Supporting Information

Performance of Density Functionals for Activation Energies of Zr-Mediated Reactions

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Table S1. Activation Energies (kcal/mol) Calculated by B3LYP with TZ and QZ Basis Sets for Four Zr-mediated Reactions in Scheme 1[a]

	$\Delta E^{\ddagger}(1)$	$\Delta E^{\ddagger}(2)$	$\Delta E^{\ddagger}(3)$	$\Delta E^{\ddagger}(4)$
TZ	9.67	11.54	5.21	18.15
QZ	9.89	11.72	6.12	18.16

[a] Activation energies for all four reactions are calculated with respect to the separated reactants.

Table S2. Activation Energies (kcal/mol) Calculated by Various Functionals with QZ Basis Set for Four Zr-mediated Reactions in Scheme 1[a]

	B3LYP	PBE0	BMK	BP86	CAM-B3LYP	M06-L	M06	M06-2X	TPSS	TPSSh	ωB97X	B2GP-PLYP	B2-PLYP	OLYP	LC-ωPBE
$\Delta E^{\ddagger}(1)$	9.89	5.67	7.98	7.40	8.63	2.25	4.01	3.17	5.50	5.70	5.52	5.33	6.40	14.88	7.14
$\Delta E^{\ddagger}(2)$	11.72	7.19	9.98	9.04	10.44	3.35	4.74	4.27	7.19	7.39	7.19	6.50	7.68	16.92	8.76
$\Delta E^{\ddagger}(3)$	6.12	2.02	4.22	4.26	3.51	-2.13	-0.51	-2.00	1.51	1.60	1.64	0.49	1.84	14.39	3.10
$\Delta E^{\ddagger}(4)$	18.16	11.33	14.02	11.73	16.12	13.10	10.35	10.72	13.87	14.34	14.11	13.75	14.72	22.54	13.51
$\Delta E^{\ddagger}(4)^b$	17.83	13.92	16.10	13.20	17.36	19.67	16.67	17.61	15.78	16.09	18.15	17.62	17.70	15.90	15.05

[a] Unless otherwise specified, activation energies for reactions are calculated with respect to the separated reactants.

[b] Activation energy for reaction 4 is calculated with respect to the reactant complex.

Table S3. Activation Energies (kcal/mol) Calculated by Various Functionals with QZ Basis Set and DFT-D3(0) Correction for Four Zr-mediated Reactions in Scheme 1[a]

	B3LYP	PBE0	BMK	BP86	CAM-B3LYP	M06-L	M06	M06-2X	TPSS	TPSSh	ωB97X	B2GP-PLYP	B2-PLYP	OLYP	LC-ωPBE
$\Delta E^{\ddagger}(1)$	4.75	2.42	2.87	1.72	5.00	1.90	3.04	2.87	1.32	1.54	4.50	3.38	3.60	3.44	3.30
$\Delta E^{\ddagger}(2)$	4.85	2.85	3.16	1.35	5.62	2.85	3.44	3.84	1.52	1.78	5.14	3.88	3.96	3.00	3.65
$\Delta E^{\ddagger}(3)$	0.12	-1.88	-1.44	-2.49	-0.70	-2.65	-1.86	-2.45	-3.57	-3.39	0.62	-1.73	-1.36	2.76	-1.37
$\Delta E^{\ddagger}(4)$	12.26	7.63	8.21	4.88	12.05	12.74	9.29	10.41	8.82	9.47	10.98	11.54	11.58	10.87	9.19
$\Delta E^{\ddagger}(4)^b$	17.00	13.47	15.07	12.29	16.79	19.69	16.67	17.63	15.18	15.48	16.43	17.26	17.22	14.44	14.44

[a] Unless otherwise specified, activation energies for reactions are calculated with respect to the separated reactants.

[b] Activation energy for reaction 4 is calculated with respect to the reactant complex.

PBE0/TZ optimized Cartesian coordinates

Cp_2ZrHCl

Zr	-0.42879400	0.33709000	-0.31776500
C	0.29747100	2.08544000	1.33855200
C	0.09518200	2.74571500	0.10818100
C	-0.95530300	1.61052600	1.78374200
H	0.85823000	3.22717500	-0.48361900
C	-1.28352200	2.68347800	-0.20292200
H	-1.13339000	1.02794000	2.67426000
C	-1.93039200	1.98738700	0.83849800
H	-1.76076900	3.11718600	-1.06831300
H	-2.98208000	1.74870100	0.88770900
C	0.64213400	0.89980700	-2.50602100
C	1.20508300	-0.33105900	-2.11257200
C	-0.73448300	0.69127000	-2.76636400
H	2.23608800	-0.50551600	-1.85231200
C	0.17742500	-1.30122000	-2.13226900
H	-1.43700100	1.43368500	-3.11281400
C	-1.01165500	-0.67448800	-2.54874400
H	0.27701900	-2.33584000	-1.84204900
H	-1.97727700	-1.14859500	-2.63623900
Cl	-1.85697800	-1.38859800	0.59283500
H	1.18367300	-0.11529400	0.42927700
H	1.23833200	1.97205300	1.85113300
H	1.17081000	1.83518600	-2.60464200

C_2H_2

C	-0.70623200	1.21917800	0.00000000
C	0.49027300	1.21917800	0.00000000
H	-1.77014000	1.21917800	0.00000000
H	1.55418100	1.21917800	0.00000000

$Cp_2ZrHCl \cdot C_2H_2$---TS

Zr	-0.36233300	-2.30791200	-0.53472400
C	0.38352100	-0.38413300	0.89961100
C	-0.07683000	0.15377600	-0.31632500
C	-0.72697600	-0.96142500	1.56236200
H	0.52335300	0.68215400	-1.03917700
C	-1.47488200	-0.07985900	-0.40190000
H	-0.70444300	-1.47895300	2.50976400
C	-1.87133900	-0.74431200	0.77124600
H	-2.12683000	0.23356800	-1.20234400
H	-2.86615700	-1.09112000	0.99531200
C	0.67129400	-1.69162400	-2.71459700
C	1.27816700	-2.90488700	-2.33654300
C	-0.69799300	-1.94662000	-2.98225400
H	2.31810900	-3.04764600	-2.09601000
C	0.28066100	-3.90845100	-2.35954500
H	-1.42832200	-1.22462800	-3.31332700
C	-0.92861700	-3.31833600	-2.78044800
H	0.42324700	-4.94690500	-2.10296600
H	-1.87833000	-3.81966700	-2.86795200
Cl	-2.42483200	-3.69565600	-0.03179200
C	0.15313700	-4.94707700	0.99014500
C	1.03212000	-4.24485400	1.41648500
H	-0.63922200	-5.56526700	0.64086100
H	1.37345900	-2.41592700	0.02945400
H	1.83524100	-3.70192900	1.85159600
H	1.39456200	-0.34231000	1.26866400
H	1.17152400	-0.74154100	-2.81086500

C_2H_4

C	-0.27924300	0.49315800	-0.00000600
C	1.04351600	0.49314300	0.00000100
H	-0.84816600	1.41593800	0.00000800
H	-0.84818600	-0.42961000	-0.00002600
H	1.61243800	-0.42963700	-0.00001300
H	1.61245900	1.41591100	0.00002000

$Cp_2ZrHCl \cdot C_2H_4$---TS

Zr	-0.37484400	-2.32279400	-0.55924800
H	1.52460100	-3.59272100	2.06136200
C	0.35329300	-0.43809400	0.93019100
C	-0.08293500	0.13073500	-0.28055900
C	-0.77267700	-1.02474600	1.55874400
H	0.53305700	0.67246000	-0.97976400
C	-1.48020500	-0.09389500	-0.39716600
H	-0.77061400	-1.55547600	2.49921600
C	-1.90191800	-0.78362000	0.75206100
H	-2.11522200	0.23859400	-1.20359900
H	-2.90233700	-1.13111600	0.94840200
C	0.67882600	-1.65586400	-2.71412600

C	1.30959200	-2.85785800	-2.34257100
C	-0.68019100	-1.94174300	-3.00783300
H	2.34985200	-2.97590300	-2.08941400
C	0.33738900	-3.88591600	-2.39302300
H	-1.42290000	-1.23460800	-3.34341400
C	-0.87793700	-3.32120300	-2.82993600
H	0.49828200	-4.92570100	-2.15096600
H	-1.81259300	-3.84551900	-2.93899000
Cl	-2.46419200	-3.70771300	-0.16887600
C	-0.01306200	-4.82739000	1.29649800
C	1.21125000	-4.29954200	1.30340200
H	-0.75990200	-4.55379800	2.02965500
H	-0.31252800	-5.57089100	0.56967000
H	1.34936700	-2.43872400	0.03330700
H	1.97184200	-4.61084300	0.59864400
H	1.35695100	-0.40948100	1.31993200
H	1.15696700	-0.69296900	-2.79269300

$HCONH_2$

C	-0.87675800	0.04343700	0.02954900
O	0.17636800	0.02436800	-0.55824700
H	-1.20764800	-0.77837400	0.69270500
N	-1.78260300	1.04441900	-0.03397500
H	-1.59046600	1.84664700	-0.60865200
H	-2.64319700	1.00078300	0.47847700

$Cp_2ZrHCl{\cdot}HCONH_2$---TS

Zr	-0.11400500	0.00764100	-0.30071000
C	-0.17923000	2.27461800	-1.42178300
C	-1.18283700	1.49089700	-2.03245500
C	-0.54792600	2.48276600	-0.07979200
H	-1.18035600	1.15355600	-3.05713600
C	-2.19077700	1.25143400	-1.07141800
H	0.02153400	3.00552500	0.67318500
C	-1.79701500	1.85276100	0.13346300
H	-3.09911500	0.69047300	-1.22938600
H	-2.32518600	1.81012700	1.07100500
C	-1.17637900	-1.69021400	-1.79944300
C	0.19680700	-1.99004300	-1.82541400
C	-1.65825400	-1.94039800	-0.48943700
H	0.84633600	-1.91428600	-2.68166300
C	0.56567100	-2.43346800	-0.53065100
H	-2.67261500	-1.81564300	-0.14348000
C	-0.58126000	-2.42486600	0.27882200
H	1.55676100	-2.72302200	-0.21485000
H	-0.61726000	-2.66834100	1.32722700
Cl	-0.43975900	-0.00758800	2.22261800
H	0.71592200	2.63226400	-1.90503900
H	-1.76171000	-1.34122700	-2.63535600
O	1.95393700	0.30542000	0.62845100
C	2.78951400	0.43082700	-0.28316300
H	3.14490300	-0.41843100	-0.87481600
H	1.22665100	0.23681000	-1.60675200
N	3.47555200	1.55753200	-0.47337900
H	3.21289400	2.38354400	0.03775300
H	4.15697600	1.63014300	-1.20621200

$Cp_2Zr{=}NH$

Zr	-0.25889200	-2.36609400	-0.52295800
C	-0.07989900	-0.80975900	1.46825700
C	0.33477300	-0.01055400	0.37178500
C	-1.44738700	-1.08370900	1.30906800
H	1.32980000	0.38231700	0.21534100
C	-0.78882500	0.23980700	-0.43885600
H	-2.05158200	-1.68612300	1.96938200
C	-1.88212800	-0.45302900	0.11416900
H	-0.79668800	0.81188200	-1.35348400
H	-2.89084300	-0.46115800	-0.27472300
C	0.54489600	-1.59927100	-2.88955300
C	1.19196700	-2.82337300	-2.56745800
C	-0.82398500	-1.85881600	-3.02587900
H	2.25288500	-2.96083800	-2.41267600
C	0.22020000	-3.84125300	-2.54640800
H	-1.59128600	-1.13579400	-3.25824400
C	-1.03182400	-3.24427700	-2.78691900
H	0.39299600	-4.87764000	-2.30795600
H	-1.97954700	-3.76232200	-2.83114900
H	0.54634500	-1.16706800	2.27069400
H	1.02684500	-0.63928700	-2.99862800
N	-0.06053400	-3.85591000	0.51650400
H	0.05565100	-4.70035100	1.05911300

CH_4

C	-1.45890800	1.38356200	0.00000000
H	-1.09596000	0.35696600	0.00000000
H	-1.09594200	1.89685100	0.88905200
H	-1.09594200	1.89685100	-0.88905200
H	-2.54776800	1.38357600	0.00000000

$Cp_2Zr{=}NH{\cdot}CH_4$---RC

Zr	-0.00647500	0.21532700	0.32455700
C	-1.70622300	-0.82006400	-1.41591600
C	-1.57292300	-1.74054800	-0.36663100
C	-2.29926200	0.35270300	-0.88442000
H	-1.15522600	-2.73316700	-0.43968500
C	-2.08732200	-1.14418500	0.81390000
H	-2.55175400	1.24236300	-1.44321500
C	-2.56174300	0.13874200	0.48082800
H	-2.13435800	-1.60120600	1.79085200
H	-2.98726400	0.85243100	1.16714100
C	1.71249200	-1.68603600	0.29803200
C	1.57921000	-1.40204000	-1.08185600
C	2.33136300	-0.57564900	0.91774900
H	1.14665400	-2.05399500	-1.82466400
C	2.04341900	-0.09969900	-1.29781800
H	2.56729100	-0.48328000	1.96533300
C	2.51134000	0.41585100	-0.05709800
H	2.07369200	0.41365200	-2.24839400
H	2.94157900	1.39207000	0.10812700
C	0.07958700	2.75680200	-1.08554700
H	-0.76723100	3.39943700	-1.31694000
H	1.01778300	3.25552900	-1.31853100
H	-1.40034800	-0.96955100	-2.44058600
H	1.45025700	-2.61506300	0.78342600
N	-0.02232000	1.11810500	1.91924900
H	-0.06206400	1.56098300	2.82638700
H	0.05988100	2.56731400	0.00250700
H	0.00355700	1.86233700	-1.71161400

$Cp_2Zr{=}NH{\cdot}CH_4$---TS

Zr	-1.13502400	-2.08507400	-0.91666600
C	0.43683700	-0.81580400	0.74716100
C	0.06949100	0.11892200	-0.23003800
C	-0.73476000	-1.18141200	1.45939900
H	0.73107700	0.59204900	-0.93887900
C	-1.33029100	0.32050700	-0.14132500
H	-0.78123200	-1.87707300	2.28352500
C	-1.81517300	-0.45856300	0.92945900
H	-1.91731100	0.98589300	-0.75732300
H	-2.84501100	-0.53757400	1.23688700
C	0.14790100	-1.47977600	-3.06105500
C	1.10752600	-2.16245700	-2.28532600
C	-0.85869100	-2.40548900	-3.42808000
H	1.99761500	-1.73316200	-1.85201700
C	0.67008200	-3.48974500	-2.13068000
H	-1.73639500	-2.18869900	-4.01685600
C	-0.53868300	-3.64292500	-2.85231600
H	1.18115800	-4.26710400	-1.58178600
H	-1.13119000	-4.54212100	-2.91647800
C	-1.23105800	-4.17148500	0.45176400
H	-1.79771600	-4.25548900	1.38072400
H	-1.26487400	-5.12531300	-0.07592600
H	1.43285300	-1.19116200	0.93000200
H	0.19277600	-0.44375500	-3.36281600
N	-2.95607000	-2.55710900	-1.03229300
H	-3.91857000	-2.85854200	-1.04501600
H	-2.24045100	-3.48490300	-0.23834200
H	-0.19109100	-3.99542000	0.73926000