Supplementary Information for

Performance of recent density functionals to discriminate between Olefin and Nitrogen Binding to Palladium

Raymond Grüber and Paul Fleurat-Lessard*

Université de Lyon, Institut de Chimie de Lyon, CNRS, Ecole Normale Supérieure de Lyon, 46 allée d'Italie, 69364 Lyon Cedex 07, France

E-mail: paul.fleurat-lessard@ens-lyon.fr

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Reference CCSD(T)/CBS		-9.00	-3.1	206.2	-39.73	209.3	-30.46
LDA							
SVWN5		-4.34	0.4	202.9	-53.46	202.5	-49.12
GGA and NGA							
HFS		-5.80	-0.4	205.7	-48.73	206.1	-42.93
HFB		-12.57	-7.8	218.1	-22.43	225.9	-9.86
PBE		-6.96	-0.4	208.2	-38.73	208.6	-31.77
PBE-D2		-4.78	0.2	208.7	-42.11	208.5	-37.33
OPBE		-5.56	2.1	206.2	-31.03	204.1	-25.47
OLYP		-9.06	-0.1	209.6	-27.88	209.7	-18.82
SLYP		-2.30	0.5	201.2	-61.07	200.6	-58.77
BP86		-7.90	-1.1	208.6	-37.70	209.7	-29.80
BP86-D2		-4.87	-0.3	209.2	-42.45	209.5	-37.58
BP86-PFD		-3.44	-6.3	213.8	-43.79	220.2	-40.35
PW91		-7.14	-0.8	208.1	-39.51	208.9	-32.37
BLYP		-10.67	-3.1	211.8	-32.81	214.9	-22.14
BLYP-D2		-7.37	-1.7	212.3	-38.24	214.1	-30.87
B97D		-6.52	-1.7	211.1	-37.80	212.8	-31.28
B97D3		-7.12	-2.1	209.9	-38.41	212.0	-31.29
HCTH|407		-9.35	0.0	209.5	-30.78	209.5	-21.43
SOGGA11		-6.49	0.8	208.7	-28.32	207.8	-21.83
N12		-7.08	-0.1	206.6	-37.49	206.8	-30.41
Meta-GGA and meta-NGA							
TPSS		-7.64	-0.6	208.5	-37.82	209.1	-30.18
M06-L		-6.46	1.5	210.5	-36.15	209.0	-29.69
M11L		-9.86	-5.5	205.9	-33.22	211.3	-23.36
t-HCTH		-8.99	-1.5	208.2	-34.32	209.6	-25.32
MN12-L		-9.00	-3.3	203.7	-40.67	207.1	-31.67
Dispersion +D3(BJ)							
B3LYP-D3		-9.17	-4.5	208.9	-39.02	213.4	-29.84
B3PW91-D3		-6.68	-2.5	206.6	-41.39	209.1	-34.71
BLYP-D3		-7.71	-1.9	212.0	-38.41	213.9	-30.70
BMK-D3		-10.17	-0.9	210.4	-38.68	211.3	-28.52
BP86-D3		-5.14	-0.8	208.3	-42.34	209.1	-37.20
CAM-B3LYP-D3		-11.08	-5.4	206.9	-40.36	212.3	-29.27
LC-ωPBE-D3		-8.33	-2.5	205.0	-42.33	207.5	-33.99
PBE1PBE-D3		-7.41	-2.6	205.9	-41.34	208.5	-33.94
B2PLYP-D3		-7.30	-2.1	207.2	-39.62	209.4	-32.32
Hybrid GGA							
O3LYP	*11.61*	-9.97	-1.6	208.4	-29.77	209.9	-19.80
τ-HCTH-hyb	*15*	-9.24	-3.1	207.5	-37.57	210.6	-28.33
B3LYP	*20*	-11.77	-5.2	209.1	-34.40	214.3	-22.63
Rev-B3LYP		-11.31	-4.8	208.5	-35.90	213.3	-24.58
B3PW91		-9.48	-2.9	207.0	-36.53	209.9	-27.04
B3P86		-9.31	-3.0	206.4	-38.88	209.4	-29.57
mPW3PBE		-9.06	-2.7	206.6	-38.04	209.3	-28.98
B97-1	*21*	-9.85	-4.0	208.2	-35.79	212.2	-25.94
B97-2		-9.83	-3.3	207.4	-34.58	210.7	-24.74
X3LYP	*21.8*	-11.75	-5.3	208.8	-35.29	214.2	-23.54
B98	*21.98*	-10.36	-4.3	208.0	-35.53	212.3	-25.17
APF	*23*	-9.10	-2.8	206.5	-37.88	209.3	-28.77
APFD		-4.65	-8.7	211.4	-43.75	220.1	-39.10
PBE0	*25*	-8.83	-2.8	206.1	-38.82	208.9	-30.00
mPW1LYP	*25*	-12.19	-6.2	209.0	-34.99	215.2	-22.80
mPW1PBE	*25*	-9.06	-3.0	206.1	-38.04	209.1	-28.98
SOGGA11-X	*40.15*	-10.82	-5.9	207.1	-36.59	213.0	-25.77
MPW1K	*42.8*	-10.46	-5.0	205.0	-38.10	210.0	-27.64
BH&H	*50*	-10.19	-5.0	202.2	-48.65	207.3	-38.47
BH&HLYP		-13.89	-9.2	207.2	-34.72	216.4	-20.83
Reference CCSD(T)/CBS		-9.00	-3.1	206.2	-39.73	209.3	-30.46

Table S1: Relative energies (ΔE in kcal/mol), distance difference, Pd-G and Pd-N distances (in pm) for the model molecules.

Model systems							
				Azane complex		Alkene complex	
Functional	% echange (attenuation)	ΔE=E(azane) –E(ethylene) (kcal/mol)	Δd=d(PdN) -d(PdG) (pm)	d(Pd-N) (pm)	Binding E (kcal/mol)	d(Pd-G) (pm)	Binding E (kcal/mol)
Reference CCSD(T)/CBS		-9.00	-3.1	206.2	-39.73	209.3	-30.46
Hybrid meta-GGA							
TPSSh	*10*	-8.37	-1.5	207.6	-37.80	209.2	-29.43
M06	*27*	-7.24	-4.6	209.3	-37.87	213.9	-30.63
B1B95	*28*	-8.76	-2.7	206.6	-36.49	209.4	-27.73
MPW1B95	*31*	-8.72	-3.0	206.2	-37.85	209.2	-29.13
BMK	*42*	-12.64	-1.7	210.1	-35.00	211.8	-22.36
MPW1B1K	*44*	-9.52	-4.4	205.2	-38.14	209.6	-28.63
M06-2X	*54*	-11.38	-6.0	209.8	-35.96	215.7	-24.58
M06-HF	*100*	-12.32	-9.4	205.9	-38.87	215.3	-26.55
Range separated Hybrid							
LC-BP86	*0-100 (0,47)*	-9.64	-2.6	201.9	-48.50	204.5	-38.86
LC-PBE		-9.25	-2.1	201.9	-46.63	203.9	-37.38
LC-ωPBE		-10.04	-2.7	205.2	-39.48	207.9	-29.44
LC-BLYP		-12.93	-5.0	204.4	-43.12	209.4	-30.19
CAM-B3LYP	*19-65 (0,33)*	-12.57	-5.6	207.0	-37.89	212.6	-25.32
LC-TPSS	*0-100 (0,47)*	-9.78	-2.5	202.5	-45.00	205.0	-35.22
ωB97	*0-100 (0,40)*	-10.70	-3.5	207.3	-39.91	210.8	-29.21
ωB97X	*15,77-100 (0,30)*	-11.18	-4.6	207.3	-39.31	211.9	-28.13
wB97X-D	*22,20-100 (0,20)*	-9.69	-4.4	207.7	-39.10	212.1	-29.42
M11	*42,8-100 (0,25)*	-9.62	-2.5	207.7	-35.52	210.2	-25.90
HISSbPBE	*0-60-0 (0,84,0,20)*	-10.00	-4.2	205.5	-39.23	209.6	-29.22
HSE06	*25-0 (0,11)*	-9.07	-3.1	206.6	-39.05	209.7	-29.97
N12-SX	*25-0 (0,11)*	-8.53	-2.0	206.0	-38.28	208.0	-29.75
MN12-SX	*25-0 (0,11)*	-9.49	-4.0	205.4	-36.14	209.4	-26.66
Double hybrid							
B2PLYP		-8.72	-2.3	207.5	-37.32	209.8	-28.60
B2PLYP-D3		-7.30	-2.1	207.2	-39.62	209.4	-32.32
mPW2PLYP		-9.28	-3.1	207.2	-37.91	210.3	-28.63
B2GPPLYP		-8.12	-2.1	206.4	-38.61	208.5	-30.48
B2GPPLYP-D3		-6.31	-1.9	206.1	-41.60	208.0	-35.28
Ab initio							
HF		0.00	-20.1	210.0	-24.78	230.2	-6.31
MP2/aVTZ		0.10	2.8	202.6	-45.39	199.8	-45.49
MP2/aVQZ		-0.20	3.4	202.4	-45.54	199.0	-45.34
MP2/aV5Z		-0.20	6.7	202.3	-45.46	195.6	-45.27
MP3		-12.59	-7.8	206.0	-37.18	213.8	-24.58
MP2.5		-6.77	-2.0	204.1	-41.25	206.1	-34.48
MP2.68		-9.01	-3.9	204.9	-39.75	208.8	-30.73
SCS-MP2		-4.70	0.6	204.4	-40.71	203.7	-36.00
SCS-MP3		-7.96	-1.8	205.4	-38.67	207.2	-30.71
CCSD/aVTZ		-11.29	-5.1	206.1	-37.84	211.2	-26.55
CCSD(T)/aVTZ		-8.77	-3.1	206.2	-39.73	209.3	-30.96
CCSD(T)/CBS[Q/5]		-9.26	-3.3	205.8	-39.73	209.0	-30.46
Reference CCSD(T)/CBS		-9.00	-3.1	206.2	-39.73	209.3	-30.71

Table S1 (continued): Relative energies (ΔE in kcal/mol), distance difference, Pd-G and Pd-N distances (in pm) for the model molecules.

2-iodo-N-allyl-aniline					
				Amino complex	Alkene complex
Functional	% echange (attenuation)	ΔE=E(amino) – E(ethylene) (kcal/mol)	Δd=d(PdN) -d(PdG) (pm)	d(Pd-N) (pm)	d(Pd-G) (pm)
Reference		1.58	5.2	215.9	210.7
LDA					
SVWN5		11.47	7.7	210.8	203.1
GGA and NGA					
HFS		7.36	6.8	213.8	207.0
HFB		-8.08	-4.1	230.7	234.8
PBE		4.28	7.7	217.8	210.0
PBE-D2		5.11	6.5	216.7	210.2
OPBE		6.58	12.4	216.0	203.5
OLYP		-0.20	10.8	221.5	210.7
SLYP		14.82	7.5	208.5	201.0
BP86		2.95	6.7	218.2	211.4
BP86-D2		4.14	4.9	216.6	211.8
PW91		4.10	7.3	217.7	210.5
BLYP		-2.03	4.2	223.1	218.9
BLYP-D2		-0.06	1.9	220.8	218.9
B97D		0.11	2.8	219.6	216.9
B97D3		-0.07	3.7	218.8	215.1
HCTH|407		-0.89	10.7	221.8	211.1
SOGGA11		5.04	9.2	217.5	208.3
N12		5.67	9.7	217.1	207.4
Meta-GGA and meta-NGA					
TPSS		2.63	5.5	216.7	211.2
M06-L		2.53	8.4	220.3	211.9
M11-L		0.67	-3.1	214.8	217.8
τ–HCTH		1.22	7.8	219.6	211.8
MN12-L		-3.59	-6.1	208.8	214.9
Dispersion +D3(BJ)					
BP86-D3		3.22	5.8	216.3	210.6
BLYP-D3		-0.86	2.5	220.3	217.7
B3LYP-D3		-1.05	0.2	217.8	217.6
B3PW91-D3		2.53	3.9	214.7	210.8
PBE1PBE-D3		3.35	4.4	214.4	210.1
BMK-D3		-4.50	-2.4	214.7	217.1
CAM-B3LYP-D3		-2.17	-0.2	215.8	216.0
LC-ωPBE-D3		1.66	3.7	212.1	208.4
Hybrid GGA					
O3LYP	11.61	-0.37	8.3	219.8	211.5
τ-HCTH-hyb	15	0.95	4.3	217.7	213.4
B3LYP	20	-1.96	1.3	220.0	218.7
B3PW91		2.06	4.8	216.7	211.9
B3P86		2.55	4.4	215.9	211.5
mPW3PBE		2.72	5.0	216.1	211.2
B97-1	21	0.16	3.2	218.3	215.0
B97-2		0.62	4.7	217.8	213.1
X3LYP	21.8	-1.78	1.0	219.5	218.6
B98	21.98	-0.38	2.5	218.1	215.6
APF	23	2.79	4.8	215.9	211.1
APFD		2.24	-5.5	218.8	224.3
PBE0	25	3.31	4.9	215.4	210.5
mPW1LYP	25	-2.47	-0.5	220.0	220.4
mPW1PBE	25	3.04	4.7	215.5	210.7
SOGGA11-X	40.15	-0.12	1.1	217.6	216.4
MPW1K	42.8	1.91	2.1	214.5	212.4
BH&H	50	4.27	1.0	210.4	209.5
BH&HLYP		-3.41	-5.2	218.0	223.3
Reference		1.58	5.2	215.9	210.7

Table S2: Relative energies (ΔE in kcal/mol), distance difference, Pd-G and Pd-N distances (in pm) for 2-iodo-N-allyl-aniline.

2-iodo-N-allyl-aniline					
				Amino complex	Alkene complex
Functional	% echange (attenuation)	ΔE=E(amino) – E(ethylene) (kcal/mol)	Δd=d(PdN) -d(PdG) (pm)	d(Pd-N) (pm)	d(Pd-G) (pm)
Reference		1.58	5.2	215.9	210.7
Hybrid meta-GGA					
TPSSh	10	2.38	4.6	216.0	211.4
M06	27	2.21	3.1	218.3	215.3
B1B95	28	3.18	3.7	215.2	211.5
MPW1B95	31	3.33	3.3	214.8	211.5
BMK	42	-4.96	-2.0	216.3	218.4
MPW1B1K	44	2.86	1.6	213.8	212.1
M06-2X	54	-0.75	-3.5	221.9	225.3
M06-HF	100	-1.43	-8.2	216.4	224.6
Range separated Hybrid					
LC-BP86	0-100 (0,47)	3.88	3.5	208.7	205.2
LC-PBE		4.70	4.5	208.7	204.3
LC-ωPBE		1.68	4.2	213.1	208.9
LC-BLYP		-1.88	0.6	212.6	212.0
CAM-B3LYP	19-65 (0,33)	-2.16	0.2	216.7	216.4
LC-TPSS	0-100 (0,47)	3.17	3.6	209.4	205.8
ωB97	0-100 (0,40)	-1.75	2.1	216.5	214.4
ωB97X	15,77-100 (0,30)	-1.65	1.4	216.7	215.3
ωB97X-D	22,20-100 (0,20)	-1.27	2.1	216.2	214.0
M11	42,8-100 (0,25)	-0.07	-0.3	216.5	216.8
HISSbPBE	0-60-0 (0,84,0,20)	2.44	2.8	214.6	211.8
HSE06	25-0 (0,11)	2.86	4.3	216.0	211.7
N12-SX	25-0 (0,11)	4.06	5.9	215.1	209.2
MN12-SX	25-0 (0,11)	-0.87	-1.5	213.2	214.7
Ab initio					
HF		-8.09			
MP2		11.69			
MP3		-3.22			
MP2.5		4.24			
MP2.68		1.55			
SCS-MP2		5.47			
SCS-MP3		1.70			
Double hybrid					
B2PLYP		1.80	5.2	215.9	210.7
mPW2PLYP		1.37	4.2	215.6	211.5
Reference		1.58	5.2	215.9	210.7

Table S2 (continued): Relative energies (ΔE in kcal/mol), distance difference, Pd-G and Pd-N distances (in pm) for 2-iodo-N-allyl-aniline.

Model systems						
			Azane complex		Alkene complex	
Functional	ΔE=E(azane) –E(ethylene) (kcal/mol)	Δd=d(PdN) -d(PdG) (pm)	d(Pd-N) (pm)	Binding E (kcal/mol)	d(Pd-G) (pm)	Binding E (kcal/mol)
Reference CCSD(T)/CBS	-9.00	-3.1	206.2	-39.73	209.3	-30.46
GGA						
OLYP	-9.06	-0.1	209.6	-27.89	209.7	-18.82
OPBE	-5.56	2.1	206.2	-31.02	204.1	-25.47
OPW91	-5.84	1.9	206.5	-30.75	204.6	-24.91
OP86	-5.86	1.5	206.3	-32.84	204.8	-26.98
PW91LYP	-10.00	-3.0	211.0	-36.52	214.0	-26.51
PW91PBE	-6.87	-0.7	207.8	-39.78	208.5	-32.91
PW91	-7.14	-0.8	208.1	-39.51	208.9	-32.38
PW91P86	-7.18	-1.2	207.9	-41.52	209.1	-34.34
PBELYP	-10.10	-2.9	211.5	-35.51	214.4	-25.4
PBE	-6.96	-0.4	208.2	-38.73	208.6	-31.71
PBEPW91	-7.21	-0.7	208.5	-38.46	209.2	-31.25
PBEP86	-7.26	-1.0	208.3	-40.46	209.3	-33.7
BLYP	-10.67	-3.1	211.8	-32.81	214.9	-22.15
BPBE	-7.59	-0.7	208.5	-35.96	209.2	-28.37
BPW91	-7.84	-0.8	208.8	-35.70	209.6	-27.85
BP86	-7.90	-1.1	208.6	-37.70	209.7	-29.8

2-iodo-N-allyl-aniline				
			Amino complex	Alkene complex
Functional	ΔE=E(azane) –E(ethylene) (kcal/mol)	Δd=d(PdN) -d(PdG) (pm)	d(Pd-N) (pm)	d(Pd-G) (pm)
Reference	1.58	5.2	215.9	210.7
GGA				
OLYP	-0.20	10.8	221.5	210.7
OPBE	4.28	7.7	217.8	210.0
OPW91	6.01	12.4	216.4	204.1
OP86	5.94	11.5	216.0	204.4
PW91LYP	-1.00	4.0	222.0	218.0
PW91PBE	4.56	7.5	217.3	209.8
PW91	4.10	7.3	217.7	210.5
PW91P86	3.99	6.6	217.4	210.8
PBELYP	-1.29	4.3	222.6	218.4
PBE	4.28	7.7	217.8	210.0
PBEPW91	3.82	7.6	218.2	210.6
PBEP86	3.72	6.8	217.9	211.0
BLYP	-2.03	4.2	223.1	218.9
BPBE	3.48	7.7	218.1	210.5
BPW91	3.03	7.5	218.6	211.1
BP86	2.95	6.7	218.2	211.4

Table S3: Influence of the exchange and correlation functionals for the model systems and 2-iodo-N-allyl-aniline. Relative energies (ΔE in kcal/mol), distance difference, Pd-G and Pd-N distances (in pm).

Electronic energy for the Alkene complex (in Hartree)

dPdC	**2.00**	**2.05**	**2.10**	**2.15**	**2.20**	**2.25**	**2.30**	**2.35**	**2.40**
dPdG	1.87	1.93	1.98	2.04	2.09	2.14	2.20	2.25	2.30
B2PLYP/aVTZ	-1351.97068	-1351.97643	-1351.98005	-1351.98200	-1351.98266	-1351.98238	-1351.98137	-1351.97986	-1351.97800
HF/aVTZ	-1349.10509	-1349.11353	-1349.12004	-1349.12491	-1349.12853	-1349.13100	-1349.13256	-1349.13350	-1349.13396
MP2/aVTZ	-1350.46398	-1350.46702	-1350.46809	-1350.46771	-1350.46623	-1350.46408	-1350.46141	-1350.45831	-1350.45495
MP2/aVQZ	-1350.56966	-1350.57260	-1350.57360	-1350.57315	-1350.57162	-1350.56943	-1350.56673	-1350.56360	
MP2/aV5Z	-1350.61186	-1350.61478	-1350.61575	-1350.61529	-1350.61375	-1350.61155	-1350.60886	-1350.60573	
MP2 CBS from MP2(Q/5)	-1346.09856	-1346.10984	-1346.11937	-1346.12731	-1346.13403	-1346.13940	-1346.14364	-1346.14716	
MP3/aVTZ	-1350.45862	-1350.46453	-1350.46856	-1350.47107	-1350.47240	-1350.47280	-1350.47246	-1350.47156	-1350.47025
MP2,5/VTZ	-1350.46130	-1350.46577	-1350.46832	-1350.46939	-1350.46932	-1350.46844	-1350.46693	-1350.46494	-1350.46260
MP2,68/aVTZ	-1350.46034	-1350.46533	-1350.46841	-1350.46999	-1350.47043	-1350.47001	-1350.46892	-1350.46732	-1350.46535
SCS-MP2/aVTZ	-1350.42069	-1350.42458	-1350.42655	-1350.42708	-1350.42652	-1350.42524	-1350.42340	-1350.42111	-1350.41854
SCS-MP3/aVTZ	-1350.41935	-1350.42396	-1350.42667	-1350.42792	-1350.42806	-1350.42742	-1350.42616	-1350.42442	-1350.42236
MP3 SCS (c=0,5)	-1350.41667	-1350.42271	-1350.42690	-1350.42960	-1350.43115	-1350.43178	-1350.43168	-1350.43104	-1350.43002
CCSD/aVTZ			-1350.49123	-1350.49335	-1350.49425	-1350.49422	-1350.49345	-1350.49215	
CCSD(T)/aVTZ			-1350.56290	-1350.56475	-1350.56533	-1350.56497	-1350.56388	-1350.56225	

Electronic energy for the Amino complex (in Hartree)

dPdN	**1.85**	**1.90**	**1.95**	**2.00**	**2.05**	**2.10**	**2.15**	**2.20**	**2.25**	**2.30**
B2PLYP/aVTZ	-1329.98169	-1329.98864	-1329.99322	-1329.99591	-1329.99710	-1329.99711	-1329.99619	-1329.99458	-1329.99243	-1329.98992
HF/aVTZ	-1327.30415	-1327.31172	-1327.31684	-1327.32007	-1327.32179	-1327.32231	-1327.32192	-1327.32081	-1327.31914	-1327.31708
MP2/aVTZ	-1328.51691	-1328.52253	-1328.52587	-1328.52736	-1328.52741	-1328.52633	-1328.52438	-1328.52180	-1328.51875	-1328.51539
MP2/aVQZ		-1328.62292	-1328.62615	-1328.62754	-1328.62750	-1328.62635	-1328.62433	-1328.62170		
MP2/aV5Z		-1328.66334	-1328.66655	-1328.66792	-1328.66787	-1328.66670	-1328.66468	-1328.66205		
MP2 CBS from MP2(Q/5)		-1324.50315	-1324.50883	-1324.51264	-1324.51490	-1324.51596	-1324.51613	-1324.51555		
MP3/aVTZ	-1328.52730	-1328.53383	-1328.53800	-1328.54031	-1328.54113	-1328.54080	-1328.53958	-1328.53767	-1328.53524	-1328.53246
MP2,5/VTZ	-1328.52211	-1328.52818	-1328.53194	-1328.53383	-1328.53427	-1328.53357	-1328.53198	-1328.52974	-1328.52700	-1328.52393
MP2,68/aVTZ	-1328.52398	-1328.53022	-1328.53412	-1328.53616	-1328.53674	-1328.53617	-1328.53472	-1328.53260	-1328.52997	-1328.52700
SCS-MP2/aVTZ	-1328.47796	-1328.48410	-1328.48793	-1328.48989	-1328.49040	-1328.48977	-1328.48824	-1328.48606	-1328.48338	-1328.48037
SCS-MP3/aVTZ	-1328.48056	-1328.48693	-1328.49096	-1328.49313	-1328.49383	-1328.49338	-1328.49204	-1328.49003	-1328.48751	-1328.48463
CCSD/aVTZ			-1328.56	-1328.56	-1328.56	-1328.56	-1328.56	-1328.56		
CCSD(T)/aVTZ			-1328.61646	-1328.61887	-1328.61979	-1328.61952	-1328.61834	-1328.61646		

Electronic energies (in Hartree)

	[Pd(PH3)2Cl]+	**C2H4**	**NH3**
HF/aVTZ	-1271.05741		
HF/aVQZ	-1271.07149		
MP2/aVDZ	-1271.98980		
MP2/aVTZ	-1271.98980	-78.40578	-56.46546
MP2/aVQZ	-1272.07242	-78.42895	-56.48271
MP2/aV5Z	-1272.10682	-78.43687	-56.48877
MP2/CBS from MP2(Q/5)	-1272.14292	-78.44518	-56.49514
CCSD/aVTZ	-1272.02258	-78.42947	-56.47707
CCSD(T)/VTZ	-1272.07115	-78.44487	-56.48535

Table S4: Electronic energies (in Hartree) for the model systems. For all ab initio methods, single points were performed on B2PLYP/aVTZ geometries. For the **ModA** complex, both Pd-C distances were frozen at the same value. As the complex is symmetric, this does not introduce artificial constraint. The Pd-G distance was then computed and is given in the upper table. For the **ModN** complex, the Pd-N distance was frozen.

Each curve was fitted using a third order polynomial that provided the energy and distance of the minimum. These parameters are reported in Table S1.

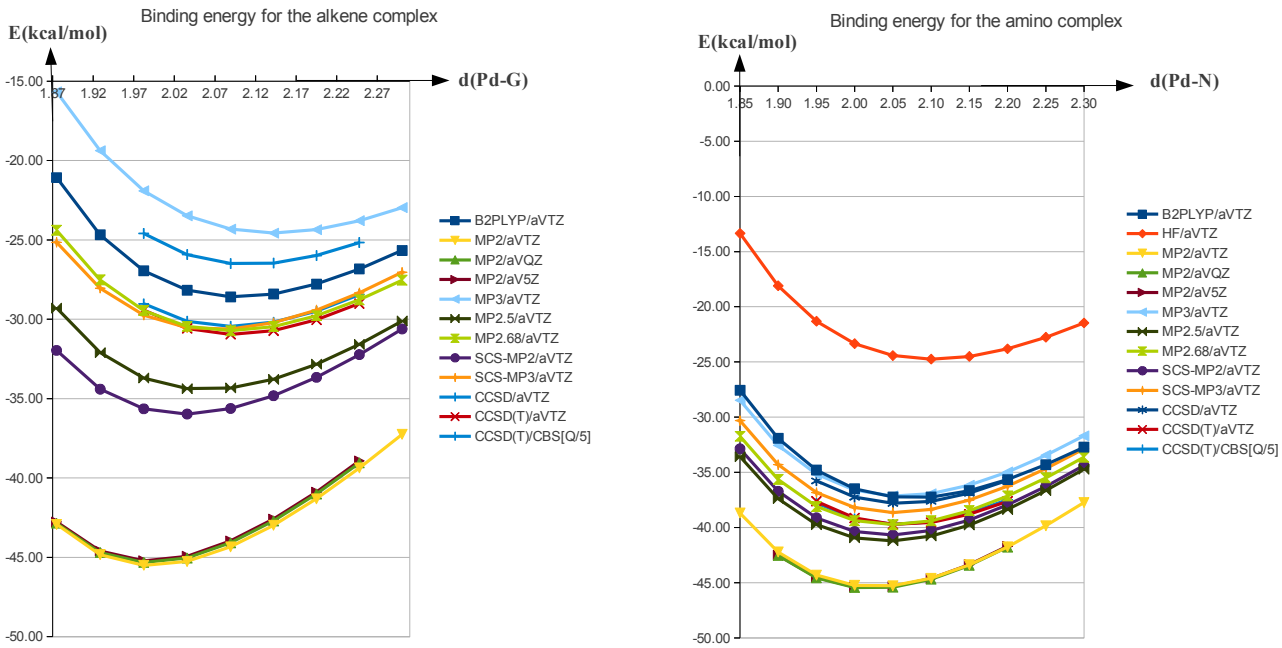

Figure SI-1: Binding energies (in kcal/mol) for alkene (as a function of the Pd-G distance) and azane (as a function of the Pd-N distance) complexes at *ab initio* level. The binding energies are computed using energies from Table S4 for $[Pd(PH_3)_2Cl]^+$, C_2H_4 and NH_3.

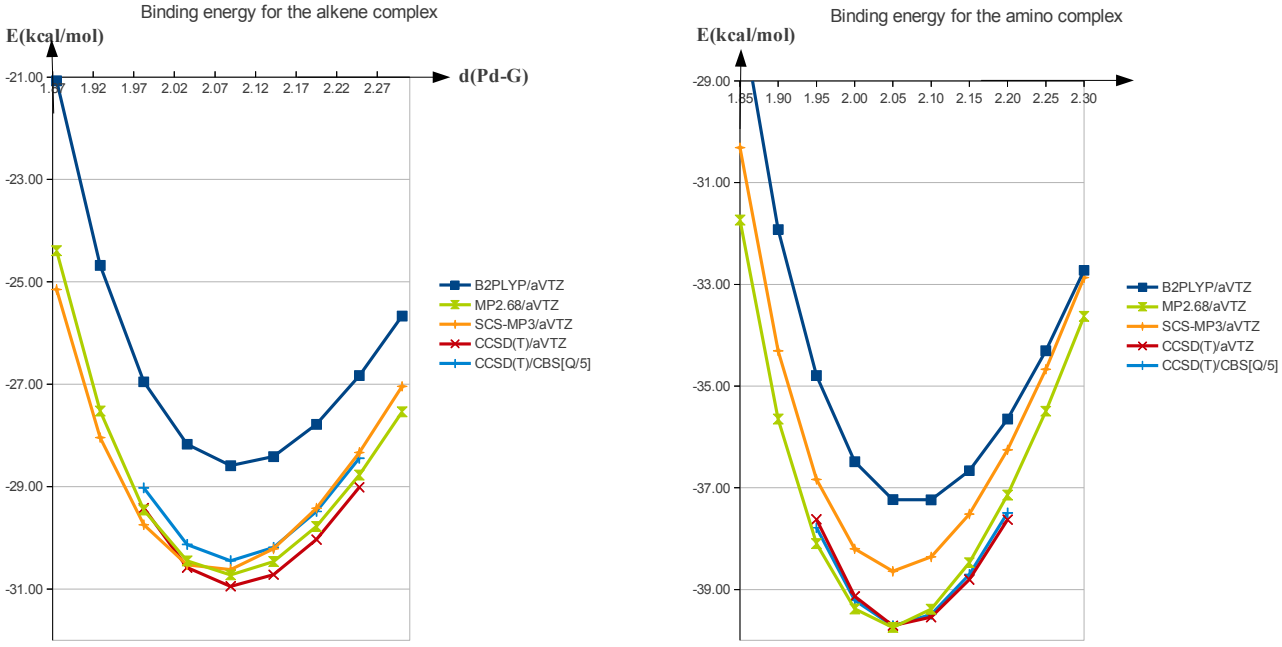

Figure SI-2: Binding energies for alkene and amino complexes for B2PLY/aVTZ, SCS-MP3/aVTZ, CCSD(T)/aVTZ, CCSD(T)/CBS and MP2.68/aVTZ.

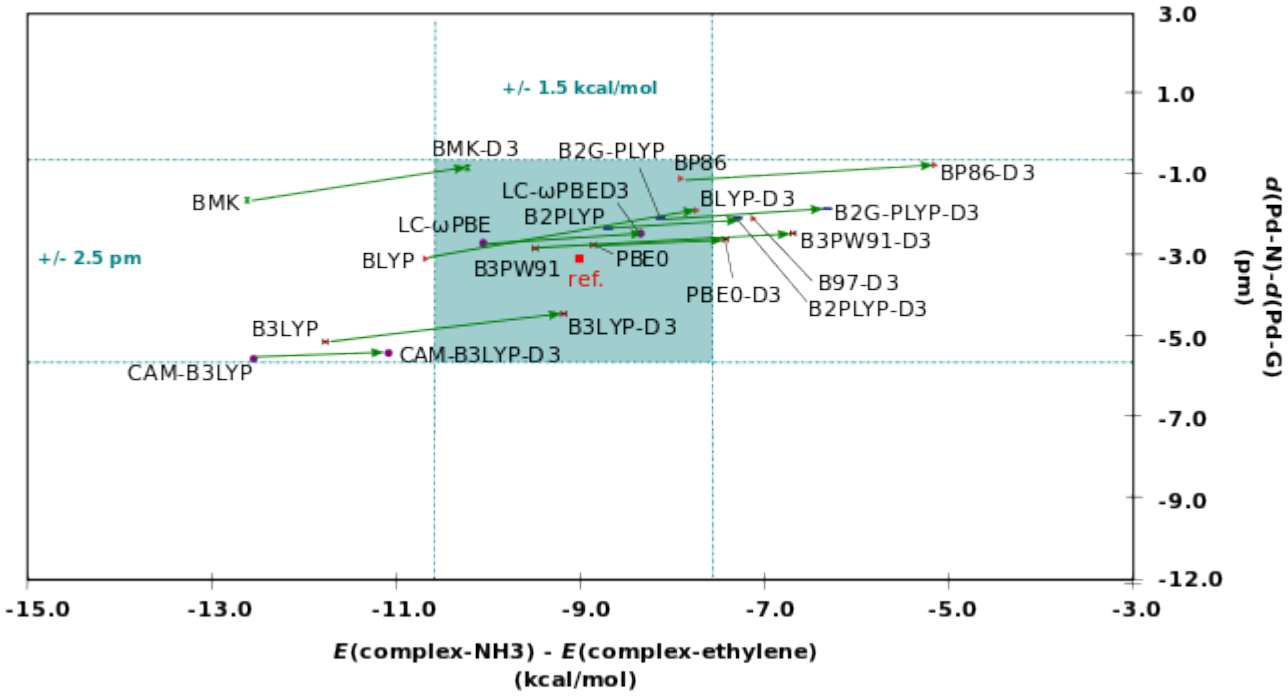

Figure SI-3: Influence of dispersion effect on ΔE and Δd. Symbol code: ■ Reference, ▶ GGA, ◀ meta GGA, ● RSH, ⋈ hybrid GGA, ⧗ hybrid meta GGA, ▬ double hybrid, ✱ ab initio.

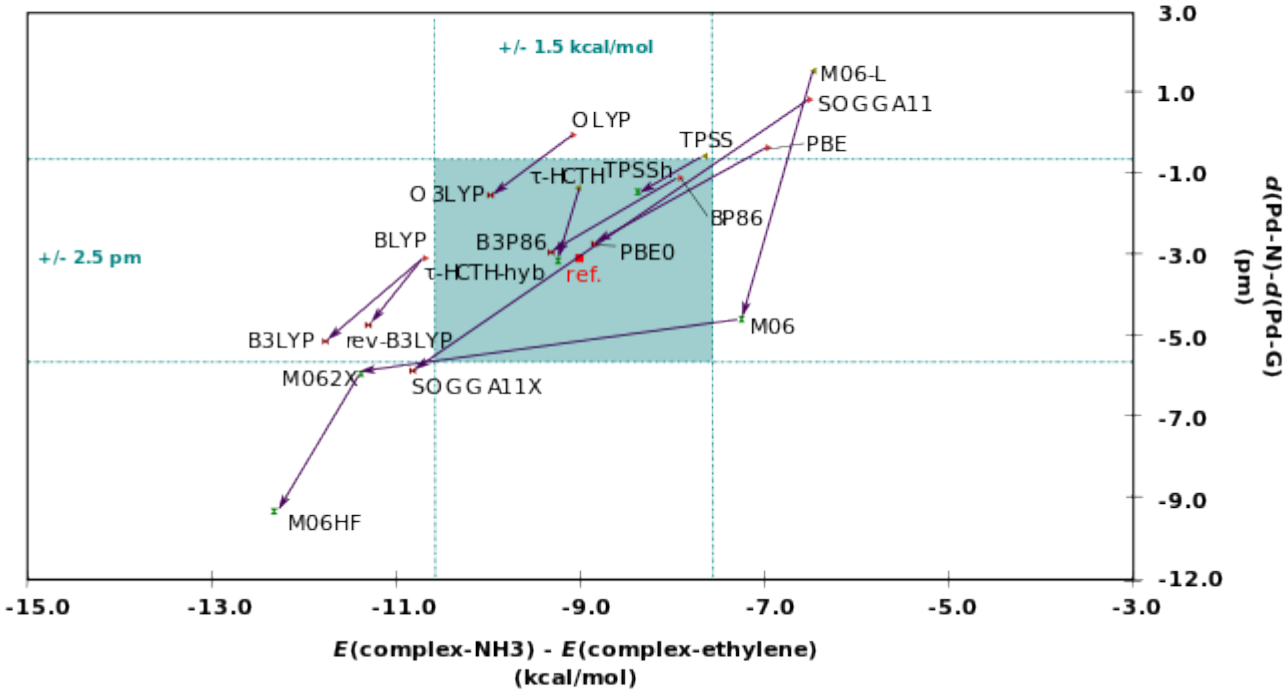

Figure SI-4: Influence of exact exchange on ΔE and Δd. Symbol code: **Symbol code:** ■ Reference, ▶ GGA, ◀ meta GGA, ● RSH, ⋈ hybrid GGA, ⧗ hybrid meta GGA.

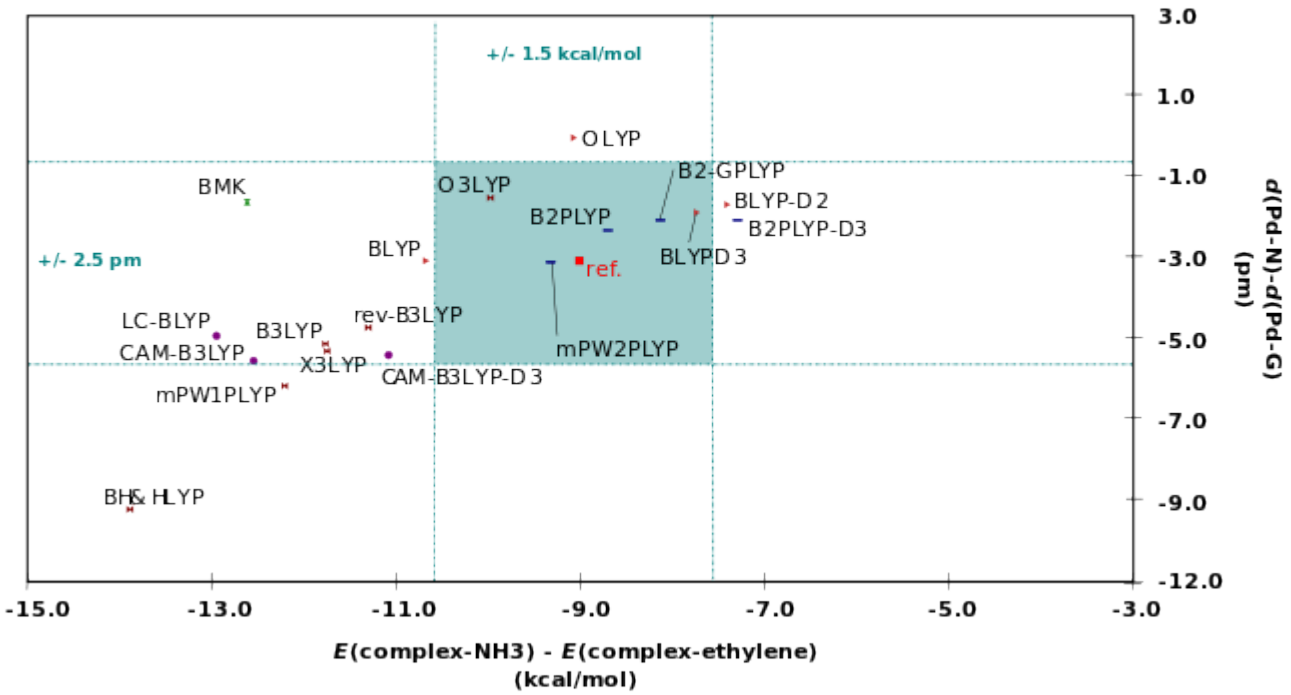

Figure SI-5: ΔE as a function of Δd for methods using the LYP correlation functional. Symbol code: ■ Reference, ▶ GGA, ● RSH, ⋈ hybrid GGA, ⧗ hybrid meta GGA, ▬ double hybrid.

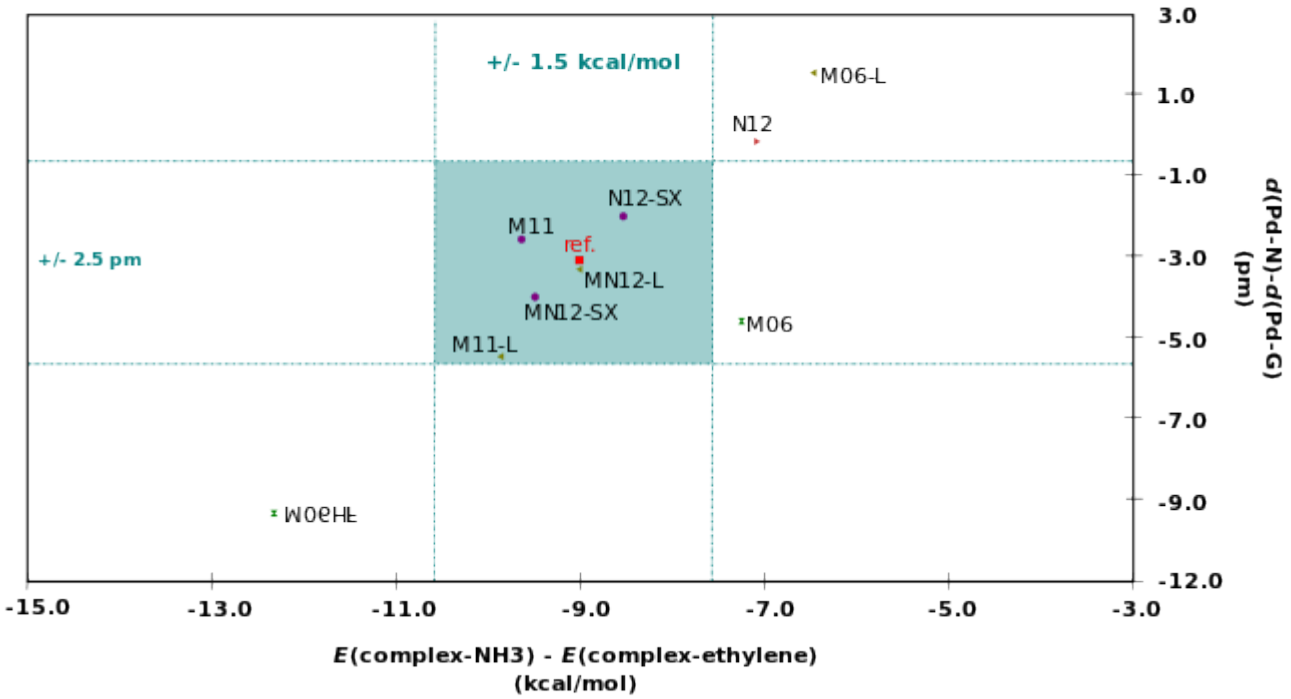

Figure SI-6: ΔE as a function of Δd for the Minesota functionals. Symbol code: ■ Reference, ▶ NGA, ◀ meta GGA/NGA, ● RSH, ⋈ hybrid GGA, ⧗ hybrid meta GGA, ▬ double hybrid, ✱ ab initio.

ModA

Energy : -1351.535629

H	2.040631	2.281767	0.974939
P	0.743391	3.652381	-1.423268
Cl	0.964445	1.404762	-3.627639
Pd	0.915338	1.338362	-1.307386
H	-0.442727	2.094612	0.917297
C	1.558542	1.330182	0.805080
C	0.183782	1.226576	0.773160
H	2.179481	0.454574	0.925588
P	1.094304	-0.965496	-1.547997
H	0.058669	-1.536378	-2.294892
H	1.129060	-1.777987	-0.405609
H	2.236787	-1.372542	-2.244656
H	-0.369609	4.099593	-2.142664
H	1.808460	4.264070	-2.092412
H	0.659724	4.398307	-0.238787
H	-0.303877	0.267419	0.867946

ModN

Energy : -1329.595367

P	3.112600	1.592623	-1.626454
Cl	0.751361	1.434207	-3.701197
Pd	0.812261	1.484724	-1.397116
P	-1.495994	1.299539	-1.488703
H	-2.137503	2.312499	-2.210466
H	-2.249308	1.270760	-0.304947
H	-1.950455	0.148880	-2.142836
H	3.578881	2.669480	-2.388934
H	3.674078	0.500210	-2.297109
H	3.927788	1.676368	-0.486858
N	0.847760	1.529478	0.676680
H	0.450463	0.679444	1.064005
H	0.302533	2.309711	1.029456
H	1.779936	1.622579	1.063280

2-iodo-N-allyl-amine – Alkene complex

Energy : -1208.687042

H	4.568950	0.280047	-0.369613
H	0.637238	-2.373756	-1.989969
H	-1.308439	-3.861863	-2.243582
H	1.571152	2.189234	-2.176660
H	3.881521	2.311723	-0.431195
C	-0.292505	-2.113962	-1.503238
P	3.478917	1.053629	0.055473
I	2.255153	-1.956894	0.957236
C	-1.391844	-2.967946	-1.640613
Pd	1.344848	0.142797	-0.387887
H	-0.579421	1.051150	-2.108163
H	3.811750	1.213665	1.409395
C	1.010091	2.150870	-1.253481
C	-0.368877	-0.971483	-0.714765
C	-0.209580	1.505958	-1.201665

C	-2.573795	-2.670145	-0.974950
H	1.276326	2.872569	-0.493487
H	-3.425955	-3.331565	-1.051340
C	-1.588710	-0.627585	-0.104340
C	-2.679007	-1.502507	-0.220715
C	-1.217224	1.776882	-0.123130
H	-2.088410	2.243480	-0.606523
N	-1.659744	0.579879	0.613819
H	-0.815928	2.495492	0.592221
H	-3.616406	-1.270251	0.262680
C	-2.865682	0.847419	1.376324
H	-2.707561	1.746939	1.968585
H	-3.070006	0.022695	2.055031
H	-3.747554	1.009032	0.741947

2-iodo-N-allyl-amine – Amino complex

Energy : -1208.684211

H	-1.326604	-3.822225	-2.196763
H	-3.714219	-3.933271	-1.551921
H	-0.707480	2.147143	-4.369182
C	-1.779002	-3.003962	-1.653035
I	1.914129	-2.953737	-2.700715
C	-3.128275	-3.062910	-1.287756
H	-1.981967	0.772626	-2.818825
C	-0.528112	2.198138	-3.304948
C	-1.048158	-1.874209	-1.300378
C	-1.220576	1.448861	-2.450272
C	-3.737590	-2.019290	-0.587608
H	0.235459	2.884993	-2.963584
H	-4.781917	-2.093087	-0.319164
C	-1.677471	-0.854217	-0.606226
C	-3.011446	-0.880287	-0.229991
C	-1.038755	1.517586	-0.968704
H	-1.956531	1.876018	-0.489369
N	-0.685653	0.204447	-0.355887
H	-0.238455	2.212542	-0.719269
H	-3.481371	-0.070903	0.311973
C	-0.406585	0.380957	1.086061
H	0.441913	1.050726	1.203363
H	-0.168220	-0.584174	1.521053
H	-1.273740	0.807005	1.595818
Pd	0.751980	-1.012934	-1.409741
P	2.751657	0.246035	-1.378422
H	3.889823	-0.337961	-0.796330
H	2.810403	1.501664	-0.742551
H	3.312357	0.610391	-2.614850

2-iodo-N-allyl-amine – Interconversion TS

Energy : -1208.666885

H	-0.175308	-2.605923	-1.291258
H	-2.216621	-3.980282	-1.122618
H	-0.007802	2.366793	-2.685520
C	-1.055353	-2.199125	-0.814258

I	2.223681	-1.185476	0.110208
C	-2.209514	-2.980947	-0.708029
H	-1.882031	0.894176	-2.169228
C	-0.614472	2.526412	-1.805800
C	-1.051508	-0.910945	-0.287187
C	-1.644301	1.717362	-1.510005
C	-3.342932	-2.492891	-0.060910
H	-0.407865	3.407085	-1.213134
H	-4.222080	-3.114951	0.033214
C	-2.201861	-0.421534	0.330147
C	-3.349149	-1.199742	0.462222
C	-2.494516	1.905745	-0.291969
H	-3.556899	1.772808	-0.529016
N	-2.072218	0.952718	0.762810
H	-2.354067	2.909123	0.108063
H	-4.229791	-0.817649	0.960190
C	-2.695325	1.257057	2.051577
H	-2.404614	2.260875	2.355005
H	-2.341377	0.546911	2.794557
H	-3.789015	1.213450	2.013293
Pd	0.304232	0.562903	-0.094775
P	1.879153	2.262351	0.414099
H	2.627560	2.091805	1.590666
H	1.510923	3.610737	0.593602
H	2.942069	2.454712	-0.485670