Supplementary data for article:

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Supporting Information

Stacking Interactions of Ni(acac) Chelates with Benzene: Calculated Interaction Energies

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Techniques of local CCSD(T) calculations

There are five categories in the local CCSD(T) (LCCSD(T)) calculation. Strong pairs are dealt with by LCCSD(T); close pairs are by LMP2, but included in LCCSD and (T) residuals; weak pairs are by LMP2; distant pairs are by LMP2 with multipole approximations; very distant pairs are neglected. The certain criteria are based on the distances and kept the same for all the calculations. When calculating the interaction energy, the pairs from two molecules are automatically detected and included in the strong pair category. In our case, close pairs are included in the strong pair category. The number of pairs of each category should be kept consistent.

Table S1. Number of pairs of each category in the LCCSD(T) calculations

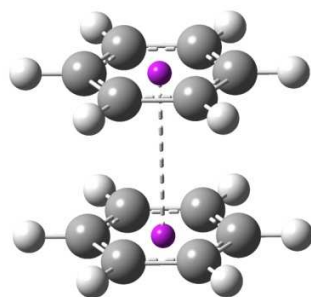| Category	[Ni($acac$)$_2$]-Benzene	[Ni($acac$)$_2$]	Benzene	Dimer of Benzene	Benzene
Strong	1058	302	96	417	96
Weak	466	442	24	48	24
Distant	228	228	0	0	0
Very Distant	18	18	0	0	0

Data in Table S1 show the number of pairs of each category in the benzene dimer and [Ni(acac)$_2$]-Benzene cases. Keep in mind the number of intermolecular pairs are 660 and 225 for [Ni(acac)$_2$]-Benzene and benzene dimer, respectively. Those numbers are consistent when counting the electrons of each molecule. It should also be mentioned density fitting technique is used throughout, and the fitting basis is AVTZ.

CCSD(T) and LCCSD(T) study on benzene dimer in sandwich conformation

CCSD(T) with larger basis set is the most accurate method to deal with the benzene dimer, and is thus taken as a benchmark. In Figure S1 the sandwich configuration of the benzene dimer is presented. The distance between the two molecules varies from 3.8 to 4.2 Å. The calculated interaction energies (kcal/mol) are collected in the Table S2. CP effect is less important for LCCSD(T) than for CCSD(T), and thus is negligible. The optimal distance is 4.0 Å at the CCSD(T) level, and 4.1 Å at the LCCSD(T) level, but the potential energy surface is quite flat around this region. The LCCSD(T) result agrees well with the reference data (e.g. -1.56 kcal/mol at the CCSD(T)/AVTZ*[S1] and -1.31 kcal/mol at the CCSD(T)/AVDZ*[S1] and estd. -1.66 kcal/mol at the CBS CCSD(T)[S2]). The failure of CCSD(T)/def2-TZVP is possibly due to the removal of the most diffuse functions compared with AVTZ (aug-cc-PVTZ).This, on the other hand, shows the advantage of the local correlation method: less dependence of the basis sets.

Table S2. Comparison between CCSD(T) and LCCSD(T) for benzene dimer in sandwich conformation. Energies are given in kcal/mol. All calculations were done with def2-TZVP basis set.

| Distance (Å)	CCSD(T)	CCSD(T) CP	LCCSD(T)	LCCSD(T) CP
3.8	-1.87	-0.88	-1.26	-1.15
3.9	-1.88	-1.01	-1.43	-1.32
4.0	-1.82	-1.06	-1.50	-1.40
4.1	-1.70	-1.04	-1.50	-1.41
4.2	-	-	-1.48	-1.39

Figure S1. Benzene dimer in sandwich conformation.

LCCSD(T) study on [Ni(acac)$_2$]-Benzene

The representative structure is shown in Figure S2a. The calculated interaction energies (kcal/mol) are collected in the Table S3. DFT calculations show the optimal distance between the two molecules is from 3.15 to 3.20. Because the energies are too close. Local CCSD(T) confirms the binding energy is strongest at the distance 3.30 Å.

Table S3. Binding energies for different normal distances.

Distance (Å)	LCCSD(T)	LCCSD(T) CP
3.20	-2.81	-1.79
3.25	-3.08	-2.14
3.30	-4.10	-3.24
3.35	-3.65	-2.86

a.   b.
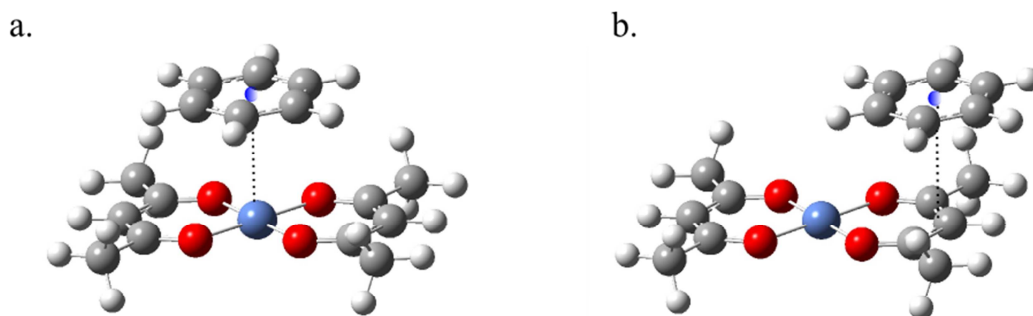
Figure S2. [Ni(*acac*)$_2$] – benzene system in geometry with *offset* a) r = 0.0 Å b) r = 3.0 Å.

DFT-D study on [Ni(acac)$_2$]-Benzene

Table S4. Calculated interaction energies for [Ni(*acac*)$_2$] with benzene in kcal/mol. All calculations were done with def2-TZVP basis set.

Theory level	Geometry with *offset* r = 0.0 Å (Figure 2a)		Geometry with *offset* r = 3.0 Å (Figure 2b)	
	Without CP	**With CP**	**Without CP**	**With CP**
LCCSD(T)	-3.83	-3.25	-	-
LCCSD(T)[†]	-4.10	-3.24	-	-
SCS-MP2[†]	-6.67	-3.71	-5.46	-3.34
MP2[†]	-8.93	-5.87	-7.43	-5.20
B2PLYP-D[†]	-7.30	-4.94	-5.80	-4.35
B3LYP-D[†]	-7.09	-6.06	-5.70	-5.03
TPSS-D[†]	-7.56	-6.49	-5.96	-5.32
BP86-D[†]	-6.97	-5.88	-5.68	-4.97

[†]Effective core potential was used for nickel atom (SDD).

References

(S1)   Hill, J. G.; Platts, J. A.; Werner, H. J. *Phys. Chem. Chem. Phys.* 2006, **8**, 4072.

(S2)   E. C. Lee, D. Kim, P. Jurecka, P. Tarakeshwar, P. Hobza, K. S. Kim, *J. Phys. Chem. A,* 2007, **111**, 3446.