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Using Single Complex to Predict the Reaction Energy Profile: A Case Study of Pd/Ni Catalyzed Ethylene Polymerization

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Hyper Parameters:

The hyper parameters were optimized via grid search with the following values:

KRR-poly:

degree in [1, 2, 3, 4]

coef0 in [0, 1, 3, 10, 30, 100, 300, 1000]

alpha = 0.001

gamma in [0.001, 0.003, 0.01, 0.03, 0.1, 0.3, 1, 3, 10]

KRR-rbf:

alpha in [0.000001, 0.00001, 0.0001, 0.001, 0.01, 0.1, 1, 10]

gamma in [0.001, 0.003, 0.01, 0.03, 0.1, 0.3, 1, 3, 10]

SVR-poly:

degree in [1, 2, 3, 4]

coef0 in [0, 1, 3, 10, 30, 100, 300, 1000]

gamma in [0.001, 0.003, 0.01, 0.03, 0.1, 0.3, 1, 3, 10]

SVR-rbf:

gamma in [0.001, 0.003, 0.01, 0.03, 0.1, 0.3, 1, 3, 10]

ANN:

layers in [0, 1, 2, 43, 4, 5]

size in [10, 20, 30, 40, 50, 60, 70, 80, 90]

activation function in [‘identity’, ‘logistic’, ‘relu’, ‘tanh’]

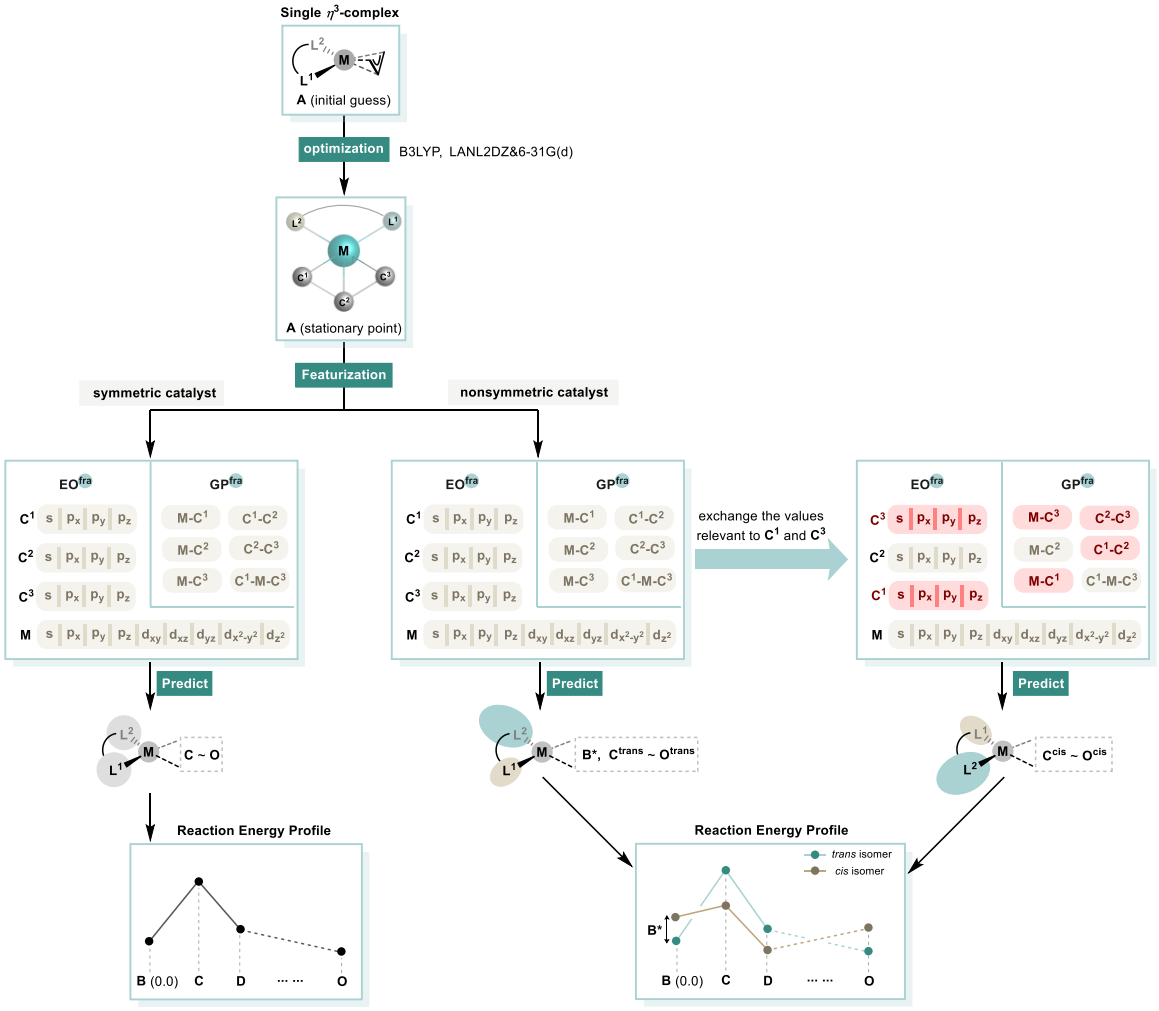
Table S1. Optimal hyper parameters via grid search.

Feature Set	LR	KRR-poly	KRR-rbf	SVR-linear	SVR-poly	SVR-rbf	ANN
EO^{fra}	—	degree=3 coef0=1 alpha=0.001 gamma=0.003	alpha=0.001 gamma=0.003	—	degree=3 coef0=10 gamma=0.03	gamma=0.03	layers=1 size=80 act=logistic
GP^{fra}	—	degree=4 coef0=1 alpha=0.001 gamma=0.3	alpha=0.00001 gamma=0.1	—	degree=4 coef0=10 gamma=0.3	gamma=1	layers=1 size=30 act=logistic
EO^{fra} + GP^{fra}	—	degree=2 coef0=3 alpha=0.001 gamma=0.003	alpha=0.001 gamma=0.003	—	degree=3 coef0=30 gamma=0.01	gamma=0.03	layers=1 size=90 act=logistic

Table S2. Values of MAE on validation set for 7 regressors and 3 feature sets.

Feature Set	LR	KRR-poly	KRR-rbf	SVR-linear	SVR-poly	SVR-rbf	ANN
EO^{fra}	1.0	0.8	0.8	1.1	0.9	2.5	0.8
GP^{fra}	1.2	0.7	0.7	1.3	0.7	1.4	0.8
EO^{fra} + GP^{fra}	0.7	0.5	0.5	0.7	0.5	1.3	0.6

a. The unit of the energy data is kcal/mol.



Scheme S1. Workflow of "using single complex to predict the reaction energy profile".

Table S3. SVR-poly model predicted and experimental energy values on testing samples.

ancillary ligand	metal	reaction process	experimental value	prediction - realistic[b]	prediction - simplified[b]	ref
α-diimine	Pd	C – D	18.0	18.4 (18.2)	19.5 (18.2)	2
α-diimine	Pd	B – F	7.2	2.7 (7.2)	4.8 (7.0)	3
α-diimine	Ni	C – D	13.5	13.0 (11.9)	12.9 (13.2)	1
DIPP	Pd	C – D	16.5	15.3 (17.6)	16.9 (17.6)	4
DIPP	Pd	B – F	10.3	13.6 (9.1)	10.8 (8.6)	4
DPPP	Pd	C – D	16.6	18.8 (18.1)	16.9 (17.6)	4
DPPP	Ni	C – D	12.7	34.8 (14.5)	12.8 (13.5)	4
PO	Pd	$C^{trans} – D^{cis}$	19.2	21.4 (19.7)	19.7 (19.9)	5

a. The unit of the energy data is kcal/mol.

b. The values in brackets are DFT calculated energy data, and the average error between realistic and simplified catalysts is 0.5 kcal/mol.

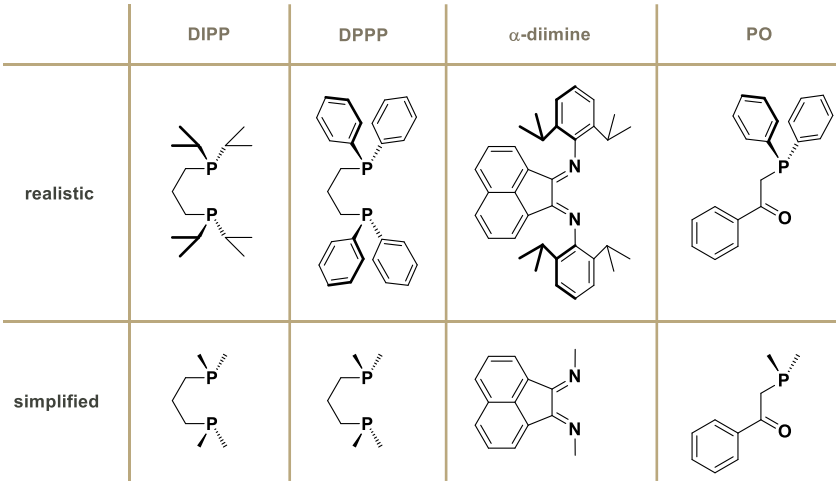


Figure S1. Simplification of ancillary ligands.

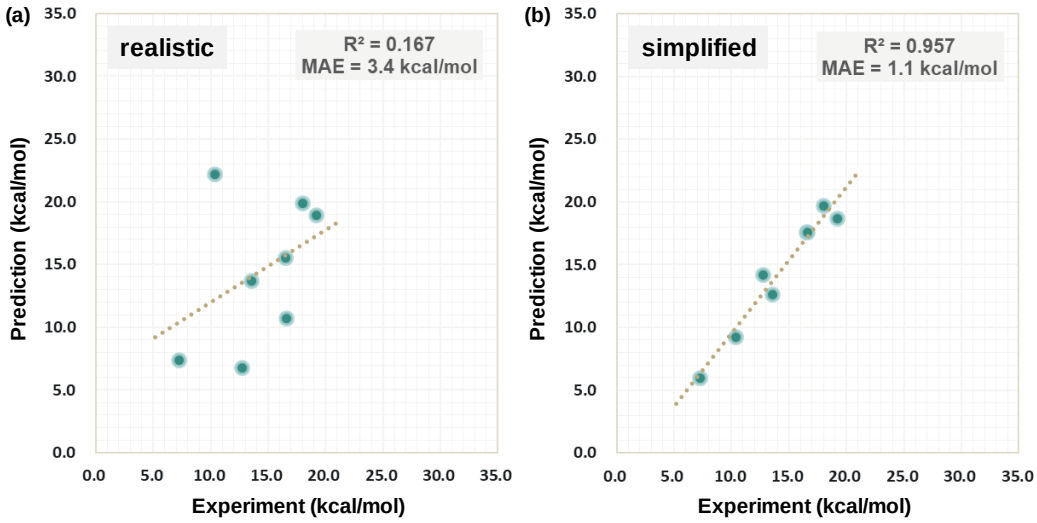


Figure S2. Linear correlation of LR model predicted and experimental energy values for realistic complexes (a) and simplified complexes (b).

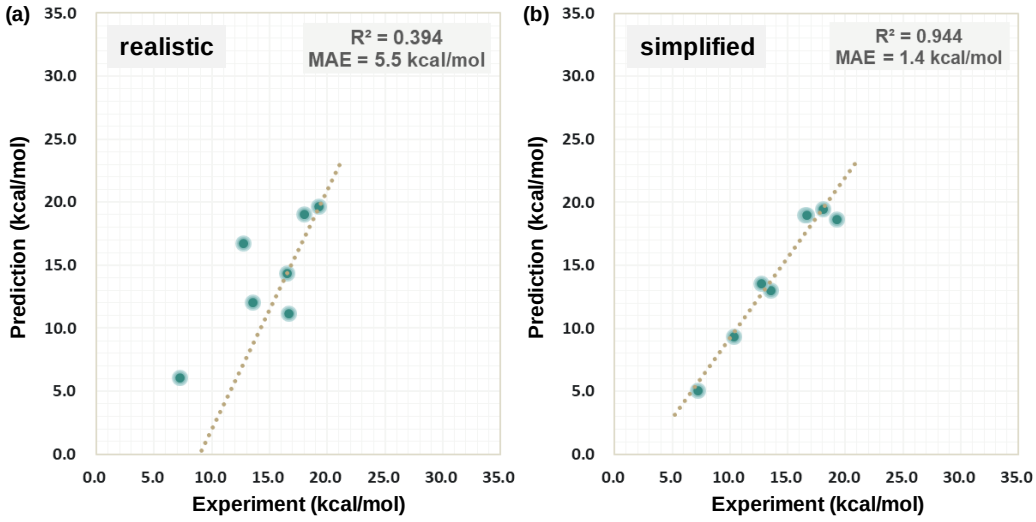


Figure S3. Linear correlation of KRR-poly model predicted and experimental energy values for realistic complexes (a) and simplified complexes (b).

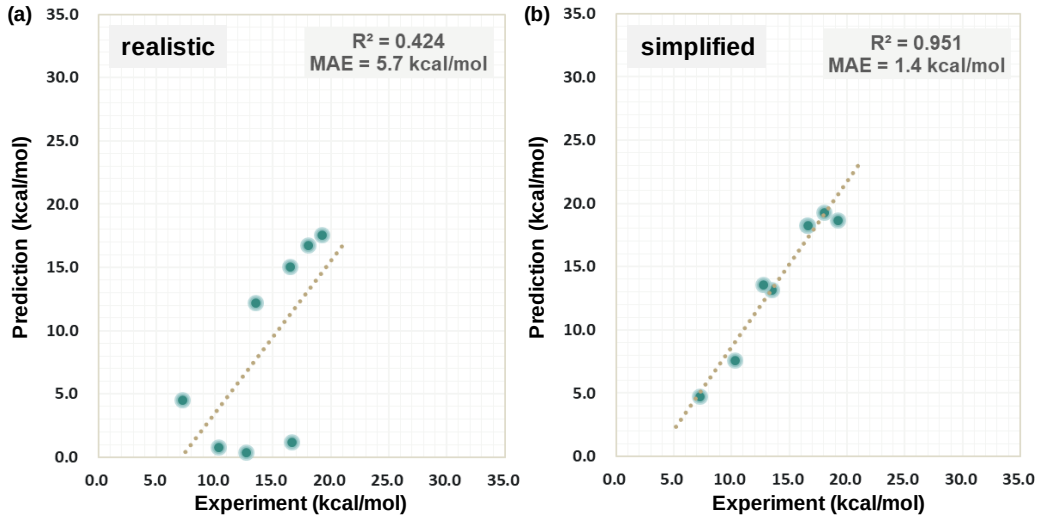


Figure S4. Linear correlation of KRR-rbf model predicted and experimental energy values for realistic complexes (a) and simplified complexes (b).

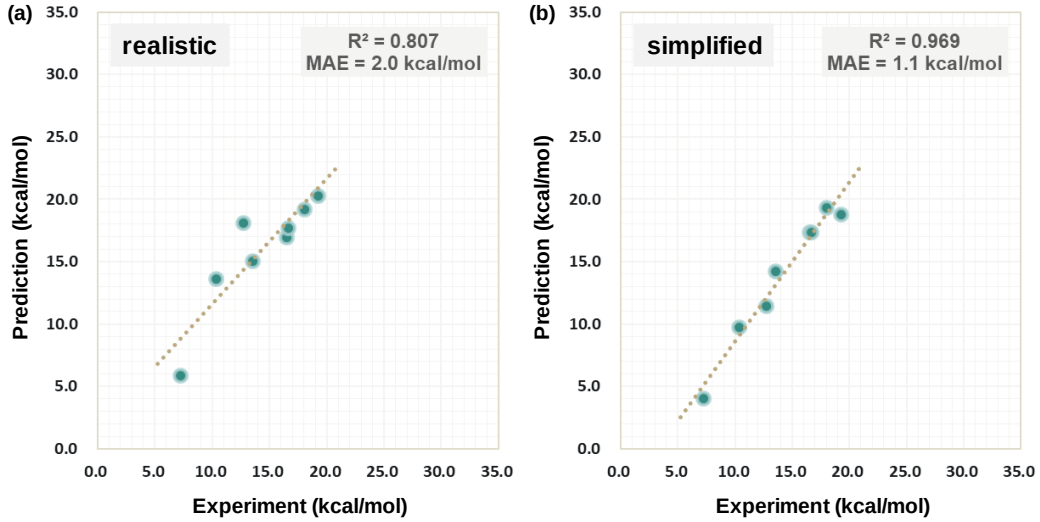


Figure S5. Linear correlation of ANN model predicted and experimental energy values for realistic complexes (a) and simplified complexes (b).

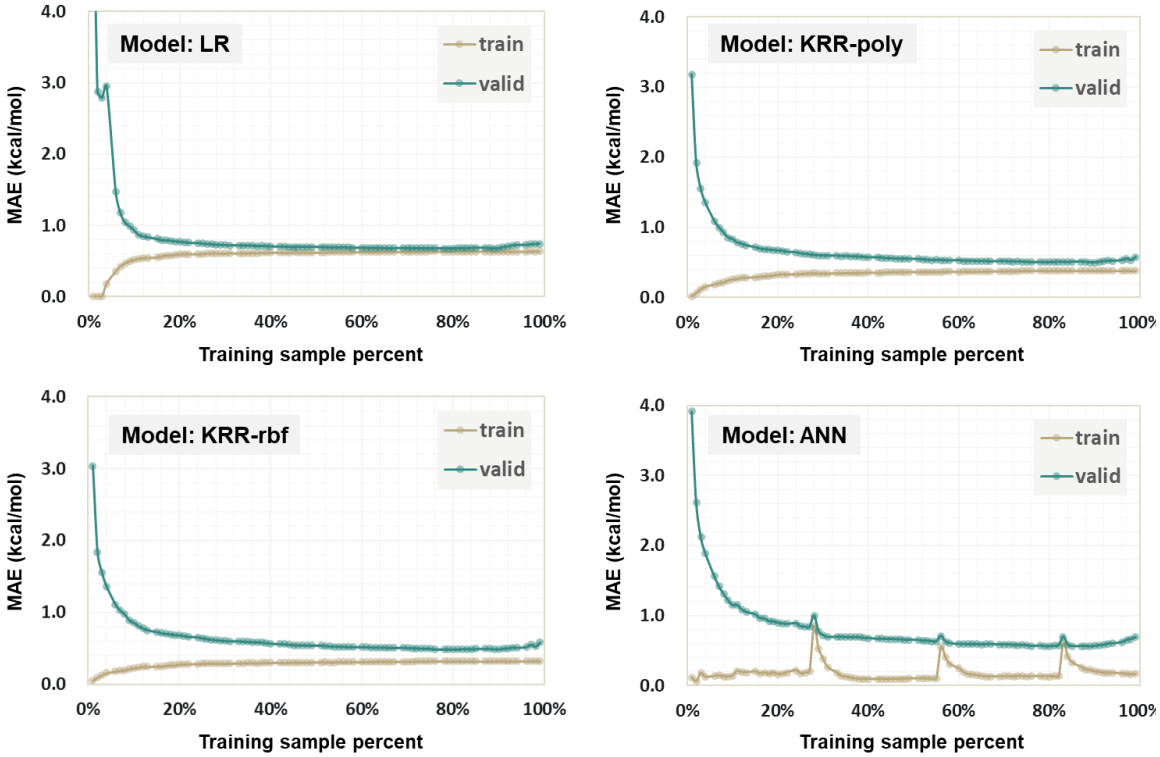


Figure S6. Performance of LR, KRR-poly, KRR-rbf and ANN regressors with different training sample size.

Data analysis

The energy barrier of ethylene insertion (property1) and the energy difference between ethylene insertion and β-H elimination (property2) were considered in catalyst screening (Figure S7a). The catalysts with low values of both property1 and property2 may result in continuous and rapid insertion of ethylene to give the linear polymer. Based on this target, we have screened the promising catalysts with from the training samples, as shown in the red cycle in Figure S7b and their structures and properties were given in Figure S7c. However, it is important to note that the ligation atoms of the screened catalysts are very weak σ-donor (F and O). There may be a risk of decomposition of the unstable catalysts while experimentally validating.

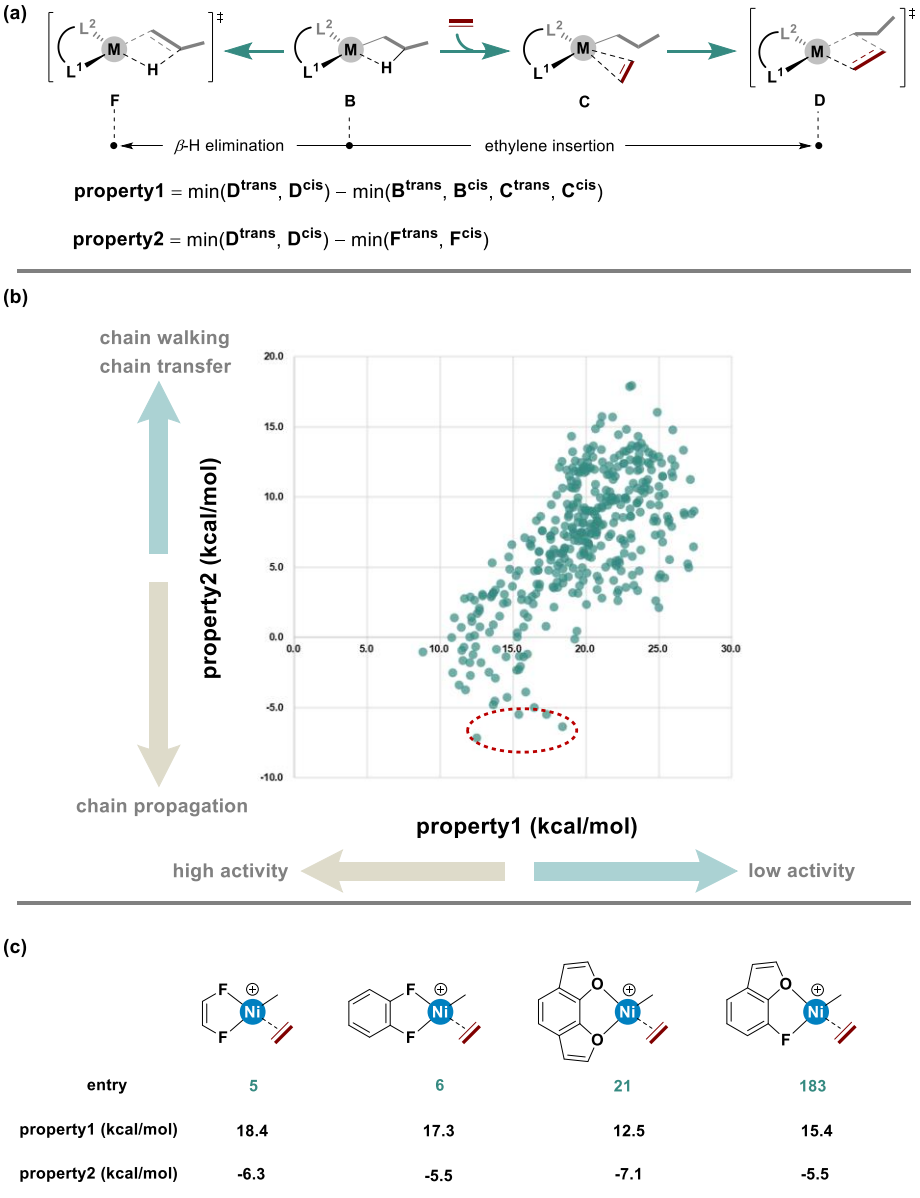


Figure S7. (a) Target properties to be studied. (b) Training samples distribution basing on property1 and property2, the points in red cycle are the screened catalysts. (c) Structures and properties of screened catalysts.

Reference

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