$

Equation 41[1] indicates that a plot of ln K_{eq} *vs* T^{-1} will have a slope of $-\Delta H^{\circ}/R$ and an intercept of $\Delta S^{\circ}/R$, and this method has been used to obtain the ΔH° and ΔS° values reported in this chapter. ΔH° is assumed to be independent of temperature, which is often the case.

$$\ln K_{eq} = -\frac{\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R} \qquad (41)$$

1. Laidler, K. J.; Meiser, J. H. *Physical Chemistry*; Benjamin/Cummings: Don Mills, Ontario, 1982; p. 156.

Kinetics

Kinetic analysis by NMR spectroscopic methods is a common technique, although the majority of applications have dealt with intramolecular processes. In this work, we are concerned with an intermolecular reaction, but a similar treatment may be used here. At the most simple level, we are looking at the exchange of a nucleus between two sites. Whether they are in the same molecule or not is irrelevant. In most of our kinetic studies we monitor the line width of the free tin reagent signal in a solution containing two equivalents of tin reagent for each equivalent of platinum(II) complex. In most systems, the second equivalent of tin reagent allows the observation of fast and slow exchange regions as well as coalescence (Me–Sn signal). In the slow exchange region, the Me–Sn signal due to unreacted tin reagent is free of the broadening effects of ^{195}Pt satellite signals, thus allowing for the more accurate determination of line widths. In the fast exchange region, the broadening effect of the platinum satellites on the averaged Me-Sn signal is diminished by the presence of a second equivalent of tin reagent, since a smaller proportion of the signal arises from the methyltin resonance of the platinum(IV) complex. In one case, the kinetic analysis for the addition of Me_2SnCl_2 to [$PtMe_2$(bipy-^{t}bu$_2$)], the signal due to the free tin reagent was interfered with by other signals; the Me_2SnCl–Pt(IV) signal was used for kinetic analysis. Satisfactory results were obtained despite the broadening effect of the ^{195}Pt satellites on the signal.

The ^{1}H Me–Sn resonances of the free tin reagent and of the platinum(IV) oxidative addition product are ideal for kinetic study due to the large frequency difference between them, which is more than 300 Hz in some cases. This difference allows for the measurement of rates over a wide range of temperatures. In the slow exchange region, a peak width is only useful if it is smaller than the frequency difference, $\delta\nu$, between the two environments. With a large $\delta\nu$, large peak widths can be tolerated and the change in peak widths with temperature is substantial, providing data of good precision. The rate constant for a process in the fast exchange region is proportional to $\delta\nu^2$ and hence, for large peak separations, very rapid processes can be studied. Another advantage of a large $\delta\nu$ is that exchange broadening can be quite substantial, and so errors in W_0

have only a small influence on the rate constants obtained. This is particularly significant for the present studies because W_0 is determined iteratively.

Kinetics data determined from the line widths of Me-Sn VT-NMR signals are not for the oxidative addition reaction, but are instead for the process described by Equation 42. Inspection shows that k_B is in fact the rate constant for the reductive elimination process; a unimolecular process with no dependence on [Pt]. Thus, the rate constant for reductive elimination, k_{red} can be expressed by Equation 43 in the slow exchange region and Equation 44 in the fast exchange region.

$$\mathrm{Sn} \underset{k_B}{\overset{k_A}{\rightleftharpoons}} \mathrm{PtSn} \qquad (42)$$

$$k_{red} = \pi(W_{Sn} - W_0) \qquad (43)$$

$$k_{red} = 4\pi\, p_{PtSn}\, p_{Sn}^2\, (\delta\nu)^2\, (W^* - W_0)^{-1} \qquad (44)$$

In Equation 44, the values of p_{Sn} and p_{PtSn} are the relative proportions of free tin reagent and platinum(IV) complex, respectively. By rearrangement of Equation 38 we obtain an expression for p_{Sn} in terms of χ_{PtSn} (Equation 45). Note that χ_{PtSn} is the mole fraction with respect to total Pt content, while p_{Sn} and p_{PtSn} are mole fractions with respect to total tin content, and therefore $p_{PtSn} \neq \chi_{PtSn}$. The value of p_{PtSn} is easily obtained by the relationship in Equation 46.

$$p_{Sn} = 1 - \chi_{PtSn} / n \qquad (45)$$

$$p_{PtSn} = 1 - p_{Sn} = \chi_{PtSn} / n \qquad (46)$$

With a series of k_{red} at different temperatures, we can now evaluate the activation parameters of the reductive elimination reaction. From Equation 47, the Eyring equation, where **k** is the Boltzmann constant and h is the Planck constant, we can derive a direct expression for $\Delta G^{\ddagger}_{red}$ from the rate constant at a given temperature (Equation 48).

$$k = \frac{kT}{h} e^{\Delta S\ddagger/R} e^{-\Delta H\ddagger/RT} = \frac{kT}{h} e^{-\Delta G\ddagger/RT} \qquad (47)$$

$$\Delta G^{\ddagger}_{red} = -RT \ln(k_{red}/T) - 23.760 \qquad (48)$$

A logarithmic form of the Eyring equation is shown in Equation 49, and inspection shows that a plot of ln (k_{red}/T) *vs* T^{-1} will give a slope of $-\Delta H^{\ddagger}_{red}/R$ and an intercept of $\Delta S^{\ddagger}/R - 23.760$ (Eyring plot).

$$\ln \frac{k_{red}}{T} = \frac{-\Delta H^{\ddagger}_{red}}{RT} + \frac{\Delta S^{\ddagger}_{red}}{R} - 23.760 \qquad (49)$$

The rate constant for the oxidative addition reaction of tin reagent to platinum(II) complex at a given temperature can be obtained directly from Equation 50, provided the equilibrium constant for oxidative addition is known at that temperature.

$$k_{ox} = k_{red} K_{eq} \quad (50)$$

The activation parameters for the oxidative addition reaction can be calculated from the activation parameters for the reductive elimination reaction along with the thermodynamic parameters of the oxidative addition reaction (Equations 51 - 53).

$$\Delta G^{\ddagger}_{ox} = \Delta G^{\ddagger}_{red} + \Delta G \quad (51)$$

$$\Delta H^{\ddagger}_{ox} = \Delta H^{\ddagger}_{red} + \Delta H \quad (52)$$

$$\Delta S^{\ddagger}_{ox} = \Delta S^{\ddagger}_{red} + \Delta S \quad (53)$$

Errors in Thermodynamic Parameters.

Experimental errors have been estimated for all directly measured parameters. Assigned errors are found in each individual data set, and the symbols used to denote these errors are as follows:

∂ mass platinum(II) complex = ∂m_{Pt}

∂ mass platinum(IV) complex = ∂m_{PtSn}

∂ volume of solvent = ∂V_s

$\partial\, {}^2J_{PtH}$ for platinum(II) complex = ∂J_{Pt}

$\partial\, {}^2J_{PtH}$ for platinum(IV) complex = ∂J_{PtSn}

$\partial\, {}^2J_{PtH}$ for averaged signal = ∂J_{ave}

∂ Sn:Pt ratio in solution = ∂n

The following formulas are used in the calculation of errors in parameters derived from the raw data:

$$\partial[\mathrm{Pt}]_{tot} = [\mathrm{Pt}]_{tot}\{(\partial m_{Pt}/m_{Pt})^2 + (\partial V_s/V_s)^2\}^{1/2} \text{ if Pt(II) cpx. was weighed} \quad (54)$$

$$\partial[\mathrm{Pt}]_{tot} = [\mathrm{Pt}]_{tot}\{(\partial m_{PtSn}/m_{PtSn})^2 + (\partial V_s/V_s)^2\}^{1/2} \text{ if Pt(IV) cpx. was weighed} \quad (55)$$

$$\partial[\mathrm{Sn}]_{tot} = [\mathrm{Sn}]_{tot}\{(\partial[\mathrm{Pt}]_{tot}/[\mathrm{Pt}]_{tot})^2 + (\partial n/n)^2\}^{1/2} \quad (56)$$

$$\partial T^{-1} = \partial T/T^2 \quad (57)$$

$$\partial\chi_{Pt}=\chi_{Pt}\{([\partial J_{ave}^2+\partial J_{PtSn}^2]^{1/2}/[J_{ave}-J_{PtSn}])^2+ ([\partial J_{Pt}^2+\partial J_{PtSn}^2]^{1/2}/[J_{Pt}-J_{PtSn}])^2\}^{1/2} \quad (58)$$

$$\partial\chi_{PtSn} = (\chi_{PtSn}/\chi_{Pt})\partial\chi_{Pt} \quad (59)$$

$$\partial p_{Sn} = (\chi_{PtSn}/n)\ \{(\partial\chi_{PtSn}/\chi_{PtSn})^2 + (\partial n/n)^2\}^{1/2} \quad (60)$$

$$\partial p_{PtSn} = (p_{PtSn}/p_{Sn})\ \partial p_{Sn} \quad (61)$$

$$\partial K_{eq} = K_{eq}\{(\partial\chi_{PtSn}/\chi_{PtSn})^2 + (\partial\chi_{Pt}/\chi_{Pt})^2 + (\partial p_{Sn}/p_{Sn})^2 + (\partial[\mathrm{Sn}]_{tot}/[\mathrm{Pt}]_{tot})^2\}^{1/2} \quad (62)$$

$$\partial \ln K_{eq} = \partial K_{eq}/K_{eq} \quad (63)$$

$$\partial\Delta G = \Delta G\{(\partial T/T)^2 + (\partial \ln K_{eq}/K_{eq})^2\}^{1/2} \quad (64)$$

$\partial\Delta H^\circ$ and $\partial\Delta S^\circ$ are derived from the regression analysis of the plot of $\ln K_{eq}$ vs T^{-1}.

Errors in Kinetic Parameters.

Experimental errors have been estimated for all measured parameters. Assigned errors are found in each individual data set and the symbols used to denote these errors are as follows (symbols presented earlier are not repeated here):

∂ in a measured line width at half height = ∂W

∂ in estimated W_0 = ∂W_0

∂ in frequency difference = $\partial \delta \nu$

The following are errors associated with the calculation of kinetic parameters. Relevant error calculations that have been outlined already will not be repeated here.

$$\partial (W - W_0) = \partial \Delta W = \{(\partial W/W)^2 + (\partial W_0/W_0)^2\}^{1/2} \quad (65)$$

$$\partial k_{red} = \pi\, \partial \Delta W \text{ in the slow exchange region} \quad (66)$$

$$\partial k_{red} = k_{red}\, \{(\partial p_{Sn}/p_{Sn})^2 + (2\partial p_{PtSn}/p_{PtSn})^2 + (2\partial \delta \nu/\delta \nu)^2 + (\partial \Delta W/\Delta W)^2\}^{1/2} \quad (67)$$

in the fast exchange region.

$$\partial \ln(k_{red}/T) = \{(\partial k_{red}/k_{red})^2 + (\partial T/T)^2\}^{1/2} \quad (68)$$

$$\partial \Delta G^{\ddagger}_{red} = (\Delta G^{\ddagger}_{red} - 23.760)\{(\partial T/T)^2 + (\partial \ln(k/T)/\ln(k/T))^2\}^{1/2} \quad (69)$$

The values for $\partial \Delta H^{\ddagger}_{red}$ and $\partial \Delta S^{\ddagger}_{red}$ are obtained from the regression analysis of the plot of $\ln(k_{red}/T)$ *vs* T^{-1} and are known to underestimate errors in these values. A number of methods have been used to get a better estimate of the errors associated with these parameters, and one of the most common is to increase the level of confidence of the error interval from 67% for the

standard deviation to 90% or 95%.[2] This amounts to multiplying the standard deviations by the *tp* factor (critical value for Student's 2-sided *t* distribution) appropriate to the confidence level and the number of degrees of freedom. We have adopted this method at the 95% confidence level. Having established the errors in the activation parameters for reductive elimination, errors associated with the derived activation parameters for oxidative addition can now be calculated.

$$\partial\Delta G^{\ddagger}_{ox} = \{(\partial\Delta G^{\ddagger}_{red}/\Delta G^{\ddagger}_{red})^2 + (\partial\Delta G/\Delta G)^2\}^{1/2} \quad (70)$$

$$\partial\Delta H^{\ddagger}_{ox} = \{(\partial\Delta H^{\ddagger}_{red}/\Delta H^{\ddagger}_{red})^2 + (\partial\Delta H/\Delta H)^2\}^{1/2} \quad (71)$$

$$\partial\Delta S^{\ddagger}_{ox} = \{(\partial\Delta S^{\ddagger}_{red}/\Delta S^{\ddagger}_{red})^2 + (\partial\Delta S/\Delta S)^2\}^{1/2} \quad (72)$$

2. Sandström, J. *op. cit.*; 1982; p. 115.

Thermodynamic Data for the Oxidative Addition of Me_3SnCl to $[PtMe_2(bipy\text{-}^tbu_2)]$ in Toluene-d_8

M.W. Pt(II) cpx. = 493.55 g mol^{-1}
M.W. Me_3SnCl = 199.25 g mol^{-1}
$n_{Sn\ tot}/n_{Pt\ tot}$ = 2.00 ± 0.05

mass Pt(IV) cpx. = 3.5 ± 0.1 mg
Vol. toluene-d_8 = 0.7192 ± 0.0005 mL
Pt(II) $^2J_{PtH}$ = 85.7 ± 0.10 Hz

$[Pt]_{tot}$ = (5.45 ± 0.16) x 10^{-3} M
$[Sn]_{tot}$ = (1.09 ± 0.041) x 10^{-2} M
Pt(IV) $^2J_{PtH}$ = 55.5 ± 0.20 Hz

T (°C) ± 1.0	T (K) ± 1.0	T^{-1} (K^{-1}) ± 0.0002	$^2J_{PtH}$ (Hz) ±0.2	$\chi_{Pt(II)}$ ± 0.011	p_{Sn} ± 0.009	K_{eq} (L mol^{-1})	ln K_{eq}	ΔG (kJ mol^{-1})
30.0	303.15	0.00330	85.5	0.962	0.981	3.74 ± 0.95	1.33 ± 0.25	-3.32 ± 0.64
20.7	293.85	0.00340	84.6	0.933	0.966	6.8 ± 1.0	1.92 ± 0.15	-4.70 ± 0.36
15.0	288.15	0.00347	83.3	0.891	0.946	11.9 ± 1.2	2.473 ± 0.097	-5.92 ± 0.23
9.1	282.25	0.00354	82.6	0.869	0.934	14.8 ± 1.2	2.697 ± 0.084	-6.33 ± 0.20
4.0	277.15	0.00361	80.4	0.798	0.899	25.8 ± 1.6	3.250 ± 0.063	-7.49 ± 0.15
-2.1	271.05	0.00369	78.5	0.737	0.869	37.6 ± 2.1	3.628 ± 0.056	-8.17 ± 0.13
-7.5	265.65	0.00376	75.9	0.654	0.827	58.7 ± 3.0	4.072 ± 0.051	-8.99 ± 0.12