SUPPORTING INFORMATION

Accelerating Computations of Organometallic Reaction Energies through Hybrid Basis Sets

Júlia M. A. Alves,[a,#] Ivanna G. R. Domingos,[b,#] Marcelo T. de Oliveira[*a,c]

a – São Carlos Institute of Chemistry, University of São Paulo, Av. Trabalhador São Carlense 400,

13566–590, São Carlos, SP, Brazil

b – Institute of Chemistry, University of São Paulo, Av. Prof. Lineu Prestes 748,

05508–000, São Paulo, SP, Brazil

c – Department of Chemistry and Physics, La Trobe Institute of Molecular Sciences,

La Trobe University, Melbourne, Victoria 3086, Australia

# These authors contributed equally.

mtavareso@usp.br

Table S1. Transition metal reactions in MOBH35 data set. Basis set partition is shown with atoms using the larger basis set in blue.

#	REACTION	#	REACTION
1		9**	
2		10**	
3		11	
4		12	
5		13	
6**		14	
7**		15	
8		16	

Table S1. Transition metal reactions in MOBH35 data set. Basis set partition is shown with atoms using the larger basis set in blue (continued).

#	REACTION
17*	
18*	
19*	
20*	

#	REACTION	#	REACTION
21		24	
22		25	
23		26	

Table S1. Transition metal reactions in MOBH35 data set. Basis set partition is shown with atoms using the larger basis set in blue (continued).

#	REACTION	#	REACTION
27		32	
28		33	
29		34**	
30**		35**	
31**			
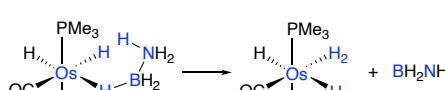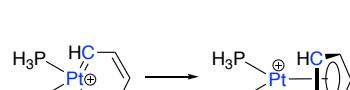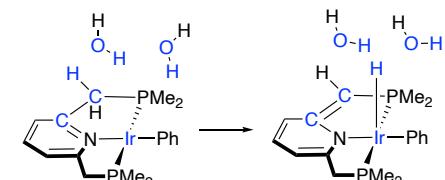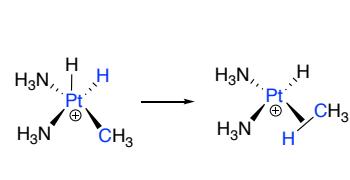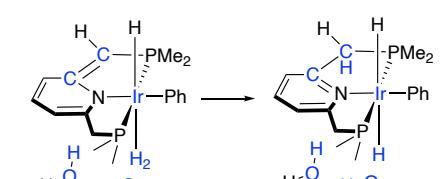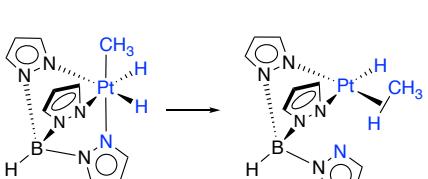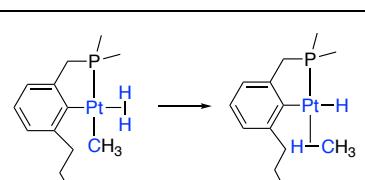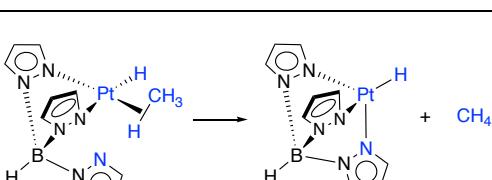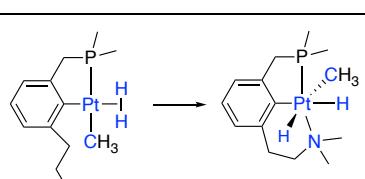
* In some cases, we were unable to locate exact atoms involved in the reaction. Therefore, we selected all phosphorus atoms for reactions #17–20.

** We favored an extended selection for those cases that the product of one reaction is the reactant in the following (6 and 7, 9 and 10, 30 and 31, 34 and 35).

Statistical parameters

• *Mean absolute deviation (MAD):*

$$MAD = \frac{1}{N} \sum_{i=1}^{N} | \sigma_i - \sigma_i^{ref} |$$

• *Percentage mean absolute relative error (%MARE):*

$$\%MARE = \left(\frac{1}{N} \sum_{i=1}^{N} | \frac{\sigma_i - \sigma_i^{ref}}{| \sigma_i^{ref} |} | \right) \times 100$$

Table S2. Mean absolute deviation (MAD), standard deviation (SD) and maximum deviation (max) parameters (kcal mol^{-1}) for various basis sets using ωB97M-V. Values are reported including and excluding reactions 8 and 9 in MOBH35 dataset.

Basis Set	Excluding Reactions #8 and #9			Including Reaction #8 and #9		
	MAD	SD	max	MAD	SD	max
def2-SV(P)	2.96	2.30	9.43	3.00	2.26	9.43
def2-SVP	2.33	2.05	8.15	2.40	2.04	8.15
ma-def2-SVP	2.26	2.08	9.70	2.34	2.08	9.70
def2-SVPD	2.51	2.95	15.66	2.57	2.91	15.66
def2-TZVP(-f)	1.61	1.42	6.66	1.67	1.47	6.66
def2-TZVP	1.64	1.40	7.24	1.72	1.45	7.24
def2-TZVPP	1.55	1.36	6.54	1.63	1.42	6.54
def2-TZVPPD*	1.52	1.32	6.03	1.61	1.38	6.33
def2-QZVPP	1.51	1.30	5.41	1.60	1.37	6.34

* For some rare cases (r8, ts8, p9 and ts9) while using ωB97M-V/def2-TZVPPD, StrongSCF criteria was required for convergence instead of TightSCF. Extensive testing showed only numerical differences with no impact on reported energies.

Table S3. Percentage mean absolute relative error (%MARE), standard deviation (SD) and maximum deviation (max) parameters (%) for various basis sets using ωB97M-V. Values are reported including and excluding reactions 8 and 9 in MOBH35 dataset.

Basis Set	Excluding Reactions #8 and #9			Including Reaction #8 and #9		
	%MARE	SD	max	%MARE	SD	max
def2-SV(P)	41.41	156.77	1281.71	42.49	153.38	1281.71
def2-SVP	30.67	89.88	875.07	32.50	91.01	875.07
ma-def2-SVP	29.59	86.86	838.35	31.34	87.67	838.35
def2-SVPD	28.24	60.00	548.29	30.97	66.90	548.29
def2-TZVP(-f)	21.48	78.11	773.91	22.32	76.68	773.91
def2-TZVP	22.05	82.44	818.42	23.31	81.49	818.42
def2-TZVPP	21.35	76.63	758.62	22.70	76.06	758.62
def2-TZVPPD*	21.11	75.47	747.19	22.47	74.96	747.10
def2-QZVPP	21.61	78.00	772.72	22.88	77.21	772.72

* For some rare cases (r8, ts8, p9 and ts9) while using ωB97M-V/def2-TZVPPD, StrongSCF criteria was required for convergence instead of TightSCF. Extensive testing showed only numerical differences with no impact on reported energies.

Table S4. Mean absolute deviation (MAD), standard deviation (SD) and maximum deviation (max) parameters (kcal mol^{-1}) for various basis sets using revDOD-PBEP86-D4. Values are reported including and excluding reactions 8 and 9 in MOBH35 dataset.

Basis Set	*Excluding Reactions #8 and #9*			*Including Reaction #8 and #9*		
	MAD	SD	max	MAD	SD	max
def2-SVP	1.92	1.75	9.25	2.02	1.91	9.25
def2-TZVP(-f)	1.49	1.58	7.05	1.62	1.84	11.32
def2-TZVP	1.45	1.51	6.84	1.57	1.76	10.76
def2-TZVPP	1.23	1.46	6.71	1.37	1.73	10.66
def2-QZVPP	1.04	1.11	4.98	1.18	1.46	10.21

Table S5. Percentage mean absolute relative error (%MARE), standard deviation (SD) and maximum deviation (max) parameters (kcal mol^{-1}) for various basis sets using revDOD-PBEP86-D4. Values are reported including and excluding reactions 8 and 9 in MOBH35 dataset.

Basis Set	*Excluding Reactions #8 and #9*			*Including Reaction #8 and #9*		
	%MARE	SD	max	%MARE	SD	max
def2-SV(P)	20.19	35.65	289.55	22.31	39.13	289.55
def2-TZVP(-f)	13.58	17.01	100.00	15.47	22.53	159.96
def2-TZVP	12.61	14.91	89.40	14.43	21.15	163.99
def2-TZVPP	11.16	14.38	86.60	13.05	20.89	164.03
def2-QZVPP	9.67	12.65	86.01	11.86	20.38	161.12

Table S6. Mean absolute deviation (MAD), standard deviation (SD) and maximum deviation (max) parameters (kcal mol^{-1}) for various hybrid basis sets using ωB97M-V. Large basis set located in atoms directly involved in the reaction. Values are reported including and excluding reactions 8 and 9 in MOBH35 dataset.

Basis Set	Excluding Reactions #8 and #9			Including Reaction #8 and #9		
	MAD	SD	max	MAD	SD	max
def2-SV(P)/def2-TZVP(-f)	1.82	1.63	8.33	1.86	1.64	8.33
def2-SVP/def2-TZVP(-f)	1.71	1.54	7.67	1.76	1.56	7.67
def2-SVP/def2-TZVPP	1.64	1.44	6.77	1.70	1.48	6.77

Table S7. Percentage mean absolute relative error (%MARE), standard deviation (SD) and maximum deviation (max) parameters (kcal mol^{-1}) for various hybrid basis sets using ωB97M-V. Large basis set located in atoms directly involved in the reaction. Values are reported including and excluding reactions 8 and 9 in MOBH35 dataset.

Basis Set	Excluding Reactions #8 and #9			Including Reaction #8 and #9		
	%MARE	SD	max	%MARE	SD	max
def2-SV(P)/def2-TZVP(-f)	24.64	74.12	682.20	25.19	72.79	682.20
def2-SVP/def2-TZVP(-f)	22.99	75.74	734.50	23.63	74.36	734.50
def2-SVP/def2-TZVPP	23.00	74.13	711.79	24.13	73.69	711.79

Table S8. Mean absolute deviation (MAD), standard deviation (SD) and maximum deviation (max) parameters (kcal mol^{-1}) for various hybrid basis sets using revDOD-PBEP86-D4. Large basis set located in atoms directly involved in the reaction. Values are reported including and excluding reactions 8 and 9 in MOBH35 dataset.

Basis Set	Excluding Reactions #8 and #9			Including Reaction #8 and #9		
	MAD	SD	max	MAD	SD	max
def2-TZVP(-f)/def2-QZVPP	1.14	1.34	6.02	1.29	1.65	10.79
def2-TZVP/def2-QZVPP	1.09	1.25	5.63	1.23	1.57	10.37
def2-TZVPP/def2-QZVPP	1.08	1.26	5.63	1.22	1.57	10.39

Table S9. Percentage mean absolute relative error (%MARE), standard deviation (SD) and maximum deviation (max) parameters (kcal mol^{-1}) for various hybrid basis sets using revDOD-PBEP86-D4. Large basis set located in atoms directly involved in the reaction. Values are reported including and excluding reactions 8 and 9 in MOBH35 dataset.

Basis Set	Excluding Reactions #8 and #9			Including Reaction #8 and #9		
	%MARE	SD	max	%MARE	SD	max
def2-TZVP(-f)/def2-QZVPP	11.90	20.32	133.63	13.94	25.32	163.82
def2-TZVP/def2-QZVPP	11.04	17.68	118.48	13.13	162.37	23.45
def2-TZVPP/def2-QZVPP	10.01	14.02	85.74	12.18	21.16	162.32

Table S10. Comparison of computational times (seconds) for some medium-sized systems with various methods. The calculations were performed on 10 Intel E5-2630v4 cores with 12 GB RAM per core [*nprocs=20; maxcore=6000*].[1]

Method	r26 *(33 atoms)*	p22 *(60 atoms)*	p24 *(86 atoms)*
ωB97M-V/			
def2-TZVPP	163	596	1916
def2-SVP/ def2-TZVPP	60	198	598
Speed-up	2.7	3.0	3.2
revDOD-PBEP86-D4/			
def2-QZVPP	434	2274	12325
def2-TZVP(-f)/def2-QZVPP	74	320	1255
Speed-up	5.9	7.1	9.8-fold faster

[1] Equipped with a solid-state drive (SSD) Samsung 960 PRO M.2 with 512 GB of storage.

Table S11. Comparison of statistical parameters for ωB97M-V/def2-SVP with and without the application of the RIJCOSX approximation.

Method	MAD	SD	max
RIJCOSX-ωB97M-V/def2-SVP	2.40	2.04	8.19
ωB97M-V/def2-SVP	2.33	2.05	8.15