Supplementary Information

NMR Probe Effects on *trans*-Philicity and *trans*-Influence Ladders in Square Planar Pt(II) Complexes

Athanassios C. Tsipis

Laboratory of Inorganic Chemistry, Department of Chemistry, University of Ioannina, Ioannina 45110, Greece

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Table S1. ^{1}H NMR Hydride Shifts (in ppm vs TMS) for selected *trans*-[Pt(PMe_3)$_2$(H)(L)]$^{0/+}$ complexes calculated by the GIAO (SO-ZORA)/PBE0/TZ2P/COSMO computational protocol in benzene solution and compared to ^{1}H NMR Hydride Shifts given by Kaupp's group[30] and to experimental data available.[40-44]

Complex	σ^{iso}(^{1}H)[a]	δ_{calcd}(^{1}H)[a]	δ_{calcd}(^{1}H)[b]	δ_{exptl}(^{1}H)	Ref.
trans-[Pt(PMe_3)(H)(H)]	35.3 (35.1)[c]	-3.3 (-3.1)[c]		-2.7	43
trans-[Pt(PMe_3)$_2$(H)(Cl)]	54.0 (54.1)	-22.0 (-22.1)	-16.2	[-16.2] -16.9	[44], 40[d]
trans-[Pt(PMe_3)$_2$(H)(Br)]	51.8 (51.9)	-19.8 (-19.9)	-15.0	-15.6	40
trans-[Pt(PMe_3)$_2$(H)(CN)]	43.4 (43.3)	-11.4 (-11.3)	-6.7	-7.8	40
trans-[Pt(PMe_3)$_2$(H)(NCMe)]$^+$	56.9 (57.0)	-24.9 (-15.0)		-18.7	42[e]
trans-[Pt(PMe_3)$_2$(H)(SCN)]	50.5 (50.6)	-18.5 (-18.6)	-12.2	-13.3	40
trans-[Pt(PMe_2)(H)(NO_2)]	56.8 (56.9)	-24.8 (-24.9)	-19.0	-19.7	40
trans-[Pt(PMe_3)$_2$(H)(NO_3)]	61.6 (61.7)	-29.6 (-29.7)	-23.6	-23.8	40
trans-[Pt(PMe_3)$_2$(H)(OH)]	54.7 (54.7)	-22.7 (-22.7)		-10.0	42
trans-[Pt(PMe_3)$_2$(H)(OH_2)]$^+$	67.0 (67.3)	-35.0 (-35.3)		-25.4	42
trans-[Pt(PMe_3)$_2$(H)(PMe_3)]$^+$	44.0 (44.0)	-12.0 (-12.0)		--12.8	43
trans-[Pt(PMe_3)$_2$(H)(Me)]	37.4 (37.3)	-5.4 (-5.3)	-4.2	-3.8 [-2.1]	[41][f]
trans-[Pt(PMe_2)(H)(Ph)]	39.8 (39.7)	-7.8 (-7.7)	-6.3	-5.7	

[a] ^{1}H NMR Hydride Shifts calculated at the GIAO (SO-ZORA)/PBE0/TZ2P/COSMO level. [b] ^{1}H NMR Hydride Shifts calculated by Kaupp's group (taken from Ref. 30). [c] Figures in parentheses are the ^{1}H NMR Hydride Shifts calculated at the GIAO (SO-ZORA)/PBE0/TZ2P-J/COSMO level of theory. [d] The δ_{exptl}(^{1}H) data given in Ref. 40 refer to the *trans*-[Pt(PEt_3)$_2$(H)(Cl)] complexes. [e] The δ_{exptl}(^{1}H) data given in Ref. 42 refer to the *trans*-[Pt(PPh_3)$_2$(H)(OH_2)]$^+$ and *trans*-[Pt(PPh_3)$_2$(H)(NCMe)]$^+$ complexes. [f] The δ_{exptl}(^{1}H) data given in Ref. 41 refer to the *trans*-[Pt(PPh_3)$_2$(H)(Me)] complexes.

Table S2. *R*(Pt-H) bond lengths (in Å) for selected *trans*-[Pt(PMe_3)$_2$(H)(L)]$^{0/+}$ complexes calculated by the PBE0/SARC-ZORA(Pt) ∪ 6-31+G(d)(E)/PCM computational protocol and compared to *R*(Pt-H) bond lengths calculated by the PBE0/Def2-TZVP (ECP) computational protocol in the gas phase.[a]

Complex	*R*(Pt-H)		Δ*R*(Pt-H)
	PBE0/SARC-ZORA(Pt) ∪ 6-31+G(d)(E)/PCM(benzene)	PBE0/Def2-TZVP (ECP) (gas phase)	
trans-[Pt(PMe_3)$_2$(H)(Cl)]	1.616	1.565	0.051
trans-[Pt(PMe_3)$_2$(H)(Br)]	1.620	1.566	0.054
trans-[Pt(PMe_3)$_2$(H)(CN)]	1.654	1.609	0.045
trans-[Pt(PMe_3)$_2$(H)(SCN)]	1.625	1.576	0.049
trans-[Pt(PMe_2)(H)(NO_2)]	1.627	1.582	0.045
trans-[Pt(PMe_3)$_2$(H)(NO_3)]	1.599	1.548	0.051
trans-[Pt(PMe_3)$_2$(H)(Me)]	1.699	1.636	0.063
trans-[Pt(PMe_2)(H)(Ph)]	1.693	1.628	0.065
			MO. = **0.053**

[a] Taken from Ref. 30.

Table S3. σ^{iso}(SO) ^{1}H NMR *trans*-philicity descriptors (in ppm) for the *trans*-[Pt(PMe_3)$_2$(H)L]$^{0/+}$ complexes calculated at the 2c-SO-ZORA level of theory employing the GIAO(SO)/PBE0/TZ2P/COSMO computational protocol in benzene solution.

Ligand	σ^{iso}(SO) ^{1}H NMR
F^-	60.80
H_2O	67.02
OCN^-	63.01
OBr^-	59.29
NO_3^-	61.57
OCl-	59.29
CCl_3COO^-	60.60
CH_3COO^-	58.76
$HCOO^-$	58.84
$C_6H_5COO^-$	58.45
OF^-	57.54
OH^-	54.68
NO_2^-	56.79
NCS^-	54.80
NCMe	56.89
Py	57.60
NCH	57.05
NH_3	56.49
NCPh	56.03
N_3^-	54.92
N_2	57.97
Cl^-	53.97
NH_2^-	46.95
Br^-	51.80
SCN^-	50.54
H_2S	52.13
SH^-	46.17
CN^-	43.40
CNMe	44.56
NHC	43.91
CNH	43.90
CNPh	43.55
t-Bu^-	41.37
Ph^-	39.83
PMe_3	44.00
CO	42.34
PPh_3	43.82
Me^-	37.40
PH_3	43.01
PF_3	41.53
$SnCl_3^-$	44.07
H^-	35.29
$B(OH)_2^-$	29.27
BH_2^-	28.30

Table S4. σ^{iso}(SO) $^{13}CH_3$ NMR *trans*-philicity descriptors (in ppm) for the *trans*-$[Pt(PMe_3)_2(CH_3)L]^{0/+}$ complexes calculated at the 2c-SO-ZORA level of theory employing the GIAO(SO)/PBE0/TZ2P/COSMO computational protocol in benzene solution.

Ligand	σ^{iso}(SO) ^{13}C NMR
BH_2^-	193.86
Ph^-	215.24
$B(OH)_2^-$	192.91
Me^-	210.27
CN^-	214.48
F^-	239.83
H^-	201.13
OF^-	233.19
OH^-	232.07
NH_2^-	220.16
OCl^-	233.19
OBr^-	234.79
Cl^-	224.55
NO_2^-	229.94
t-Bu^-	223.47
NCS^-	228.17
Br^-	219.59
N_3^-	225.45
SH^-	214.84
CH_3COO^-	232.36
$C_6H_5COO^-$	232.16
$HCOO^-$	231.47
NHC	211.13
NO_3^-	233.12
CCl_3COO^-	231.15
OCN^-	232.53
SCN^-	215.77
Py	223.82
CNPh	204.51
NCPh	219.14
NCMe	219.98
CNMe	204.50
NCH	217.93
CNH	202.44
NH_3	219.14
$SnCl_3^-$	200.82
H_2O	225.03
CO	196.78
PMe_3	199.17
N_2	211.72
H_2S	206.55
PPh_3	197.60
PH_3	176.78
PF_3	189.50

Table S5. σ^{iso}(SO) ^{13}CO NMR *trans*-philicity descriptors (in ppm) for the *trans*-[Pt(PMe_3)$_2$(CO)L]$^{+/2+}$ complexes calculated at the 2c-SO-ZORA level of theory employing the GIAO(SO)/PBE0/TZ2P/COSMO computational protocol in benzene solution.

Ligand	σ^{iso}(SO) ^{13}CO NMR
H_2O	48.79
N_2	42.27
NCH	36.23
OCN^-	34.49
NCMe	34.18
NCPh	32.79
NO_3^-	29.83
NH_3	29.62
F^-	29.34
Py	28.98
CCl_3COO^-	28.16
H_2S	27.10
$HCOO^-$	25.53
CH_3COO^-	25.08
NCS^-	24.61
$C_6H_5COO^-$	24.17
OCl^-	23.72
OBr^-	23.15
Cl^-	22.65
OF^-	22.52
Br^-	22.39
CO	22.10
NO_2^-	20.63
OH^-	19.88
N_3^-	19.66
PF_3	18.00
CNMe	17.87
CNPh	17.08
SCN^-	14.77
PH_3	13.93
PMe_3	11.31
NHC	10.69
CNH	10.69
PPh_3	9.73
NH_2^-	9.40
SH^-	8.71
CN^-	8.33
$SnCl_3^-$	2.95
Ph^-	-2.13
Me^-	-2.57
H^-	-7.85
t-Bu^-	-9.55
$B(OH)_2^-$	-13.76
BH_2^-	-17.16

Table S6. σ^{iso}(SO) $^{15}NH_2$ NMR *trans*-philicity descriptors (in ppm) for the *trans*-$[Pt(PMe_3)_2(NH_2)L]^{0/+}$ complexes calculated at the 2c-SO-ZORA (SO) level of theory employing the GIAO(SO)/PBE0/TZ2P/COSMO computational protocol in benzene solution.

Ligand	σ^{iso}(SO)
OH^-	322.54
$HCOO^-$	315.45
CH_3COO^-	317.53
NH_2^-	313.56
$C_6H_5COO^-$	316.72
NO_3^-	305.93
F^-	306.50
Py	298.64
NH_3	297.78
H_2O	285.89
OBr^-	305.20
$B(OH)_2^-$	311.65
OCl-	304.63
NCH	293.78
OF^-	300.35
CCl_3COO^-	311.66
t-Bu^-	280.36
OCN^-	288.35
NO_2^-	288.65
N_2	277.00
N_3^-	284.99
NCS^-	290.13
Ph^-	277.06
CNH	279.14
CNMe	279.46
Cl^-	277.26
PMe_3	271.20
Me^-	266.73
PH_3	266.41
Br^-	268.73
BH_2^-	226.80
SCN^-	264.58
SH^-	263.87
H^-	255.34
NCMe	267.37
NCPh	266.50
CN^-	268.83
NHC	257.33
PF_3	250.14
H_2S	240.63
CNPh	240.05
$SnCl_3^-$	230.32
PPh_3	223.89
CO	224.48

Table S7. σ^{iso}(SO) $^{17}OH_2$ NMR *trans*-philicity descriptors (in ppm) for the *trans*-$[Pt(PMe_3)_2(OH_2)L]^{+/2+}$ complexes calculated at the 2c-SO-ZORA (SO) level of theory employing the GIAO(SO)/PBE0/TZ2P/COSMO computational protocols in benzene solution.

Ligand	σ^{iso}(SO) $^{17}OH_2$ NMR
H_2O	513.76
F^-	463.62
OCN^-	452.51
NO_3^-	456.87
CCl_3COO^-	447.87
CH_3COO^-	441.37
$C_6H_5COO^-$	441.72
N_2	450.34
$HCOO^-$	441.52
OBr^-	425.93
NCH	446.24
NH_3	439.67
OH^-	426.28
OCl^-	423.54
NCS^-	431.83
Py	434.83
OF^-	419.11
NO_2^-	417.74
Cl^-	409.95
NCMe	427.00
N_3^-	402.78
H_2S	407.34
NCPh	434.02
CNMe	406.90
CNH	411.75
CN^-	408.87
NH_2^-	389.45
SCN^-	386.89
NHC	372.09
CO	397.80
PF_3	383.92
Br^-	383.52
PH_3	379.36
CNPh	386.44
SH^-	361.08
Me^-	362.59
$B(OH)_2^-$	350.33
PPh_3	358.63
PMe_3	359.46
Ph^-	359.72
H^-	356.79
$SnCl_3^-$	344.63
t-Bu^-	323.37
BH_2^-	327.04

Table S8. σ^{iso}(SO) ^{35}Cl NMR *trans*-philicity descriptors (in ppm) for the *trans*-[Pt(PMe_3)$_2$(Cl)L]$^{0/+}$ complexes calculated at the 2c-SO-ZORA (SO) level of theory employing the GIAO(SO)/PBE0/TZ2P/COSMO computational protocol in benzene solution.

Ligand	σ^{iso}(SO) ^{35}Cl NMR
F^-	1225.20
OBr^-	1203.85
OCN^-	1176.67
OCl^-	1202.23
NO_3^-	1186.38
OH^-	1204.76
CH_3COO^-	1189.16
OF-	1193.92
$C_6H_5COO^-$	1188.74
CCl_3COO^-	1177.68
HCOO-	1182.18
NO_2^-	1187.39
NCS^-	1173.53
H_2O	1096.56
N_3^-	1160.22
NH_2^-	1166.19
Py	1129.75
Cl^-	1129.33
Ph^-	1154.24
Br^-	1112.91
NH_3	1101.96
Me^-	1137.19
NCMe	1097.13
CN^-	1129.32
NCPh	1095.76
H^-	1129.00
SH^-	1105.04
BH_2^-	1123.03
NCH	1079.90
SCN^-	1086.11
$B(OH)_2^-$	1117.91
NHC	1096.59
t-Bu^-	1094.34
N_2	1021.80
CNMe	1052.94
CNPh	1041.67
CNH	1037.34
H_2S	1002.84
$SnCl_3^-$	1005.93
PPh_3	998.39
PMe_3	995.56
PH_3	983.81
CO	989.68
PF_3	940.66

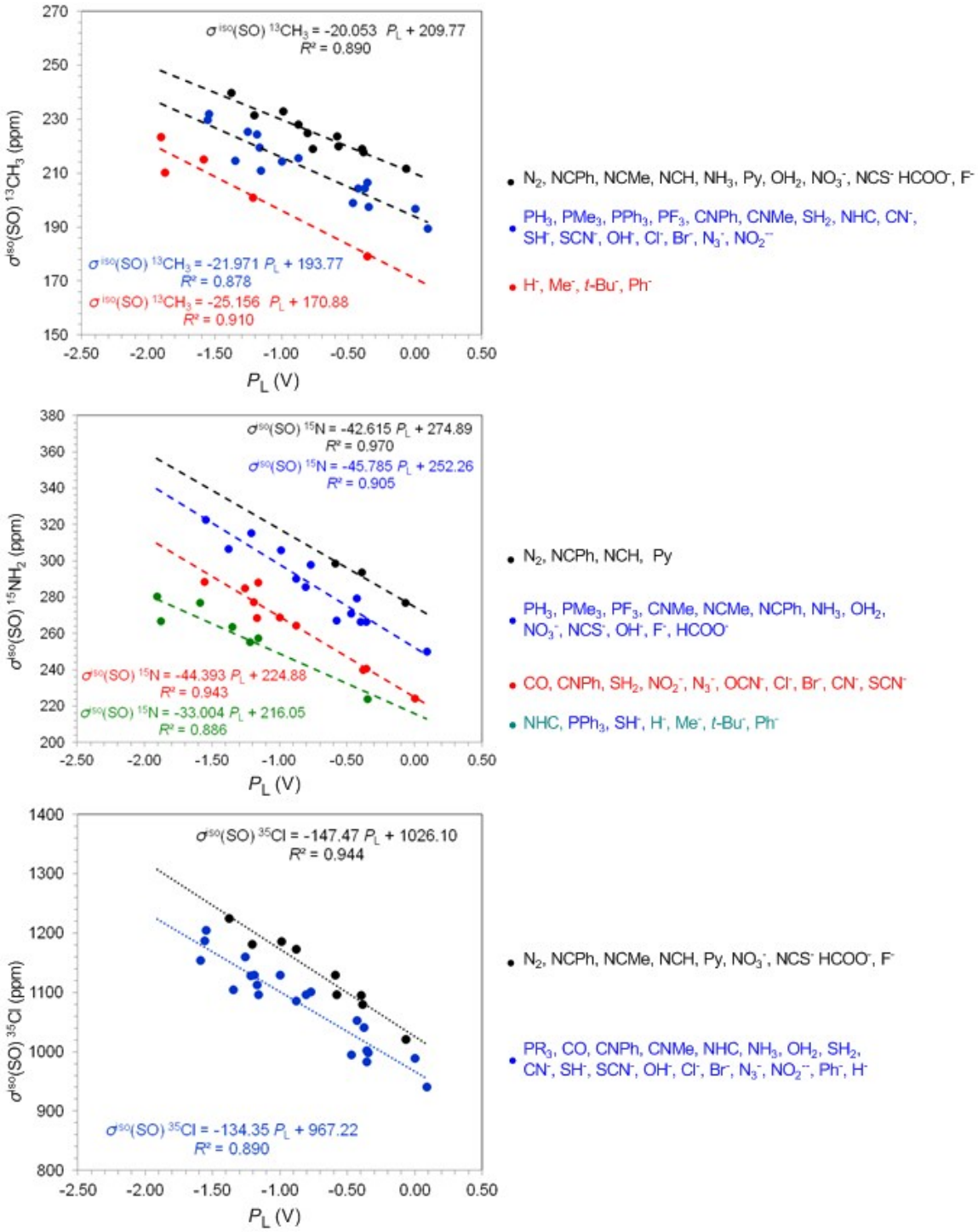

Figure S1. Linear plots of the σ^{iso}(SO) X (X = $^{13}CH_3$, $^{15}NH_2$,, ^{35}Cl) vs P_L correlations for square planar *trans*-$[Pt(PMe_3)_2(X)L]^{0/+}$ (X = X = CH_3, NH_2, Cl) complexes calculated by the GIAO(2c-SO-ZORA)/PBE0/TZ2P/COSMO computational protocol in benzene solution.

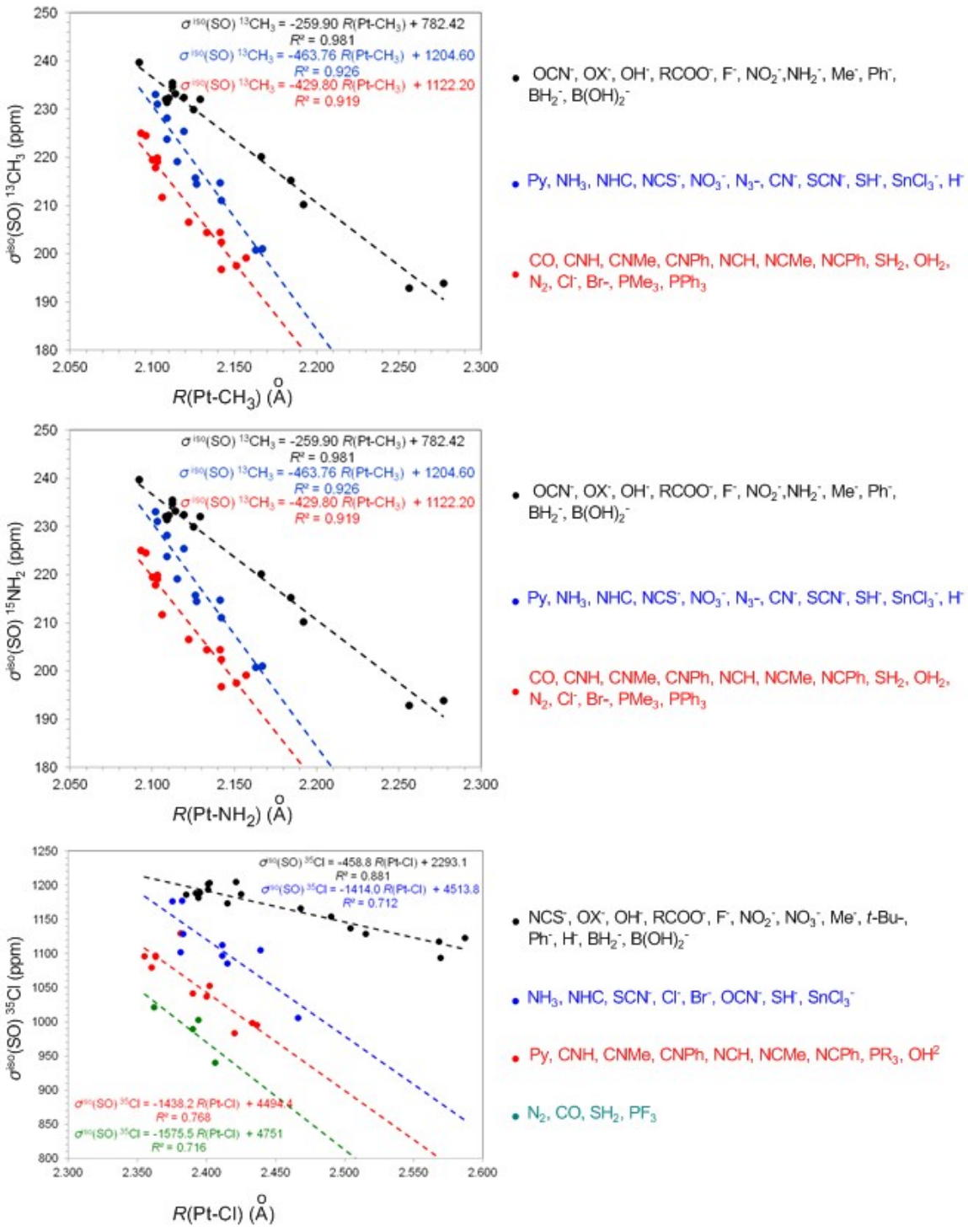

Figure S2. Linear plots of the σ^{iso}(SO) X (X = CH_3, NH_2, Cl) shieldings *vs* *R*(Pt-X) correlations for square planar *trans*-[Pt(PMe_3)$_2$(X)L]$^{0/+}$ (X = CH_3, NH_2, Cl) complexes calculated by the GIAO(2c-SO-ZORA)/PBE0/TZ2P/COSMO computational protocol in benzene solution.

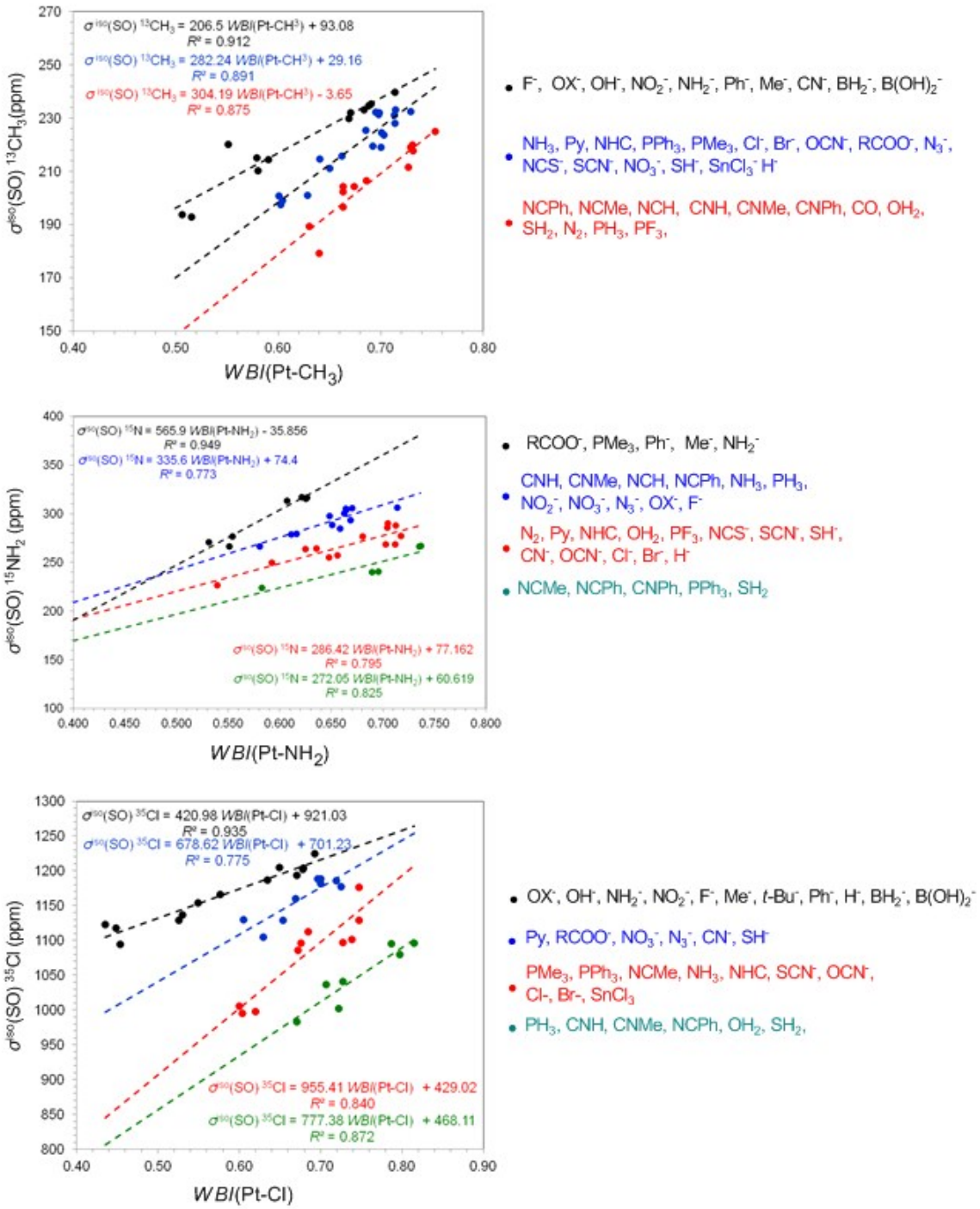

Figure S3. Linear plots of the σ^{iso}(SO) X (X = CH_3, NH_2, Cl) shieldings *vs* *WBI*(Pt-X) correlations for square planar *trans*-$[Pt(PMe_3)_2(X)L]^{0/+}$ (X = CH_3, NH_2, Cl) complexes calculated by the GIAO(2c-SO-ZORA)/PBE0/TZ2P/COSMO computational protocol in benzene solution.

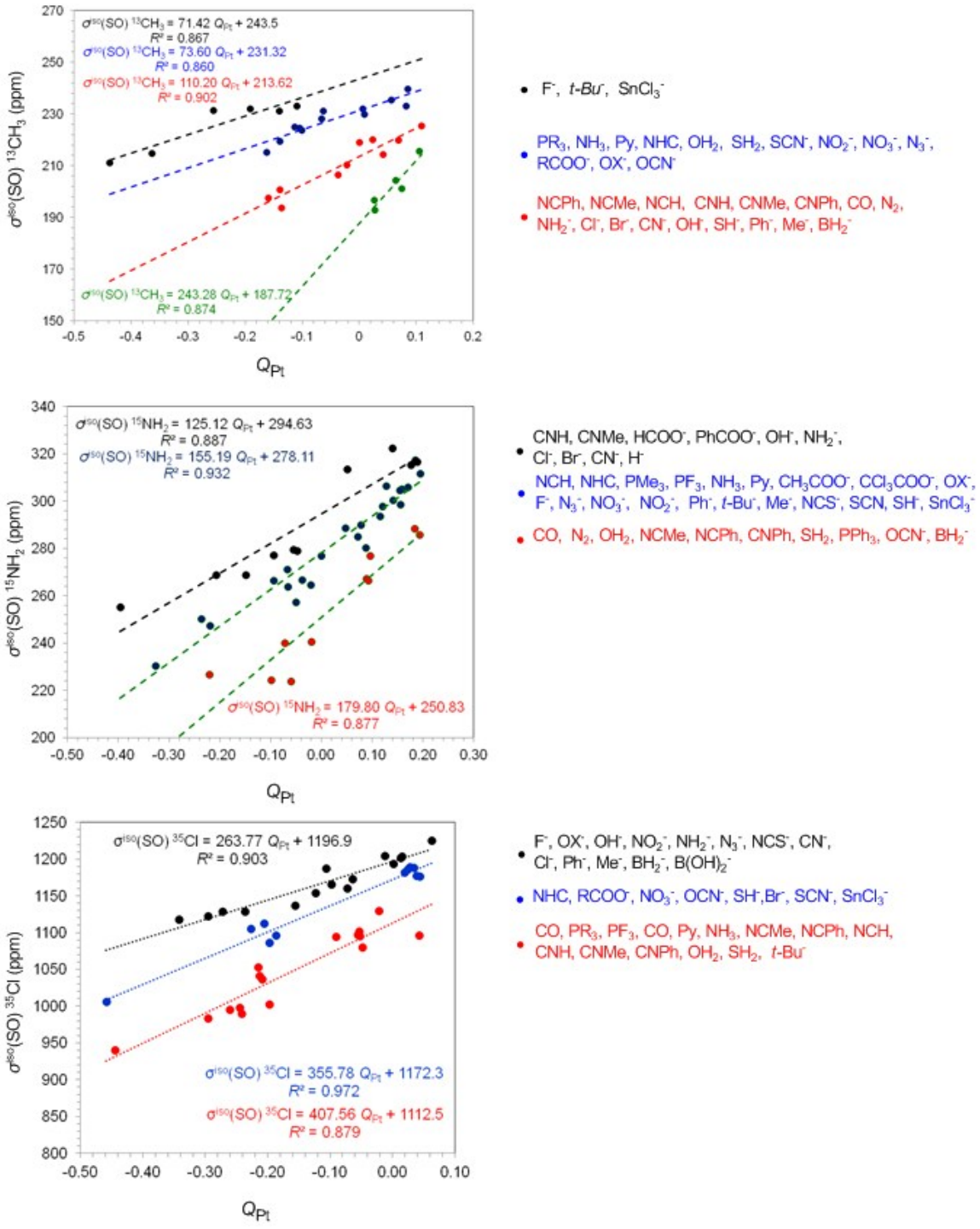

Figure S4. Linear plots of the σ^{iso}(SO) X (X = CH_3, NH_2, Cl) shieldings *vs* Q_{Pt} correlations for square planar *trans*-$[Pt(PMe_3)_2(X)L]^{0/+}$ (X = CH_3, NH_2, Cl) complexes calculated by the GIAO(2c-SO-ZORA)/PBE0/TZ2P/COSMO computational protocol in benzene solution.