Supplementary Material (ESI) for Dalton Transactions

Supporting Information

Quantification of Mutual Trans Influence of Ligands in Pd(II) Complexes: A Combined Approach Using Isodesmic Reactions and AIM Analysis

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(1) Table S1. SCF energies E (in a.u.) of all geometries at MPWB1K- COSMO/BS1 level.

$[PdCl_3H_2O]^-$, E = -1584.09541137	$[PdCl_3CO]^-$, E = -1620.96688807
$[PdCl_3Py]^-$, E = -1755.88995161	$[PdCl_3NH_3]^-$, E = -1564.25453667
$[PdCl_3SMe_2]^-$, E = -1985.71128760	$[PdCl_3C_2H_4]^-$, E = -1586.24498739
$[PdCl_3AsH_3]^-$, E = -3743.17116718	$[PdCl_3PH_3]^-$, E = -1850.87524624
$[PdCl_3AsMe_3]^-$, E = -3861.08693813	$[PdCl_3PMe_3]^-$, E = -1968.79627957
$[PdCl_3PEt_3]^-$, E = -2086.66529766	$[PdCl_3ONO]^{2-}$, E = -1712.87492674
$[PdCl_3F]^{2-}$, E = -1607.66446611	$[PdCl_4]^{2-}$, E = -1968.12116931
$[PdCl_3Br]^{2-}$, E = -4079.61490270	$[PdCl_3N_3]^{2-}$, E = -1671.96383042
$[PdCl_3NO_2]^{2-}$, E = -1712.88962942	$[PdCl_3OH]^{2-}$, E = -1583.62846621
$[PdCl_3CN]^{2-}$, E = -1600.65643902	$[PdCl_3C_6H_5]^{2-}$, E = -1739.37234667
$[PdCl_3H]^{2-}$, E = -1508.42417198	$[PdCl_3CH_3]^{2-}$, E = -1547.71228455
$[PdCl_3SiH_3]^{2-}$, E = -1799.15401533	$[PdCl_2H_2O]$, E = -1123.60320367
$[PdCl_2CO]$, E = -1160.48095317	$[PdCl_2Py]$, E = -1295.41321093
$[PdCl_2NH_3]$, E = -1103.77837583	$[PdCl_2SMe_2]$, E = -1525.24143631

$[PdCl_2C_2H_4]$, E = -1125.77407607	$[PdCl_2AsH_3]$, E = -3282.70757895
$[PdCl_2PH_3]$, E = -1390.41189604	$[PdCl_2AsMe_3]$, E = -3400.63133922
$[PdCl_2PMe_3]$, E = -1508.34201363	$[PdCl_2PEt_3]$, E = -1626.21246997
$[PdCl_2ONO]^-$, E = -1252.39792104	$[PdCl_2F]^-$, E = -1147.18757806
$[PdCl_3]^-$, E = -1507.65221781	$[PdCl_2Br]^-$, E = -3619.14927801
$[PdCl_2N_3]^-$, E = -1211.49760964	$[PdCl_2NO_2]^-$, E = -1252.42289625
$[PdCl_2OH]^-$, E = -1123.16457851	$[PdCl_2CN]^-$, E = -1140.19420140
$[PdCl_2C_6H_5]^-$, E = -1278.93243509	$[PdCl_2H]^-$, E = -1047.98275444
$[PdCl_2CH_3]^-$, E = -1087.27494392	$[PdCl_2SiH_3]^-$, E = -1338.71945016
$[PdCl_2]$, E = -1047.15180156	$[PdCl_2COBr]^-$, E = -3732.45986273
$[PdCl_2H_2OBr]^-$, E = -3695.58911374	$[PdCl_2PH_3CN]^-$, E = -1483.39990229
$[PdCl_2NH_3Br]^-$, E = -3675.74712684	$[PdCl_2PH_3NO_2]^-$, E = -1595.63582456
$[PdCl_2\ AsH_3CN]^-$, E = -3375.69712860	$[PdCl_2FPH_3]^-$, E = -1490.41814350
$[PdCl_2NH_3\ NO_2]^-$, E = -1309.01998923	$[PdCl_2PyAsH_3]$, E = -3530.93468985
$[PdCl_2COPy]$, E = -1408.72946711	$[PdCl_2ONON_3]^{2-}$, E = -1416.71742767
$[PdCl_2H_2ONH_3]$, E = -1180.22411073	$[PdCl_2COCN]^-$, E = -1253.49677671
$[PdCl_2HCH_3]^{2-}$, E = -1087.96363617	$[PdCl_2BrOH]^{2-}$, E = -3695.12082312
$[PdCl_2OHPH_3]^-$, E = -1466.37844263	$[PdCl_2NH_3SMe_2]$, E = -1581.84046357
$[PdCl_2OHCN]^{2-}$, E = -1216.15979452	$[PdCl_2(H_2O)_2]$, E = -1200.06086964
$[PdCl_2H_2ON_3]^-$, E = -1287.93917013	$[PdCl_2H_2OCH_3]^-$, E = -1163.69600490
$[PdCl_2PyCH_3]^-$, E = -1335.47639721	$[PdCl_2PH_3SiH_3]^-$, E = -1681.89359033
$[PdCl_2NH_3CH_3]^-$, E = -1143.83807649	$[PdCl_2CNCH_3]^{2-}$, E = -1180.22770329
$[PdCl_2AsH_3SiH_3]^-$, E = -3574.19212857	$[PdCl_2COH]^-$, E = -1161.26928203
$[PdCl_2OHH]^{2-}$, E = -1123.91446353	$[PdCl_2AsH_3C_6H_5]^-$, E = -3514.41240989
$[PdCl_2NO_2H]^{2-}$, E = -1253.18159795	$[PdCl_2H_2OSiH_3]^-$, E = -1415.13630745
$[PdCl_2PH_3C_6H_5]^-$, E = -1622.11389869	$[PdCl_2SMe_2CH_3]^-$, E = -1565.29894798
$[PdCl_2FSiH_3]^{2-}$, E = -1438.69168467	$[PdCl_2SMe_2SiH_3]^-$, E = -1816.73890905
$[PdCl_2COSiH_3]^-$, E = -1451.99794713	$[PdCl_2(AsMe_3)_2]$, E = -5754.03840377
$[PdCl_2FH]^{2-}$, E = -1147.96429472	$[PdCl_2(PMe_3)_2]$, E = -1969.45515665
$[PdCl_2(AsMe_3)(PMe_3)]$, E = -3861.74682423	$[PdCl_2CN(PMe_3)]^-$, E = -1601.31826678
$[PdCl_2(AsMe_3)(PEt_3)]$, E = -3979.61623989	$[PdCl_2H_2O\ (PMe_3)]$, E = -1584.77304790
$[PdCl_2H_2O(AsMe_3)]$, E = -3477.06264116	$[PdCl_2(AsMe_3)CH_3]^-$, E = -3440.65752551
$[PdCl_2(PMe_3)SiH_3]^-$, E = -1799.80233764	$[PdCl_2C_6H_5CH_3]^{2-}$, E = -1318.91188476
$[PdCl_2OH(PMe_3)]^-$, E = -1584.29663414	$[PdCl_2CH_3SiH_3]^{2-}$, E = -1378.68824353
$[PdCl_2C_6H_5SiH_3]^{2-}$, E = -1570.35138503	$[PdCl_2(SiH_3)_2]^{2-}$, E = -1630.12830064
$[PdCl_2(CH_3)_2]^{2-}$, E = -1127.24685742	$[PdCl_2HSiH_3]^{2-}$, E = -1339.40208335

(2) Table S2. Comparison of E_1 values calculated at two different levels of theory.

Trans Ligand	B3LYP-COSMO/ BS1	MPWB1K-COSMO/ BS1
H_2O	7.84	5.15
CO	12.08	9.09
NH_3	18.17	15.22
C_2H_4	21.68	18.51
PH_3	25.92	23.26
F^-	17.79	14.76
Cl^-	23.03	19.74
Br^-	25.48	21.83

CH_3^-	42.29	39.58
SiH_3^-	43.75	41.32

(3) Table S3. Comparison of E_1 values with water and chloroform as solvent obtained at MPWB1K-COSMO/BS1 method.

Trans Ligand	Water as solvent	Chloroform as solvent
H_2O	5.15	6.73
CO	9.09	10.22
NH_3	15.22	17.32
C_2H_4	18.51	20.35
PH_3	23.26	25.66
F^-	14.76	33.57
Cl^-	19.74	37.83
Br^-	21.83	39.71
CH_3^-	39.58	58.91
SiH_3^-	41.32	59.87

(4) Table S4. Comparison of ρ(r) values at bcp of trans Pd-X bond in $[PdCl_3X]^{n-}$ obtained at two different levels of theory.

Trans Ligand	MPWB1K-COSMO/ BS1	MPWB1K-COSMO/ DGDZVP
H_2O	0.08481	0.08086
CO	0.07921	0.07609
NH_3	0.07456	0.07063
C_2H_4	0.07473	0.07002
PH_3	0.06657	0.06316
F^-	0.07564	0.07177
Cl^-	0.07484	0.07099
Br^-	0.07272	0.06848
CH_3^-	0.04497	0.04096
SiH_3^-	0.04237	0.03908

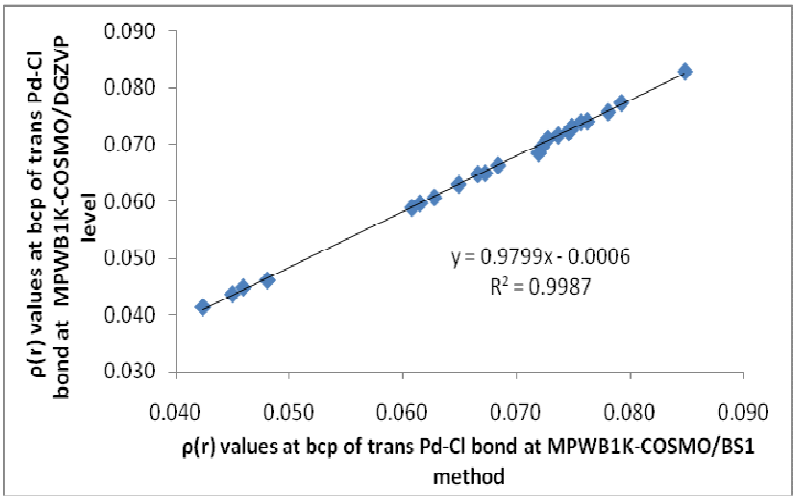

Figure S1. Correlation between **ρ(r)** values calculated at MPWB1K-COSMO/BS1 and single point energy calculations at MPWB1K-COSMO/DGDZVP methods.

(5) Table S5. E_{2pred}, actual and predicted dissociation energy (in kcal/mol) of the bonds Pd-X and Pd-Y bonds in $[Pd^{II}Cl_2XY]^{n-}$ of 53 complexes.

The equations used for predictions are,

$$E_{2pred} = -2709.906\rho_{1X} - 2217.285\rho_{1Y} + 19763.654\rho_{1X}\rho_{1Y} + 274.334$$
$$D_{2Xpred} = D_{1X} + 1924.836\rho_{1X} + 2217.285\rho_{1Y} - 19763.654\rho_{1X}\rho_{1Y} - 198.584$$
$$D_{2Ypred} = D_{1Y} + 2709.906\rho_{1X} + 1431.93\rho_{1Y} - 19763.654\rho_{1X}\rho_{1Y} - 198.584$$

Sl. No.	Ligands in the trans positions		E_{2pred}	Calculated D_{2X}	Predicted D_{2X}	Calculated D_{2Y}	Predicted D_{2Y}
	X	Y					
1	H_2O	Br^-	5.15	21.21	27.33	42.81	41.72
2	NH_3	Br^-	18.20	39.07	40.90	32.04	28.67
3	PH_3	CN^-	35.44	30.76	29.68	43.30	42.84
4	NO_2^-	PH_3	26.45	30.02	31.31	35.29	38.65
5	NH_3	NO_2^-	18.79	38.60	40.30	41.12	38.95
6	Py	AsH_3	19.20	31.64	35.02	40.57	41.85
7	ONO^-	N_3^-	14.10	27.44	29.63	40.22	40.20
8	CO	CN^-	17.39	22.94	26.71	60.76	60.89
9	OH^-	PH_3	33.07	42.37	38.39	35.88	32.03
10	Br^-	OH^-	24.86	24.19	22.03	45.50	46.58
11	OH^-	CN^-	34.57	41.77	36.89	47.83	43.70
12	H_2O	H_2O	-1.39	32.40	33.87	32.40	33.85
13	OH^-	PMe_3	37.60	34.88	33.87	47.84	45.24
14	CN^-	PMe_3	41.02	35.93	37.27	42.82	41.81
15	Py	CH_3^-	35.82	15.54	18.40	93.07	95.72
16	PH_3	SiH_3^-	55.73	10.95	9.39	68.84	68.19
17	AsH_3	SiH_3^-	52.39	9.95	8.68	70.63	71.53

18	CO	H^-	29.74	12.87	14.35	88.15	87.82
19	NO_2^-	H^-	42.87	14.28	14.89	69.56	74.68
20	PH_3	$C_6H_5^-$	50.61	15.55	14.51	76.27	75.05
21	H_2O	SiH_3^-	21.57	6.79	10.91	101.11	102.36
22	F^-	SiH_3^-	38.74	8.31	11.04	82.90	85.18
23	SMe_2	CH_3^-	40.52	13.40	12.82	89.51	91.02
24	CO	SiH_3^-	32.06	7.83	12.03	90.99	91.87
25	F^-	H^-	36.18	14.15	13.61	80.87	81.38
26	PMe_3	PMe_3	46.10	35.97	36.75	35.97	36.73
27	$AsMe_3$	PEt_3	44.90	31.88	32.89	38.65	39.45
28	$AsMe_3$	CH_3	60.34	18.58	17.44	69.85	71.20
29	$C_6H_5^-$	CH_3^-	87.11	35.45	38.56	40.53	44.44
30	CH_3^-	CH_3^-	92.72	35.80	38.84	35.80	38.82
31	SiH_3^-	SiH_3^-	101.04	23.13	22.90	23.13	22.89
32	H^-	SiH_3^-	94.38	21.83	23.19	29.70	29.55
33	H^-	CH_3^-	90.98	25.63	26.59	41.42	40.57
34	CO	Br^-	12.28	27.97	31.81	38.42	34.59
35	AsH_3	CN^-	32.89	28.93	28.18	44.27	45.38
36	F^-	PH_3	21.27	29.66	28.52	46.36	43.83
37	CO	Py	10.00	31.52	34.09	45.07	44.20
38	H_2O	NH_3	4.15	24.91	28.32	53.54	54.92
39	NH_3	SMe_2	17.52	39.81	41.57	37.30	35.80
40	H_2O	N_3^-	5.42	22.29	27.05	50.55	48.88
41	H_2O	$AsMe_3$	10.54	15.88	21.93	66.82	67.22
42	H_2O	PMe_3	11.23	15.68	21.25	71.56	71.60
43	H_2O	CH_3^-	20.16	9.42	12.31	111.66	111.38
44	NH_3	CH_3^-	38.84	17.29	20.26	90.88	92.71
45	CN	CH_3^-	56.46	21.19	21.83	74.44	75.09
46	OH^-	H^-	51.43	20.51	20.03	64.03	66.12
47	AsH_3	$C_6H_5^-$	47.47	14.52	13.60	78.05	78.19
48	SMe_2	SiH_3^-	42.50	10.55	10.84	78.74	81.42
49	$AsMe_3$	$AsMe_3$	42.97	33.95	34.82	33.95	34.80
50	$AsMe_3$	PMe_3	44.21	32.53	33.58	37.44	38.62
51	PMe_3	SiH_3^-	65.25	16.98	17.60	55.43	58.67
52	$C_6H_5^-$	SiH_3^-	90.40	32.31	35.27	29.47	33.52
53	CH_3^-	SiH_3^-	96.17	33.84	35.39	25.92	27.75