Square-Planar Pt(II) and Ir(I) Complexes as the Lewis Bases: Donor-Acceptor Adducts with Group 13 Trihalides and Trihydrides

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SUPPORTING INFORMATION:

Table S1: Comparison of optimized bond lengths for cis/trans- $Pt(H_2O)_2F_2]\cdot BH_3$ adducts. All optimizations were performed with the MWB-60(f)/6-311++G** basis set. MAE = Mean Absolute Error with respect to the CCSD reference values.

Method	Isomer	Pt-B	Pt-O	Pt-F	B-H	O-H	MAE
CCSD	cis	2.273	1.927	2.081	1.206	0.970	0
	trans	2.301	1.961	2.036	1.203	0.969	0
MP2	cis	2.186	1.917	2.054	1.210	0.976	0.027
	trans	2.206	1.952	2.012	1.206	0.974	0.027
B3PW91-GD3BJ	cis	2.256	1.935	2.074	1.210	0.978	0.009
	trans	2.284	1.966	2.037	1.206	0.976	0.007
M062X-GD3	cis	2.291	1.927	2.108	1.200	0.972	0.011
	trans	2.305	1.963	2.056	1.199	0.972	0.007
BLYP-GD3BJ	cis	2.312	1.973	2.122	1.211	0.991	0.031
	trans	2.344	2.007	2.080	1.206	0.990	0.032
PBE-GD3BJ	cis	2.243	1.929	2.066	1.212	0.977	0.012
	trans	2.268	1.960	2.031	1.207	0.975	0.010
TPSS-GD3BJ	cis	2.252	1.952	2.086	1.213	0.991	0.016
	trans	2.273	1.983	2.053	1.208	0.989	0.018
BP86-GD3BJ	cis	2.243	1.958	2.090	1.221	0.995	0.022
	trans	2.268	1.991	2.057	1.216	0.994	0.024
LC-wPB-GD3BJ E	cis	2.249	1.926	2.060	1.207	0.975	0.010
	trans	2.273	1.955	2.026	1.204	0.973	0.010
CAM-B3LYP-GD3BJ	cis	2.312	1.933	2.075	1.201	0.975	0.012
	trans	2.345	1.963	2.037	1.197	0.974	0.012
B97D3	cis	2.299	1.955	2.106	1.216	0.983	0.021
	trans	2.337	1.988	2.062	1.211	0.982	0.022
B3LYP-GD3BJ	cis	2.321	1.946	2.096	1.203	0.977	0.018
	trans	2.355	1.978	2.054	1.199	0.976	0.020
BPBE-GD3BJ	cis	2.232	1.957	2.091	1.221	0.993	0.024
	trans	2.257	1.989	2.056	1.216	0.992	0.026
M06L-GD3	cis	2.394	1.951	2.098	1.197	0.975	0.035
	trans	2.319	1.989	2.072	1.196	0.978	0.020
wB97XD	cis	2.327	1.934	2.093	1.206	0.972	0.015
	trans	2.365	1.969	2.048	1.203	0.971	0.017
M06HF-GD3	cis	2.258	1.908	2.052	1.205	0.970	0.012
	trans	2.270	1.936	2.015	1.204	0.969	0.016
BMK-GD3BJ	cis	2.262	1.916	2.101	1.199	0.973	0.010
	trans	2.291	1.974	2.069	1.195	0.972	0.013
M06L-GD3	cis	2.293	1.953	2.120	1.199	0.977	0.020
	trans	2.319	1.989	2.072	1.196	0.978	0.020

Table S2: Binding energies for cis/trans- $Pt(H_2O)_2H_2]\cdot BH_3$ adducts calculated on CCSD/ MWB-60(f)/6-311++G** optimized structures. The basis set superposition error (BSSE) was included (ΔE_{BOND}) or not included (ΔE_{BOND}^{noBSSE}). All energy evaluations were performed with the BS2 basis set. MAE = Mean Absolute Error with respect to the CCSD(T) reference values.

DFT functionals with D3BJ dispersion correction:

Method	Isomer	CCSD(T)	B3PW91	BLYP	B3LYP	PBE0	PBE	TPSS	BP86
ΔE_{BOND}	cis	-14.5	-21.5	-20.5	-17.7	-21.5	-26.5	-25.0	-25.7
ΔE_{BOND}^{noBSSE}		-21.2	-22.4	-21.3	-18.6	-22.5	-27.4	-26.0	-26.6
ΔE_{BOND}	trans	-11.8	-18.2	-16.7	-14.6	-18.3	-22.4	-21.1	-21.6
ΔE_{BOND}^{noBSSE}		-18.4	-19.0	-17.4	-15.3	-19.1	-23.2	-21.9	-22.3
MAE_{BOND}		0	6.65	5.40	2.98	6.76	11.24	9.85	10.44
MAE_{BOND}^{noBSSE}		0	0.91	0.53	2.85	1.01	5.49	4.14	4.67

Method	Isomer	BPBE	BMK	CAM-B3LYP	LC-wPBE	B97D3
ΔE_{BOND}	cis	-26.0	-19.4	-15.5	-17.8	-20.0
ΔE_{BOND}^{noBSSE}		-27.0	-20.3	-16.3	-18.7	-20.9
ΔE_{BOND}	trans	-22.0	-16.1	-12.7	-15.2	-16.6
ΔE_{BOND}^{noBSSE}		-22.8	-16.9	-13.4	-16.0	-17.4
MAE_{BOND}		10.83	4.53	0.91	3.30	5.12
MAE_{BOND}^{noBSSE}		5.11	1.17	4.92	2.43	0.66

DFT functionals with D3 dispersion correction:

Method	Isomer	M062X	M06L	M06HF	M06	ωB97XD
ΔE_{BOND}	cis	-14.1	-18.7	-14.9	-13.8	-15.1
ΔE_{BOND}^{noBSSE}		-15.1	-20.1	-16.7	-14.9	-16.0
ΔE_{BOND}	trans	-12.0	-16.1	-13.2	-12.0	-12.6
ΔE_{BOND}^{noBSSE}		-12.8	-17.3	-14.9	-13.0	-13.4
MAE_{BOND}		0.28	4.25	0.86	0.49	0.69
MAE_{BOND}^{noBSSE}		5.88	1.10	3.97	5.81	5.10

Table S3 The Gibbs free energy differences between the adducts with M·Y and X·Y dative bonds (in kcal/mol) calculated at the M062X-D3/B2//B3PW91-D3BJ/B1 level. Negative values reflect a larger stability of the adduct with M·Y dative bond. n.a. = the adduct with the X·Y dative bond does not exist.

M = Pt												
Y	B				Al				Ga			
X\Z	H	F	Cl	Br	H	F	Cl	Br	H	F	Cl	Br
H	0.6	-8.7	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
CH_3	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
F	11.4	23.6	23.9	26.0	21.8	27.4	27.7	29.6	12.8	22.0	20.3	18.6
Cl	4.8	4.2	7.7	10.1	7.3	9.7	10.3	10.8	5.1	7.7	8.3	8.2
Br	4.8	2.5	-0.6	7.9	5.5	6.0	7.0	7.8	4.4	5.0	6.3	7.2
M = Ir												
Y	B				Al				Ga			
X\Z	H	F	Cl	Br	H	F	Cl	Br	H	F	Cl	Br
H	-6.4	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
CH_3	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
F	-8.1	3.7	-5.8	-9.2	1.8	4.4	1.4	-0.5	-4.7	n.a.	-10.4	-11.7
Cl	-18.8	-18.3	-27.7	-29.7	n.a.	n.a.	n.a.	n.a.	-13.4	n.a.	n.a.	n.a.
Br	-19.6	-21.9	-31.0	-32.9	n.a.	n.a.	n.a.	n.a.	-14.4	n.a.	n.a.	n.a.

Table S4: Energies (in a.u.) of $5dz^2$ and valence pz NAO's for isolated fully optimized MX and YZ_3 molecules, respectively. All molecules are supposed to lie in the xy plane. Data were obtained at M062X-D3/BS2//M062X-D3/BS1 level.

Structure	PtNCN	PtH	$PtCH_3$	PtF	PtCl	PtBr
$5dz^2$ NAO energy	-0.28208	-0.25161	-0.25377	-0.30987	-0.332	-0.33501

Structure	IrNNN	IrH	$IrCH_3$	IrF	IrCl	IrBr
$5dz^2$ NAO energy	-0.18679	-0.13732	-0.14071	-0.15413	-0.17585	-0.18143

Structure	BH_3	BF_3	BCl_3	BBr_3	AlH_3	AlF_3
pz NAO energy	0.00601	0.00182	-0.11245	-0.13538	-0.00342	0.0584

Structure	$AlCl_3$	$AlBr_3$	GaH_3	GaF_3	$GaCl_3$	$GaBr_3$
pz NAO energy	-0.04615	-0.06608	-0.0102	0.02567	-0.06564	-0.07801

Table S5: Pt-Y bond lengths (d(Pt-Y), in Å); Local topological properties of Pt·Y bonds in the PtNCN·YZ_3 adducts calculated at the position of BCP's: the electron density ($\rho(BCP)$) and the Laplacian of electron density ($\nabla^2\rho(BCP)$); mean values of Pt-Y-Z angles ($\overline{\propto}$, in deg); transferred charge ($\Delta q, \text{in e}$) for the PtX·YZ_3 adducts. The data were calculated at M062X-D3/BS2//M062X-D3/BS1 level.

Y = B						
X	Z	d(Pt-Y)	$\rho(BCP)$	$\nabla^2\rho(BCP)$	$\overline{\propto}$	Δq
H	H	2.210	0.0745	-0.0371	103.0	-0.461
	F	2.218	0.0817	-0.1091	104.9	-0.356
	Cl	2.128	0.1039	-0.1639	107.7	-0.578
	Br	2.100	0.1099	-0.1790	108.7	-0.635
CH_3	H	2.211	0.0751	-0.0349	103.0	-0.443
	F	2.219	0.0827	-0.1127	105.1	-0.355
	Cl	2.146	0.1019	-0.1546	108.5	-0.568
	Br	2.121	0.1075	-0.1675	109.7	-0.619
F	H	2.280	0.0621	-0.0007	99.5	-0.351
	F	2.466	0.0466	0.0023	98,8	-0.176
	Cl	2.293	0.0728	-0.0548	104.1	-0.394
	Br	2.247	0.0805	-0.0745	105.8	-0.453
Cl	H	2.338	0.0553	0.0037	99.0	-0.313
	F	2.987	0.0139	0.0366	92.4	-0.025
	Cl	2.401	0.0596	-0.0203	103.3	-0.343
	Br	2.306	0.0727	-0.0513	105.9	-0.439
Br	H	2.349	0.0541	0.0048	98.9	-0.310
	F	3.017	0.0132	0.0354	92.4	-0.021
	Cl	3.339	0.0071	0.0217	91.3	-0.020
	Br	2.310	0.0724	-0.0499	105.9	-0.442

Y = Al						
X	Z	d(Pt-Y)	$\rho(BCP)$	$\nabla^2\rho(BCP)$	$\bar{\propto}$	Δq
H	H	2.470	0.0462	0.1261	102.8	-0.335
	F	2.394	0.0546	0.1578	105.3	-0.284
	Cl	2.385	0.0568	0.1599	107.1	-0.417
	Br	2.380	0.0577	0.1608	107.6	-0.450
CH_3	H	2.487	0.0454	0.1186	102.7	-0.306
	F	2.394	0.0553	0.1565	105.2	-0.269
	Cl	2.401	0.0566	0.1473	108.0	-0.380
	Br	2.399	0.0572	0.1455	108.7	-0.403
F	H	2.620	0.0338	0.0765	99.2	-0.227
	F	2.507	0.0426	0.1113	102.9	-0.212
	Cl	2.501	0.0458	0.1091	103.0	-0.304
	Br	2.505	0.0460	0.1039	103.3	-0.317
Cl	H	2.650	0.0317	0.0685	99.2	-0.221
	F	2.519	0.0412	0.1071	103.1	-0.214
	Cl	2.564	0.0395	0.0847	104.7	-0.313
	Br	2.569	0.0398	0.0797	105.4	-0.340
Br	H	2.659	0.0313	0.0658	99.4	-0.230
	F	2.518	0.0413	0.1074	103.4	-0.233
	Cl	2.563	0.0399	0.0844	105.6	-0.334
	Br	2.568	0.0401	0.0798	106.0	-0.370

Y = Ga						
X	Z	d(Pt-Y)	$\rho(BCP)$	$\nabla^2\rho(BCP)$	$\bar{\propto}$	Δq
H	H	2.578	0.0524	0.0837	101.1	-0.310
	F	2.427	0.0727	0.1140	105.8	-0.336
	Cl	2.442	0.0721	0.1017	106.3	-0.434
	Br	2.442	0.0723	0.0990	106.6	-0.458
CH_3	H	2.592	0.0516	0.0802	101.0	-0.287
	F	2.425	0.0737	0.1126	105.7	-0.323
	Cl	2.454	0.0711	0.0935	107.7	-0.405
	Br	2.460	0.0707	0.0886	108.2	-0.421
F	H	2.747	0.0356	0.0694	96.9	-0.193
	F	2.532	0.0584	0.0887	103.4	-0.244
	Cl	2.599	0.0506	0.0742	103.1	-0.273
	Br	2.612	0.0494	0.0712	103.5	-0.281
Cl	H	2.795	0.0317	0.0653	96.7	-0.176
	F	2.539	0.0567	0.0883	103.7	-0.251
	Cl	2.626	0.0483	0.0699	104.0	-0.305
	Br	2.647	0.0467	0.0660	104.4	-0.316
Br	H	2.808	0.0308	0.0642	96.7	-0.180
	F	2.542	0.0562	0.0882	103.9	-0.273
	Cl	2.626	0.0487	0.0689	105.1	-0.323
	Br	2.643	0.0473	0.0660	105.0	-0.343

Table S6: Ir-Y bond lengths (d(Pt-Y), in Å); Local topological properties of Ir·Y bonds in the IrNNN·YZ_3 adducts calculated at the position of BCP's: the electron density ($\rho(BCP)$) and the Laplacian of electron density ($\nabla^2\rho(BCP)$); mean values of Ir-Y-Z angles ($\overline{\propto}$, in deg); transferred charge ($\Delta q, \text{in e}$) for the IrX·YZ_3 adducts. The data were calculated at M062X-D3/BS2//M062X-D3/BS1 level.

Y = B						
X	Z	d(Pt-Y)	$\rho(BCP)$	$\nabla^2\rho(BCP)$	$\overline{\propto}$	Δq
H	H	2.131	0.1002	-0.1294	108.5	-0.662
	F	2.104	0.1180	-0.2145	109.3	-0.565
	Cl	2.046	0.1328	-0.2129	111.6	-0.781
	Br	2.023	0.1376	-0.2204	112.4	-0.829
CH_3	H	2.139	0.0998	-0.1287	107.6	-0.655
	F	2.109	0.1176	-0.2140	109.2	-0.560
	Cl	2.054	0.1319	-0.2089	111.8	-0.771
	Br	2.030	0.1369	-0.2174	112.7	-0.815
F	H	2.146	0.0962	-0.1082	106.5	-0.634
	F	2.119	0.1135	-0.2067	108.2	-0.545
	Cl	2.063	0.1285	-0.2086	111.0	-0.733
	Br	2.041	0.1332	-0.2161	111.8	-0.768
Cl	H	2.159	0.0936	-0.1029	106.4	-0.614
	F	2.132	0.1106	-0.1975	108.1	-0.525
	Cl	2.079	0.1255	-0.1974	111.2	-0.718
	Br	2.056	0.1305	-0.2057	111.6	-0.782
Br	H	2.163	0.0929	-0.1013	106.3	-0.611
	F	2.136	0.1097	-0.1942	108.1	-0.522
	Cl	2.077	0.1259	-0.2004	110.7	-0.736
	Br	2.058	0.1302	-0.2037	111.6	-0.784

Y = Al						
X	Z	d(Pt-Y)	$\rho(BCP)$	$\nabla^2\rho(BCP)$	$\overline{\propto}$	Δq
H	H	2.398	0.0589	0.1593	105.7	-0.455
	F	2.341	0.0674	0.1827	107.3	-0.369
	Cl	2.338	0.0696	0.1817	110.0	-0.506
	Br	2.332	0.0703	0.1840	110.3	-0.537
CH_3	H	2.412	0.0581	0.1513	105.7	-0.438
	F	2.362	0.0663	0.1676	107.8	-0.374
	Cl	2.345	0.0693	0.1768	109.9	-0.490
	Br	2.341	0.0699	0.1780	110.4	-0.517
F	H	2.438	0.0552	0.1409	104.8	-0.418
	F	2.374	0.0641	0.1646	106.7	-0.357
	Cl	2.362	0.0671	0.1703	108.6	-0.484
	Br	2.358	0.0677	0.1716	109.0	-0.506
Cl	H	2.445	0.0544	0.1382	104.5	-0.400
	F	2.377	0.0634	0.1632	106.3	-0.335
	Cl	2.374	0.0657	0.1620	109.0	-0.465
	Br	2.371	0.0662	0.1620	109.5	-0.488
Br	H	2.454	0.0539	0.1336	104.4	-0.414
	F	2.378	0.0632	0.1635	106.3	-0.334
	Cl	2.377	0.0653	0.1601	109.1	-0.465
	Br	2.374	0.0659	0.1605	109.6	-0.490

Y = Ga						
X	Z	d(Pt-Y)	$\rho(BCP)$	$\nabla^2\rho(BCP)$	$\overline{\propto}$	Δq
H	H	2.488	0.0700	0.0822	104.8	-0.471
	F	2.388	0.0862	0.0987	109.0	-0.481
	Cl	2.392	0.0867	0.0880	110.1	-0.574
	Br	2.391	0.0869	0.0856	110.4	-0.598
CH_3	H	2.504	0.0690	0.0759	104.6	-0.468
	F	2.393	0.0860	0.0958	108.8	-0.471
	Cl	2.398	0.0863	0.0845	109.9	-0.560
	Br	2.398	0.0863	0.0816	110.1	-0.584
F	H	2.524	0.0655	0.0775	103.7	-0.431
	F	2.410	0.0834	0.0960	108.0	-0.466
	Cl	2.416	0.0835	0.0854	108.7	-0.543
	Br	2.416	0.0835	0.0824	108.9	-0.559
Cl	H	2.534	0.0642	0.0757	103.4	-0.408
	F	2.414	0.0824	0.0951	107.9	-0.440
	Cl	2.424	0.0823	0.0824	109.1	-0.522
	Br	2.426	0.0821	0.0786	109.5	-0.546
Br	H	2.540	0.0637	0.0741	103.1	-0.420
	F	2.414	0.0823	0.0952	107.9	-0.438
	Cl	2.427	0.0818	0.0811	109.2	-0.527
	Br	2.429	0.0817	0.0773	109.6	-0.546

Table S7: The PtX·YZ_3 adducts: ETS-NOCV energy decomposition terms ΔE_{Pauli}, ΔE_{elst}, ΔE_{orb}, ΔE_{disp} obtained at BLYP-D3BJ/QZ4P//M062X-D3/BS1 level. ΔE_{def}^{YZ3}, ΔE_{def}^{PtNCN}, ΔE_{Bind}, ΔH^{298} and ΔG^{298} energy values calculated at M062X-D3/BS2//M062X-D3/BS1 level. All values are in kcal/mol.

[a]values calculated with respect to dimeric Y_2Z_6 structures.

Y = B										
X	Z	ΔE_{Pauli}	ΔE_{elst}	ΔE_{orb}	ΔE_{disp}	ΔE_{def}^{PtX}	ΔE_{def}^{YZ3}	ΔE_{Bind}	ΔH^{298}	ΔG^{298}
H	H	95.2	-53.5	-72.3	-5.9	1.1	10.4	-23.5	-2.3[a]	3.4[a]
	F	109.7	-74.8	-67.7	-6.2	0.6	26.7	-17.5	-16.1	-4.7
	Cl	175.4	-108.7	-106.9	-13.4	1.1	32.7	-24.5	-22.6	-10.0
	Br	199.4	-123.1	-119.2	-15.1	1.3	33.5	-28.8	-26.7	-14.1
CH_3	H	99.5	-56.9	-72.8	-7.6	1.1	10.3	-25.1	-3.6[a]	2.9[a]
	F	115.0	-77.2	-69.8	-8.4	1.0	27.2	-18.2	-16.7	-3.7
	Cl	177.1	-109.6	-107.2	-16.9	2.1	34.7	-24.3	-22.2	-7.6
	Br	199.8	-123.1	-119.2	-19.2	2.8	36.5	-27.8	-25.6	-11.1
F	H	80.2	-44.5	-56.0	-6.4	0.8	5.5	-15.6	5.8[a]	11.7[a]
	F	64.5	-41.6	-31.9	-7.0	0.6	9.3	-6.4	-5.3	5.2
	Cl	129.8	-76.3	-71.4	-14.0	1.7	19.8	-8.0	-6.6	5.5
	Br	153.3	-90.4	-84.7	-16.0	2.4	22.9	-10.0	-8.7	3.3
Cl	H	70.3	-37.9	-49.4	-7.4	0.5	4.9	-13.0	8.1[a]	14.7[a]
	F	21.2	-15.6	-7.9	-6.5	0.0	1.0	-7.9	-6.6	3.2
	Cl	108.2	-62.0	-57.5	-16.3	2.5	17.0	-3.3	-1.9	10.6
	Br	139.1	-80.3	-75.9	-18.7	3.8	22.6	-4.4	-2.9	10.5
Br	H	69.7	-37.4	-48.9	-5.9	0.6	4.8	-12.3	8.9[a]	15.0[a]
	F	21.3	-15.6	-7.9	-6.2	0.1	1.0	-7.8	-6.5	3.1
	Cl	20.5	-11.6	-6.3	-13.4	0.1	0.4	-7.7	-6.2	3.9
	Br	139.5	-79.9	-75.7	-15.1	0.1	0.4	-3.6	-2.1	11.7

Y = Al										
X	Z	ΔE_{Pauli}	ΔE_{elst}	ΔE_{orb}	ΔE_{disp}	ΔE_{def}^{PtX}	ΔE_{def}^{YZ3}	ΔE_{Bind}	ΔH^{298}	ΔG^{298}
H	H	85.1	-66.9	-53.3	-6.7	0.9	8.5	-34.3	-14.6[a]	-8.2[a]
	F	90.0	-82.3	-60.5	-7.6	1.0	16.1	-51.5	-49.5	-36.2
	Cl	113.4	-89.4	-74.5	-12.0	0.8	18.4	-48.8	-31.9[a]	-24.9[a]
	Br	126.6	-95.9	-79.8	-13.2	0.8	18.4	-49.3	-34.1[a]	-27.0[a]
CH_3	H	86.9	-67.0	-52.8	-9.2	1.1	8.2	-34.0	-14.0[a]	-6.9[a]
	F	93.9	-82.2	-61.7	-10.5	1.1	15.4	-51.4	-49.2	-35.2
	Cl	119.2	-91.0	-76.8	-16.7	1.6	19.8	-47.7	-30.5[a]	-21.8[a]
	Br	131.9	-97.4	-81.8	-18.5	2.0	20.1	-47.5	-32.2[a]	-24.1[a]
F	H	59.9	-44.5	-37.5	-7.0	0.8	4.6	-20.1	-0.6[a]	4.6[a]
	F	70.3	-58.0	-48.0	-8.0	1.0	11.4	-31.6	-30.0	-18.1
	Cl	91.7	-65.4	-55.4	-14.4	1.8	11.6	-26.5	-9.9[a]	-3.6[a]
	Br	100.4	-69.6	-58.3	-16.0	2.0	11.4	-26.3	-11.6[a]	-5.3[a]
Cl	H	59.0	-41.9	-37.6	-8.6	0.7	4.8	-19.4	-0.1[a]	6.3[a]
	F	71.5	-56.6	-49.8	-10.0	0.7	12.2	-31.4	-29.9	-17.1
	Cl	80.8	-55.2	-51.7	-16.4	0.6	13.4	-24.6	-8.1[a]	-1.6[a]
	Br	89.9	-59.6	-54.6	-18.3	0.7	13.9	-23.8	-9.3[a]	-2.4[a]
Br	H	60.1	-42.6	-38.2	-9.1	0.5	5.0	-19.4	0.2[a]	6.5[a]
	F	73.8	-57.9	-51.2	-10.6	0.6	12.9	-31.7	-30.1[a]	-17.4[a]
	Cl	87.2	-58.6	-57.3	-17.3	0.5	15.3	-24.3	-8.0[a]	-1.6[a]
	Br	92.8	-61.6	-55.9	-19.5	0.7	14.8	-23.6	-9.0[a]	-1.4[a]

Y = Ga										
X	Z	ΔE_{Pauli}	ΔE_{elst}	ΔE_{orb}	ΔE_{disp}	ΔE_{def}^{PtX}	ΔE_{def}^{YZ3}	ΔE_{Bind}	ΔH^{298}	ΔG^{298}
H	H	80.9	-63.0	-46.1	-6.6	0.8	6.8	-28.0	-12.4[a]	-5.8[a]
	F	115.1	-101.0	-71.5	-7.5	1.1	17.1	-55.3	-53.2	-39.7
	Cl	129.3	-101.1	-75.8	-12.5	1.4	17.4	-46.1	-32.0[a]	-25.1[a]
	Br	138.5	-104.7	-78.4	-13.9	1.4	17.3	-45.0	-32.6[a]	-27.5[a]
CH_3	H	82.7	-63.4	-45.8	-9.0	0.8	6.5	-28.1	-12.6[a]	-5.5[a]
	F	119.7	-101.9	-73.0	-10.4	1.3	16.3	-55.4	-53.3	-39.5
	Cl	132.6	-100.0	-79.0	-16.3	1.4	18.6	-46.3	-32.0[a]	-23.6[a]
	Br	140.2	-102.1	-81.0	-18.1	1.6	18.7	-44.3	-31.5[a]	-23.7[a]
F	H	51.4	-38.1	-30.0	-6.9	0.5	2.9	-16.8	-1.5[a]	3.9[a]
	F	88.6	-71.7	-56.7	-7.9	1.2	12.3	-34.5	-32.8	-20.5
	Cl	82.0	-58.6	-49.2	-12.7	0.7	10.7	-24.4	-10.8[a]	-5.1[a]
	Br	85.1	-58.6	-48.8	-14.1	0.8	10.5	-22.9	-10.8[a]	-6.2[a]
Cl	H	47.6	-34.0	-28.6	-8.3	0.4	2.9	-16.3	-1.2[a]	4.9[a]
	F	90.1	-70.4	-58.8	-9.9	1.1	13.6	-34.7	-33.2	-20.0
	Cl	84.3	-57.9	-50.3	-15.9	0.5	12.2	-23.8	-10.9[a]	-2.6[a]
	Br	87.5	-58.3	-49.5	-17.8	0.5	11.9	-21.9	-10.0[a]	-4.2[a]
Br	H	48.2	-34.1	-29.0	-8.8	0.4	2.9	-16.3	-1.1[a]	4.6[a]
	F	92.6	-71.7	-60.5	-10.5	0.9	14.3	-35.3	-33.7	-20.5
	Cl	90.2	-61.0	-55.6	-16.8	0.4	13.9	-23.7	-10.2[a]	-3.1[a]
	Br	90.4	-60.2	-50.7	-19.0	0.6	12.9	-21.6	-9.6[a]	-2.9[a]

Table S8: The IrX·YZ_3 adducts: ETS-NOCV energy decomposition terms ΔE_{Pauli}, ΔE_{elst}, ΔE_{orb}, ΔE_{disp} obtained at BLYP-D3BJ/QZ4P//M062X-D3/BS1 level. ΔE_{def}^{YZ3}, ΔE_{def}^{PtNCN}, ΔE_{Bind}, ΔH^{298} and ΔG^{298} energy values calculated at M062X-D3/BS2//M062X-D3/BS1 level. All values are in kcal/mol.

[a]values calculated with respect to dimeric Y_2Z_6 structures.

Y = B										
X	Z	ΔE_{Pauli}	ΔE_{elst}	ΔE_{orb}	ΔE_{disp}	ΔE_{def}^{IrX}	ΔE_{def}^{YZ3}	ΔE_{Bind}	ΔH^{298}	ΔG^{298}
H	H	145.7	-83.5	-120.5	-6.8	0.6	21.1	-47.2	-26.2[a]	-19.7[a]
	F	178.9	-128.2	-121.7	-7.9	1.7	48.6	-43.5	-41.9	-30.0
	Cl	250.1	-162.7	-170.3	-15.3	0.8	51.4	-60.8	-58.3	-45.0
	Br	280.4	-180.2	-187.5	-17.2	1.0	51.4	-68.1	-65.4	-52.1
CH_3	H	148.9	-86.7	-118.9	-7.7	0.5	19.3	-48.3	-26.9[a]	-20.5[a]
	F	181.4	-129.9	-120.9	-8.7	0.5	47.6	-44.6	-42.8	-29.0
	Cl	254.2	-165.8	-171.4	-16.8	1.0	52.0	-60.7	-58.2	-44.6
	Br	285.2	-183.5	-188.7	-19.1	1.5	52.1	-67.6	-65.0	-50.5
F	H	142.7	-84.2	-110.9	-7.1	1.4	16.8	-43.5	-22.4[a]	-15.5[a]
	F	175.1	-125.1	-112.2	-8.1	1.5	42.5	-38.5	-37.1	-24.0
	Cl	251.5	-163.2	-166.8	-15.4	2.1	47.7	-53.4	-51.5	-37.8
	Br	281.3	-180.1	-183.9	-17.4	2.6	47.8	-59.6	-57.6	-43.8
Cl	H	137.8	-81.2	-107.0	-7.6	1.0	16.5	-41.3	-20.0[a]	-12.4[a]
	F	169.3	-120.0	-108.9	-8.6	1.0	42.0	-35.9	-34.4	-20.4
	Cl	242.3	-156.4	-162.6	-16.2	2.4	48.9	-48.7	-46.7	-33.3
	Br	270.4	-173.5	-173.7	-18.9	3.8	46.5	-54.8	-52.7	-39.7
Br	H	136.7	-80.6	-106.0	-7.7	1.0	16.4	-40.6	-19.3[a]	-11.5[a]
	F	167.9	-118.8	-108.2	-8.7	1.0	41.8	-35.0	-33.8	-20.3
	Cl	241.2	-156.2	-157.3	-16.9	3.0	46.2	-48.0	-45.9	-32.0
	Br	268.3	-172.3	-172.6	-19.1	4.1	46.3	-53.9	-51.7	-37.4

Y = Al										
X	Z	ΔE_{Pauli}	ΔE_{elst}	ΔE_{orb}	ΔE_{disp}	ΔE_{def}^{IrX}	ΔE_{def}^{YZ3}	ΔE_{Bind}	ΔH^{298}	ΔG^{298}
H	H	131.0	-102.1	-83.1	-8.1	-0.2	12.6	-57.6	-38.0[a]	-30.8[a]
	F	130.6	-122.1	-84.9	-9.1	-0.1	21.1	-79.4	-77.1	-63.5
	Cl	166.0	-138.0	-109.4	-15.0	1.2	27.1	-79.1	-61.6[a]	-54.3[a]
	Br	182.3	-146.3	-116.5	-16.7	1.1	26.6	-81.1	-65.6[a]	-58.5[a]
CH_3	H	132.1	-102.8	-82.1	-9.2	-0.2	12.3	-56.7	-36.8[a]	-29.3[a]
	F	134.2	-125.7	-84.2	-10.5	0.5	22.4	-77.4	-75.0	-60.0
	Cl	169.0	-139.3	-108.8	-16.8	0.1	26.3	-79.1	-61.6[a]	-52.9[a]
	Br	184.4	-146.8	-116.1	-18.6	0.3	26.2	-80.9	-65.1[a]	-56.2[a]
F	H	123.0	-97.4	-75.3	-8.2	0.5	11.1	-50.2	-30.6[a]	-23.7[a]
	F	127.3	-118.4	-79.9	-9.2	1.2	19.4	-69.8	-67.9	-54.6
	Cl	161.3	-133.3	-100.2	-15.3	1.4	22.8	-69.8	-52.7[a]	-44.2[a]
	Br	176.0	-140.3	-107.2	-17.0	1.5	22.4	-71.3	-56.0[a]	-47.9[a]
Cl	H	121.4	-94.6	-74.4	-9.0	0.4	10.9	-48.0	-28.3[a]	-21.0[a]
	F	125.0	-113.8	-79.0	-10.1	0.6	18.7	-67.5	-65.6	-51.2
	Cl	157.6	-128.4	-99.8	-16.5	0.8	24.0	-67.1	-49.9[a]	-40.9[a]
	Br	172.5	-135.7	-107.1	-18.3	1.0	24.0	-68.3	-53.1[a]	-43.8[a]
Br	H	121.4	-94.6	-73.0	-9.4	0.6	11.0	-47.4	-27.8[a]	-19.8[a]
	F	124.2	-112.7	-78.8	-10.4	0.2	18.7	-67.0	-64.9	-50.4
	Cl	156.8	-127.4	-99.9	-16.9	0.7	24.4	-66.2	-49.1[a]	-39.9[a]
	Br	171.4	-134.3	-106.6	-18.8	0.9	24.1	-67.4	-52.2[a]	-43.2[a]

Y = Ga										
X	Z	ΔE_{Pauli}	ΔE_{elst}	ΔE_{orb}	ΔE_{disp}	ΔE_{def}^{IrX}	ΔE_{def}^{YZ3}	ΔE_{Bind}	ΔH^{298}	ΔG^{298}
H	H	137.8	-107.4	-78.1	-8.0	-0.2	11.7	-49.3	-33.8[a]	-26.8[a]
	F	175.8	-158.3	-107.6	-9.6	2.3	26.5	-85.4	-82.9	-68.4
	Cl	193.5	-156.9	-120.1	-14.7	1.2	27.2	-79.2	-64.6[a]	-57.0[a]
	Br	204.8	-160.5	-124.4	-16.3	1.1	26.6	-78.9	-65.9[a]	-59.4[a]
CH_3	H	141.7	-110.3	-78.1	-9.3	0.3	11.8	-48.6	-32.9[a]	-24.5[a]
	F	176.9	-158.9	-106.0	-10.4	1.0	25.4	-85.3	-82.9	-67.9
	Cl	196.7	-158.5	-119.6	-16.3	0.2	26.3	-79.3	-64.6[a]	-55.7[a]
	Br	207.2	-161.3	-123.6	-18.2	0.2	25.6	-78.8	-65.7[a]	-59.6[a]
F	H	128.5	-101.4	-70.7	-8.1	0.5	10.0	-42.9	-27.8[a]	-21.4[a]
	F	168.9	-151.5	-98.6	-9.6	2.6	23.3	-76.0	-74.0	-59.8
	Cl	187.4	-151.1	-110.4	-15.0	1.5	23.1	-69.3	-55.1[a]	-46.6[a]
	Br	197.8	-154.0	-114.6	-16.6	1.4	22.4	-68.8	-56.1[a]	-48.5[a]
Cl	H	125.0	-97.4	-69.1	-8.9	0.2	9.7	-40.9	-25.5[a]	-18.2[a]
	F	164.1	-145.9	-97.4	-10.3	1.4	23.1	-74.3	-72.3	-57.2
	Cl	182.7	-145.5	-109.7	-16.1	0.7	24.2	-66.8	-52.6[a]	-43.2[a]
	Br	192.2	-148.1	-113.6	-17.9	0.9	23.9	-66.0	-53.3[a]	-45.0[a]
Br	H	126.1	-97.9	-68.4	-9.3	0.4	9.8	-40.4	-25.0[a]	-17.0[a]
	F	163.7	-145.0	-97.9	-10.6	1.2	23.6	-73.7	-71.6	-56.3
	Cl	181.3	-144.0	-109.7	-16.5	0.7	24.4	-66.0	-52.0[a]	-43.0[a]
	Br	191.1	-146.7	-113.5	-18.3	0.8	24.1	-65.1	-52.5[a]	-44.5[a]

Table S9: Dependence of $\rho(BCP)$ and $\nabla^2\rho(BCP)$ on the Ir·B and Ir·Al bonding distances in IrH·BBr_3 and IrH·$AlBr_3$ adducts, respectively, calculated by M062X-D3/BS2, M062X-D3/ADZP and MP2/ADZP methods.

IrH·BBr_3						
Ir·B distance (Å)	M062X-D3/BS2		M062X-D3/ADZP		MP2/ADZP	
	$\rho(BCP)$	$\nabla^2\rho(BCP)$	$\rho(BCP)$	$\nabla^2\rho(BCP)$	$\rho(BCP)$	$\nabla^2\rho(BCP)$
1.8	0.1907	-0.2010	0.1860	-0.2135	0.1765	-0.1437
1.9	0.1658	-0.3151	0.1633	-0.2707	0.1542	-0.2253
2	0.1432	-0.2434	0.1420	-0.1793	0.1336	-0.1523
2.1	0.1226	-0.1512	0.1225	-0.1100	0.1146	-0.0894
2.2	0.1046	-0.0949	0.1054	-0.0687	0.0979	-0.0517
2.3	0.0893	-0.0600	0.0908	-0.0468	0.0835	-0.0312
2.4	0.0761	-0.0377	0.0782	-0.0359	0.0713	-0.0204
2.5	0.0649	-0.0231	0.0676	-0.0303	0.0610	-0.0141
2.6	0.0554	-0.0134	0.0584	-0.0258	0.0524	-0.0096
2.7	0.0472	-0.0066	0.0504	-0.0205	0.0452	-0.0059
2.8	0.0403	-0.0019	0.0435	-0.0142	0.0395	-0.0032
2.9	0.0344	0.0015	0.0374	-0.0081	0.0347	-0.0014
3	0.0293	0.0040	0.0321	-0.0027	0.0308	-0.0002

IrH·$AlBr_3$						
Ir·Al distance (Å)	M062X-D3/BS2		M062X-D3/ADZP		MP2/ADZP	
	$\rho(BCP)$	$\nabla^2\rho(BCP)$	$\rho(BCP)$	$\nabla^2\rho(BCP)$	$\rho(BCP)$	$\nabla^2\rho(BCP)$
1.9	0.1385	0.9486	0.1291	0.9636	0.1247	0.9486
2	0.1165	0.6553	0.1093	0.6371	0.1046	0.6266
2.1	0.0991	0.4524	0.0941	0.4284	0.0894	0.4213
2.2	0.0852	0.3107	0.0820	0.2964	0.0775	0.2916
2.3	0.0738	0.2095	0.0721	0.2115	0.0676	0.2092
2.4	0.0645	0.1372	0.0637	0.1547	0.0598	0.1478
2.5	0.0568	0.0851	0.0565	0.1135	0.0526	0.1093
2.6	0.0503	0.0481	0.0502	0.0815	0.0464	0.0793
2.7	0.0446	0.0219	0.0446	0.0554	0.0411	0.0545

Table S10: $NH_3 \cdot YZ_3$ adducts: N-Y bond lengths (d(N-Y), in Å); Local topological properties of N·Y bonds calculated at the position of BCP's: the electron density ($\rho(BCP)$) and the Laplacian of electron density ($\nabla^2\rho(BCP)$); mean values of N-Y-Z angles ($\overline{\propto}$, in deg); transferred charge ($\Delta q, \text{in e}$) for the $NH_3 \cdot YZ_3$ adducts. The data were calculated at M062X-D3/BS2//M062X-D3/BS1 level.

Y	Z	d(N-Y)	$\rho(BCP)$	$\nabla^2\rho(BCP)$	$\overline{\propto}$	Δq
B	H	1.648	0.1060	0.4046	104.9	-0.355
	F	1.670	0.1129	0.1758	104.0	-0.307
	Cl	1.610	0.1329	0.2164	105.2	-0.359
	Br	1.599	0.1366	0.2278	105.2	-0.354
Al	H	2.058	0.0513	0.2416	99.2	-0.167
	F	1.983	0.0623	0.3068	100.6	-0.141
	Cl	1.994	0.0629	0.2923	101.4	-0.183
	Br	1.987	0.0650	0.1803	100.9	-0.180
Ga	H	2.181	0.0581	0.1836	98.2	-0.168
	F	2.054	0.0788	0.2747	100.1	-0.156
	Cl	2.077	0.0760	0.2474	100.7	-0.195
	Br	2.083	0.0809	0.1102	100.7	-0.200

Table S11: The $NH_3 \cdot YZ_3$ adducts: ETS-NOCV energy decomposition terms ΔE_{Pauli}, ΔE_{elst}, ΔE_{orb}, ΔE_{disp} obtained at BLYP-D3BJ/QZ4P//M062X-D3/BS1 level. ΔE_{def}^{YZ3}, ΔE_{def}^{PtNCN}, ΔE_{Bind}, ΔH^{298} and ΔG^{298} energy values calculated at M062X-D3/B2//M062X-D3/BS1 level. Experimental values of ΔH_{exp}^{298} were taken from ref. 1. All values are in kcal/mol.

[a]values calculated with respect to monomeric YZ_3 structures.

[b]values calculated with respect to dimeric Y_2Z_6 structures.

Y	Z	ΔE_{Pauli}	ΔE_{elst}	ΔE_{orb}	ΔE_{disp}	ΔE_{def}^{YZ3}	ΔE_{def}^{NH3}	ΔE_{Bind}	ΔH^{298}	ΔH_{exp}^{298}	ΔG^{298}
B	H	118.0	-78.8	-79.1	-2.3	13.2	0.0	-31.5	-8.2[b]		-2.8[b]
	F	143.4	-98.0	-79.5	-2.7	23.8	0.2	-22.8	-20.4[a]		-10.1[a]
	Cl	209.6	-125.4	-120.5	-5.5	24.0	0.2	-27.9	-25.0[a]		-14.1[a]
	Br	229.1	-133.7	-131.4	-6.3	22.1	0.3	-31.1	-28.0[a]		-17.2[a]
Al	H	65.8	-60.9	-32.5	-2.7	3.9	0.0	-30.1	-9.8[b]		-5.2[b]
	F	70.3	-74.6	-36.0	-3.1	6.9	0.1	-44.3	-42.0[a]		-32.0[a]
	Cl	89.2	-80.6	-44.8	-5.1	7.5	0.1	-40.1	-37.8[a] -22.9[b]	-32.8	-18.6[b]
	Br	97.9	-83.7	-48.1	-5.8	6.6	0.1	-39.7	-37.3[a] -24.3[b]	-34.4	-19.8[b]
Ga	H	63.2	-54.7	-28.6	-2.7	3.3	0.0	-23.6	-7.7[b]		-3.2[b]
	F	87.7	-81.7	-41.1	-3.0	6.3	0.1	-41.8	-39.6[a]		-30.1[a]
	Cl	99.4	-81.8	-46.1	-4.9	6.6	0.1	-34.7	-32.5[a] -20.5[b]	-32.1	-16.3[b]
	Br	104.8	-82.3	-47.8	-5.4	6.3	0.1	-32.8	-30.5[a] -20.1[b]	-32.8	-16.8[b]

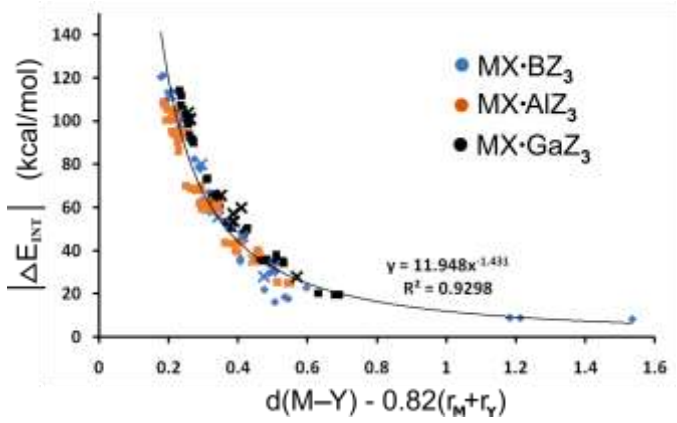

Figure S1: Exponential dependence of the absolute value of interaction energy $|\Delta E_{INT}|$ on the modified M-Y distance [d(M-Y)-0.82(r_M+r_Y)]. Covalent radii values of r_M (r_{Pt} = 1.36 Å; r_{Ir} = 1.41 Å) and r_Y (r_B = 0.84 Å; r_{Al} = 1.21 Å; r_{Ga} = 1.22 Å) were taken from Ref. 69. d(M-Y) and $|\Delta E_{INT}|$ values were obtained at M062X-D3/BS2//M062X-D3/BS1 level. Points corresponding to the adducts of IrNNN and PtNCN are distinguished by crosses.

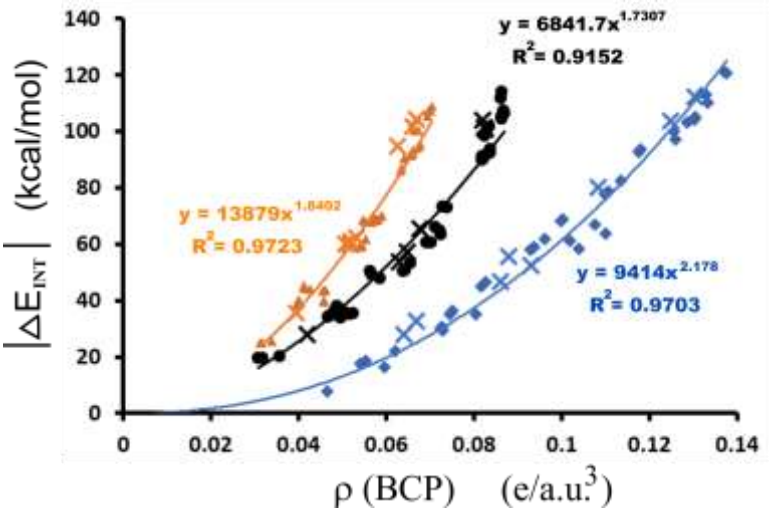

Figure S2: Dependence of ΔE_{INT} on $\rho(BCP)$. Blue, orange and black points correspond to adducts of B, Al and Ga, respectively. Adducts of NNN and NCN pincer ligands are distinguished by crosses. ΔE_{INT} and $\rho(BCP)$ were calculated at M062X-D3/BS2//M062X-D3/BS1 level.

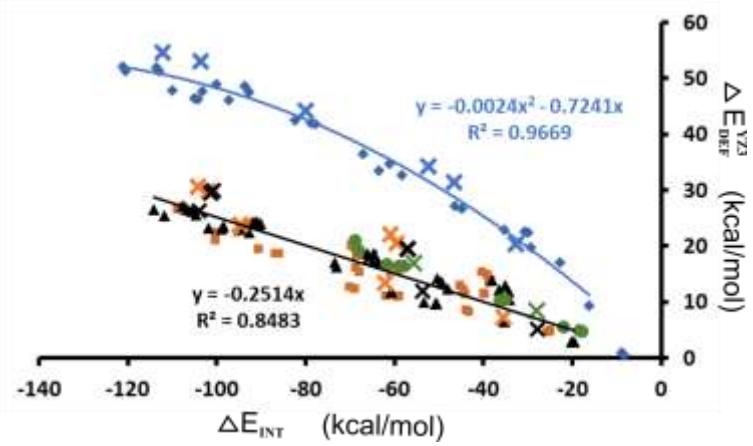

Figure S3: Dependence of ΔE_{Def}^{YZ3} on ΔE_{INT}. Blue, orange and black points correspond to adducts of B, Al and Ga, respectively. Adducts of NNN and NCN pincer ligands are distinguished by crosses. For Al and Ga adducts one common regression line was constructed (black curve). The adducts of BH_3 (green points) are not included in either extrapolations. ΔE_{INT} and ΔE_{Def}^{YZ3} were calculated at M062X-D3/BS2//M062X-D3/BS1 level.

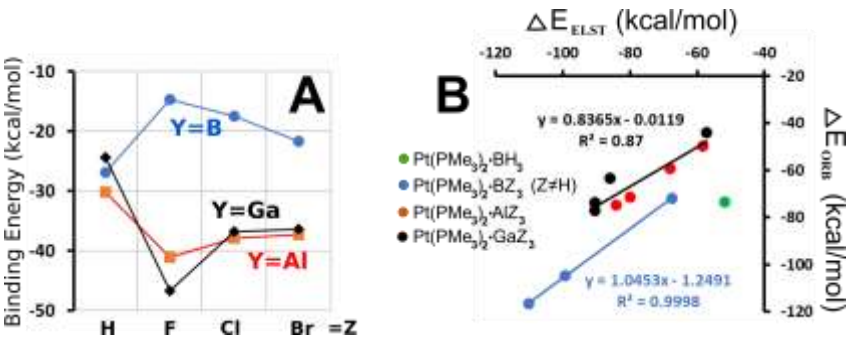

Figure S4: $Pt(PMe_3)_2 \cdot YZ_3$ adducts: A) Dependence of binding energies of $Pt(PMe_3)_2$ with YZ_3 on the nature of Z (cf. Figure 4). B) Correlation between $\Delta \boldsymbol{E_{orb}}$ and $\Delta \boldsymbol{E_{elst}}$ terms for the $Pt(PMe_3)_2 \cdot YZ_3$ adducts (cf. Figure 2). One regression line was constructed for adducts of both Al and Ga (black line). All data were taken from Ref. 44.