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# Binding energy of $d^{10}$ transition metals to alkenes by wave function theory and density functional theory☆

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ABSTRACT

The structures of $Pd(PH_3)_2$ and $Pt(PH_3)_2$ complexes with ethene and conjugated $C_nH_{n+2}$ systems ($n$ = 4, 6, 8, and 10) were studied. Their binding energies were calculated using both wave function theory (WFT) and density functional theory (DFT). Previously it was reported that the binding energy of the alkene to the transition metal does not depend strongly on the size of the conjugated $C_nH_{n+2}$ ligand, but that DFT methods systematically underestimate the binding energy more and more significantly as the size of the conjugated system is increased. Our results show that recently developed density functionals predict the binding energy for these systems much more accurately. New benchmark calculations carried out by the coupled cluster method based on Brueckner orbitals with double excitations and a quasiperturbative treatment of connected triple excitations (BCCD(T)) with a very large basis set agree even better with the DFT predictions than do the previous best estimates. The mean unsigned error in absolute and relative binding energies of the alkene ligands to $Pd(PH_3)_2$ is 2.5 kcal/mol for the ωB97 and M06 density functionals and 2.9 kcal/mol for the M06-L functional. Adding molecular mechanical damped dispersion yields even smaller mean unsigned errors: 1.3 kcal/mol for the M06-D functional, 1.5 kcal/mol for M06-L-D, and 1.8 kcal/mol for B97-D and ωB97X-D. The new functionals also lead to improved accuracy for the analogous Pt complexes. These results show that recently developed density functionals may be very useful for studying catalytic systems involving Pd $d^{10}$ centers and alkenes.



## 1. Introduction

Palladium interactions with alkenes and conjugated π systems are very important in a number of catalytic contexts [1–13]. Although density functional theory (DFT) has been very useful for understanding and predicting transition metal chemistry [14], Ikeda et al. [15] concluded that DFT significantly underestimates the binding energies of Pd and Pt $d^{10}$ centers to ethene and conjugated π systems with 2–5 double bonds, with the errors increasing in magnitude as the ligand becomes larger. DFT would be formally exact if one were able to use the exact density functional [16], but the exact functional is not available so errors occur due to the use of approximate functionals. For $Pt(PH_3)_2C_nH_{n+2}$, Ikeda et al. tested eight approximate functionals against high-level wave function theory (WFT), which they assumed to be accurate, and they found deviations in the predicted bond strengths of 8–19 kcal/mol for $n$ = 2 increasing to 9–26 kcal/mol for $n$ = 10. For the widely used BP86 [17,18] and B3LYP [17,19–21] functionals, the deviations increased from 0.4–8 kcal/mol for $n$ = 2 to 15–22 kcal/mol for $n$ = 10. All tested DFT calculations predicted that the binding energy decreases by 11–17 kcal/mol as $n$ increases from 2 to 10, but the most accurate WFT prediction decreased by only 1 kcal/mol. Similar results were found by comparing WFT calculations to results obtained with two approximate functionals for $Pd(PH_3)_2C_nH_{n+2}$. Primarily based on the incorrect prediction of the trend with $n$, Ikeda et al. concluded that the failure of their DFT calculations is not due to overestimating charge transfer or to excessive delocalization of charge on the conjugated π systems but is due in part to underestimation of dispersion interactions and partly due to the underestimation of correlation energy and polarization energy caused by the use of a single Slater determinant representation of the electron density. They concluded that it is necessary to use a multiconfigurational treatment to attain good accuracy. This is a very serious issue because, although there are some attempts to formulate DFT in a multiconfigurational framework [22–26], retention of the formalism based on a single Slater determinant [16] is computationally appealing, and this formalism has accounted for most of the success of DFT. We therefore decided to re-examine this problem with more accurate density functional approximations, while retaining the framework of a single Slater determinant. In re-examining the

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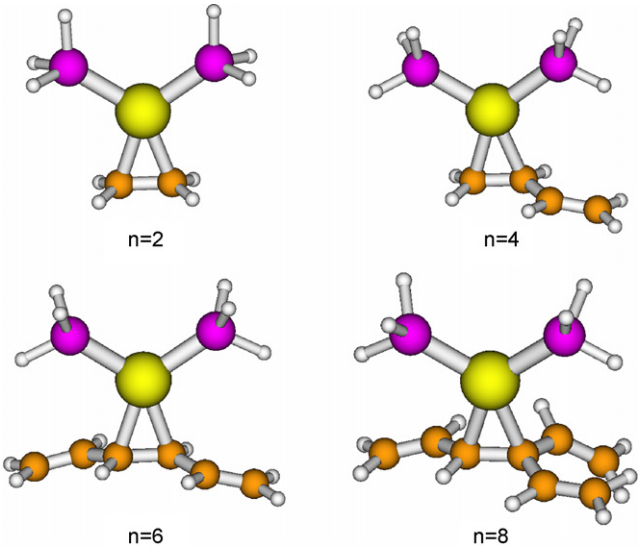


**Fig. 1.** Structures of Pd and Pt complexes for $n = 2$–8.

problem, we confirm that the trends are similar for the Pd complexes and the Pt complexes and then we focus mainly on the Pd complexes.

## 2. Methods

All structures, in particular $Tr(PH_3)_2$ where Tr = Pd or Pt, $C_nH_{n+2}$ where $n = 2$, 4, 6, 8, and 10, and $Tr(PH_3)_2C_nH_{n+2}$, were optimized. The initial structures for the optimization of the complexes were taken from Ikeda et al. [15] The $Tr(PH_3)_2$ and $C_nH_{n+2}$ structures were optimized within the symmetry groups $D_{3h}$, $D_{2h}$, $C_{2h}$, $C_{2h}$, $C_1$, and $D_2$ for $Tr(PH_3)_2$, $C_2H_4$, $C_4H_6$, $C_6H_8$, $C_8H_{10}$, and $C_{10}H_{12}$, respectively. The $Tr(PH_3)_2C_nH_{n+2}$ complexes have $C_{2v}$, $C_1$, $C_2$, $C_1$, and $C_2$ symmetry for $n = 2, 4, \ldots, 10$, respectively. The complexes for $n = 2$–8 are shown in Fig. 1. For $n = 10$ our calculations revealed two possible conformations (Fig. 2). One of them, denoted 10a, corresponds to the conformation from Ref. [15]. The second one, denoted 10b, has a less planar conjugated system $C_nH_{n+2}$ and it was not mentioned in Ref. [15]. However, the 10b complex has an energy of about 2 kcal/mol lower than 10a. To make it possible to compare our results for $n = 10$ with the previous results, we calculate binding energies for both conformations.

As previously [15], we define the binding energy as the difference between the energy of $Tr(PH_3)_2C_nH_{n+2}$ and the sum of the energies of $Tr(PH_3)_2$ and $C_nH_{n+2}$ (at optimized geometries). All binding energies are zero-point exclusive because the focus here is on electronic effects.

In all basis sets Pd and Pt atoms have 18 active electrons, and the core electrons (28 for Pd and 60 for Pt) are replaced by a relativistic effective core potential (RECP). In all cases we used spherical-harmonic subshells for d, f, and g basis functions.

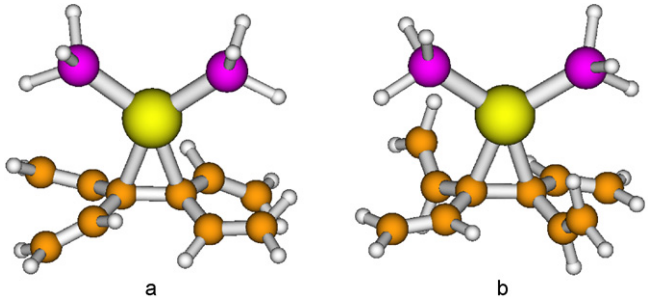


**Fig. 2.** Two possible conformations for $n = 10$.

**Table 1**
Density functionals used in this work.

| | |
|---|---|
| Generalized gradient approximations (GGAs) | |
| BP86 [17,18] | BLYP [17,19] |
| Meta-GGAs | |
| M06-L [43–45] | |
| Hybrid GGAs | |
| B3PW91 [17,19,20] | B3LYP [17,19–21] |
| PBE0 [46,47] | B1LYP [17,19,48] |
| B98 [49] | B97-1 [50] |
| B97-2 [51] | |
| Long-range-corrected hybrid GGAs | |
| ωB97 [52] | ωB97X [52] |
| Hybrid meta-GGAs | |
| M05 [53] | M05-2X [45,54] |
| M06 [44,45] | M06-2X [44,45] |
| DFT + molecular mechanical damped dispersion | |
| B97-D [55] | ωB97X-D [56] |
| M06-L-D [43,57] | M06-D [44,57] |

We used four basis sets for DFT calculations, and they are numbered in order of increasing quality. BS1 denotes the LANL2DZ RECP and basis set [27] (with the 341/321/31 contraction scheme for Pd and 331/321/21 for Pt) for the transition metal and 6-31G(d,p) for P [28], C, and H [29,30]. This basis set is similar to BS1 in Ref. [15], where f functions were added for the transition metals.

BS2 denotes the uncontracted LANL2DZ basis with an f polarization subshell from Ehlers et al. [31] for the transition metal (denoted as LANL08(f) in Ref. [32]) and 6-311G(d,p) for P (the 6-311 basis set for P is from McLean and Chandler [33] as modified in the *Gaussian* program [34] with a d subshell from Francl et al. [28]) and for C and H (the 6-311(d,p) basis set for these elements is from Krishnan et al. [35]).

BS3 denotes the MWB28 RECP and basis set for Pd and the MWB60 RECP and basis set for Pt from the Stuttgart–Dresden–Dunning (SDD) family [36] with 2fg polarization functions for the transition metal [37] (with a 311111/22111/411/11/1 contraction for both Pd and Pt) and cc-pVTZ for P [38], C, and H [39].

BS4 denotes the def2-TZVPP RECP and basis set (with a 211111/4111/411/11/1 contraction for Pd and 311111/4111/411/11/1 for Pt) [40] for the transition metal and the MG3S basis set [41,42] for P, C, and H. Note that the RECP of def2-TZVPP is taken to be the same as the SDD one, but the basis sets are different.

The tested density functionals [17–21,43–57] are listed in Table 1, where they are grouped according to their type. The final type included in the table involves adding damped dispersion terms based on atomic parameters; these are analytic functions added post-SCF, so these calculations may be considered to be a combination of DFT with molecular mechanics. The damped dispersion is only parameterized [55] for H through Xe, so these methods are available for Pd complexes but not for Pt complexes.

The integration grid for density functional calculations is a pruned (99, 590) grid [34] which is denoted as "ultrafine" in the *Gaussian* program. DFT calculations with 13 functionals were performed with consistently optimized geometries and with M06-BS3 geometries; additional calculations were performed to compare electronic energies at fixed geometries, and for this we used geometries optimized by M06/BS3. All optimized structures were confirmed to be local minima by frequency analysis except for a few cases; in those cases we nevertheless accepted the located stationary point as relevant because our goal was to compare energies for structures similar to the initial structures specified in the first paragraph.

**Table 2**
WFT calculations of the binding energy (kcal/mol) $Pd(PH_3)_2C_nH_{n+2}$ ($n$ = 2, 6, 10) for various basis sets[a].

| $n$ | NC | MP2 | MP3 | MP4(DQ) | MP4(SDQ) | MP4 | CCSD | BCCD | CCSD(T) | BCCD(T) |
|---|---|---|---|---|---|---|---|---|---|---|
| BS3 | | | | | | | | | | |
| 2 | 195 | 33.7 | 15.9 | 21.5 | 23.6 | 33.1 | 18.8 | 18.6 | 23.2 | 23.4 |
| 6 | 291 | 35.6 | 13.5 | 20.6 | 24.2 | 37.3 | 17.8 | 17.5 | 23.4 | 23.8 |
| 10a | 387 | 36.8 | 10.8 | 19.6 | 24.3 | 40.0 | 16.8 | 16.3 | 23.5 | 23.9 |
| 10b | 387 | 41.0 | 14.4 | 23.0 | 27.3 | 42.6 | 20.4 | 19.9 | 27.1 | 27.5 |
| mDZ | | | | | | | | | | |
| 2 | 209 | 32.8 | 15.6 | 21.2 | 23.2 | 32.0 | 18.4 | 28.2 | 22.6 | 22.9 |
| 6 | 321 | 37.3 | 15.6 | 22.8 | 26.3 | 38.9 | 19.9 | 19.5 | 25.5 | 25.8 |
| 10a | 433 | 40.9 | 15.1 | 24.1 | 28.6 | 44.0 | 21.1 | 20.6 | 28.1 | 28.4 |
| 10b | 433 | 45.6 | 19.2 | 27.9 | 32.0 | 47.1 | 25.1 | 24.7 | 32.2 | 32.2 |
| mVTZ | | | | | | | | | | |
| 2 | 436 | 28.3 | 10.8 | 16.4 | 17.7 | 27.2 | 13.5 | 13.4 | 17.8 | 17.9 |
| 6 | 612 | 28.7 | 7.2 | 14.0 | 16.5 | 29.4 | 11.2 | 10.9 | 16.6 | 16.8 |
| 10a | 788 | 27.6 | 2.5 | 10.9 | 14.2 | 29.6 | 8.1 | 7.7 | 14.4 | 14.7 |
| 10b | 788 | 31.4 | 5.7 | 13.9 | 16.9 | 32.0 | 11.2 | 10.9 | 17.6 | 18.0 |
| aug-mVTZ | | | | | | | | | | |
| 2 | 590 | 28.9 | 11.2 | 16.9 | 18.4 | 28.1 | 14.1 | 13.9 | 18.5 | 18.6 |
| 6 | 866 | 29.8 | 8.0 | 14.9 | 17.6 | 30.8 | 12.1 | 11.8 | 17.6 | 17.8 |
| 10a | 1142 | 29.4 | 3.8 | 12.3 | 15.9 | 31.7 | 9.5 | 9.1 | 16.1 | |
| 10b | 1142 | 33.1 | 6.9 | 15.2 | 18.4 | 34.0 | 12.6 | 12.2 | 19.2 | |
| mQZVP | | | | | | | | | | |
| 2 | 583 | 28.3 | 10.6 | 16.4 | 18.0 | 27.6 | 13.5 | 13.3 | 17.8 | 17.8 |
| 6 | 867 | 28.7 | 6.9 | 14.0 | 16.9 | 30.0 | 11.2 | 10.9 | 16.5 | 16.7 |
| 10a | 1151 | 27.9 | 2.4 | 11.1 | 14.9 | 30.5 | 8.2 | 7.8 | 14.6 | 14.7 |
| 10b | 1151 | 31.5 | 5.5 | 13.9 | 17.4 | 32.7 | 11.2 | 10.8 | 17.7 | 17.8 |
| mVQZ | | | | | | | | | | |
| 2 | 696 | 28.1 | 10.4 | 16.0 | 17.5 | 27.2 | 13.2 | 13.1 | 17.6 | 17.6 |
| 6 | 1036 | 28.4 | 6.6 | 13.5 | 16.1 | 29.4 | 10.7 | 10.4 | 16.2 | 16.2 |

[a] $N_C$ denotes number of contracted functions in the molecule. The geometry is calculated by M06/BS3.

DFT calculations were carried out for both Pd and Pt systems, and WFT calculations were also carried out for both systems to improve the best estimates.

Because energies obtained from WFT depend strongly on basis set, we used several additional basis sets for our WFT calculations for Pd complexes. We use the label mDZ to denote the MWB28 basis with 2fg polarization functions [37] for Pd, aug-cc-pVDZ for P [38] and C [39], and cc-pVDZ for H [39]. We use the label mVQZ to denote the MWB28 basis with polarization and augmented functions from Ref. [58] (denoted there as AVQZ) for Pd, and cc-pVQZ for P [38], C, and H [39]. We use the label mVTZ to denote the MWB28 basis with polarization and augmented functions from Ref. [58] for Pd and cc-pVTZ for P, C, and H. We use the label aug-mVTZ to denote the MWB28 basis with polarization and augmented functions from Ref. [58] for Pd, and aug-cc-pVTZ for P [38], C, and H [39]. We use the label mQZVP to denote mVQZ with h functions removed from Pd and with def2-QZVP [59] for P, C, and H but removing g functions from P and C and f functions from H.

In addition to using one-electron basis sets, we also performed some calculations with explicitly correlated basis functions by using the CCSD(T)-F12 method of Knizia et al. [60]. These calculations include both configuration state functions formed from one-electron basis functions and configuration state functions containing the correlating factor

$$F = \exp(-\beta r_{12}) \quad (1)$$

where $\beta$ is a parameter and $r_{12}$ is the distance between two electrons. For the one-electron basis in these calculations we used BS3 (for Pd and Pt complexes) and mVQZ for Pd complexes. WFT calculations were also carried out with the def2-QZVPP [59] basis set for Pt and cc-pVQZ for P, C, and H for the Pt complexes with $n$ = 2 and 4. CCSD(T)-F12 calculations also require two auxiliary basis sets for density fitting. For P, C, and H atoms we used density fitting basis sets implemented in MOLPRO for the corresponding orbital bases, in particular cc-pVTZ-mp2fit [61] and cc-pVTZ-jkfit [62] for cc-pVTZ basis sets and cc-pVQZ-mp2fit [61] and cc-pVQZ-jkfit [62] for cc-pVQZ basis sets. For transition metal atoms we used def2-TZVPP-mp2fit [63] and def2-TZVPP-jkfit [64] for BS3 and def2-QZVPP-mp2fit [63] and def2-QZVPP-jkfit [64] for larger basis sets. The last four basis sets were taken from the TURBOMOLE library [65]. Note that the density fitting basis sets are very large, for example, in terms of contracted functions, the largest for Pd is [11s11p9d8f6g3h2i] and the largest for P is [13s11p9d4fgh].

Our WFT calculations are all performed at the geometries optimized by M06/BS3 because, as we shall see in the results section, this DFT method gives the best accuracy of all examined DFT methods that do not involve molecular mechanical corrections. The following WFT methods were used, listed roughly in order of increasing level of completeness and expected reliability: MP2 [66], MP3 [67], MP4DQ [67], MP4SDQ [67], MP4 [67], CCSD [68,69], BCCD [70,71], CCSD(T) [72,73], and BCCD(T) [70].

In order to ascertain the effect of the incompleteness of our basis sets, we checked for basis set superposition error. The usual way of making such a correction is the counterpoise method of Boys and Bernardi [74]; we will call this the Boys–Bernardi counterpoise correction (BBCC). The BBCC vanishes for a complete basis set, but it is known that it often overestimates the correction for finite basis sets [75–83]. Since the basis set limit often lies about midway between the uncorrected result and the result obtained with BBCC, we define a smaller correction to be called the conser-

**Table 3**
CCSD(T)-F12 vs. CCSD(T) for $Pd(PH_3)_2C_nH_{n+2}$ complexes.

| $n$ | CCSD(T)/BS3 | CCSD(T)-F12/BS3 | CCSD(T)/mVQZ | CCSD(T)-F12/mVQZ |
|---|---|---|---|---|
| 2 | 23.2 | 18.0 | 17.6 | 17.7 |
| 6 | 23.4 | 16.8 | 16.2 | 16.2 |
| 10a | 23.5 | 14.5 | | |
| 10b | 27.1 | 17.4 | | |

**Table 4**
Effect of counterpoise corrections on the binding energies in $Pd(PH_3)_2C_nH_{n+2}$ ($n$ = 2, 6, and 10) complexes as calculated with the BS3 basis set[a].

| $n$ | M06 | | | MP4(SDQ) | | | CCSD(T) | | |
|---|---|---|---|---|---|---|---|---|---|
| | None | CCC | BBCC | None | CCC | BBCC | None | CCC | BBCC |
| 2 | 13.4 (0.0) | 13.1 (0.3) | 12.7 (0.7) | 23.6 (0.0) | 19.0 (4.5) | 14.5 (9.1) | 23.2 (0.0) | 18.3 (4.8) | 13.5 (9.7) |
| 6 | 11.5 (0.0) | 11.0 (0.4) | 10.6 (0.9) | 24.3 (0.0) | 18.7 (5.6) | 13.1 (11.1) | | | |
| 10a | 9.1 (0.0) | 8.6 (0.5) | 8.0 (1.1) | 24.3 (0.0) | 17.4 (7.0) | 10.4 (14.0) | | | |
| 10b | 11.5 (0.0) | 10.9 (0.6) | 10.3 (1.1) | 27.3 (0.0) | 19.9 (7.4) | 12.5 (14.7) | | | |

[a] The corrections to binding energies (kcal/mol) are given in parentheses.

**Table 5**
Effect of basis set superposition error on binding energies (kcal/mol) in $Pd(PH_3)_2C_2H_4$ complexes for the CCSD(T) method with different basis sets.

| $n$ | CCSD(T)/BS3 | | | CCSD(T)/mVQZ | | | CCSD(T)-F12/mVQZ | | |
|---|---|---|---|---|---|---|---|---|---|
| | None | CCC | BBCC | None | CCC | BBCC | None | CCC | BBCC |
| Correction | 0 | 4.8 | 9.7 | 0 | 0.6 | 1.1 | 0 | 0.4 | 0.7 |
| Binding energy | 23.2 | 18.3 | 13.5 | 17.6 | 17.0 | 16.5 | 17.7 | 17.3 | 17.0 |

[a]Corrections to binding energies (kcal/mol) are given above the corrected binding energy.

**Table 6**
Binding energies (kcal/mol) for M06-L and B3PW91 functionals for consistently optimized geometries and various basis sets.

| $n$ | M06-L | | | | B3PW91 | | | | Best estimate[a] |
|---|---|---|---|---|---|---|---|---|---|
| | BS1 | BS2 | BS3 | BS4 | BS1 | BS2 | BS3 | BS4 | |
| Pd | | | | | | | | | |
| 2 | 17.0 | 16.8 | 17.1 | 16.5 | 15.4 | 15.7 | 15.9 | 14.8 | 17.6[b] |
| 4 | 15.8 | 16.0 | 15.9 | 15.3 | 12.3 | 13.7 | 13.2 | 12.6 | n.a.[c] |
| 6 | 13.1 | 13.8 | 13.4 | 12.8 | 8.2 | 10.6 | 9.7 | 9.3 | 16.2[b] |
| 8 | 12.3 | 13.4 | 12.8 | 12.2 | 5.2 | 8.8 | 7.5 | 7.3 | n.a. |
| 10a | 9.7 | 11.0 | 10.2 | 9.7 | 0.4 | 2.2 | 3.2 | 3.1 | 14.2[d] |
| 10b | 11.3 | 12.9 | 11.8 | 11.3 | 2.3 | 4.5 | 5.3 | 5.1 | 17.3[d] |
| Pt | | | | | | | | | |
| 2 | 19.7 | 21.3 | 19.0 | 19.2 | 18.4 | 21.4 | 19.2 | 18.9 | 21.7[e]/21.5[f] |
| 4 | 17.0 | 19.1 | 16.6 | 16.8 | 14.4 | 18.5 | 16.0 | 15.8 | 20.8[e]/20.5[f] |
| 6 | 12.6 | 15.3 | 12.6 | 12.8 | 9.1 | 14.3 | 11.6 | 11.4 | 19.0[e] |
| 8 | 10.8 | 13.9 | 11.0 | 11.2 | 5.5 | 11.8 | 8.8 | 8.7 | 18.3[e] |
| 10a | 7.4 | 10.8 | 7.6 | 7.9 | 0.1 | 4.8 | 4.0 | n.f.[g] | n.f.[g] |
| 10b | 10.4 | 14.3 | 10.6 | 10.9 | 3.6 | 8.7 | 7.6 | 7.5 | 20.5[e] |

[a] When two values are given, the best estimate is the second one because it employs a bigger basis set.
[b] BCCD(T)/mVQZ//M06/BS3.
[c] n.a. denotes not available.
[d] $[BCCD(T)/mQZVP]_{n=10} + [BCCD(T)/mVQZ]_{n=6} - [BCCD(T)/mQZVP]_{n=6}$ at M06/BS3 geometries.
[e] CCSD(T)-F12/BS3//M06/BS3.
[f] CCSD(T)-F12/def2-QZVPP(Pt),cc-pVQZ(P,C,H)//M06/BS3.
[g] Not found with M06/BS3 method.

vative counterpoise correction (CCC) that is equal to one half the BBCC.

All DFT calculations were carried out with *Gaussian03* [34], a locally modified version of *Gaussian03* [84], and *Gaussian09* [85]. Partial atomic charges were calculated by the NBO [86] and Hirshfeld [87] methods using *Gaussian09*.

WFT calculations were carried out with MOLPRO [88] and *Gaussian03*. In these calculations, the 1s orbitals of carbon atom and the 1s, 2s, and 2p orbitals of phosphorus atom are treated as frozen cores. All other orbitals (with the exception of the core orbitals of Pd that are substituted by a RECP) are unfrozen. This core option is the default in the *Gaussian* program, but it is not the default in MOLPRO, so we defined frozen core orbitals explicitly in MOLPRO for consistency with *Gaussian* calculations.

## 3. Results and discussion

### 3.1. WFT benchmarks for Pd complexes

Ikeda et al. carried out benchmarks by the CCSD(T) method for Pt complexes with $n$ = 2, 4, and 6 and found good agreement with MP4(SDQ) calculations. Therefore, they used MP4(SDQ) calculations as best estimates for Pt with $n$ = 8, 10 and for Pd with $n$ = 2, 6, and 10. To further convince ourselves that the binding energies and trends in the WFT calculations are reliable, we performed calculations for Pd systems with 9 WFT levels of correlation treatment combined with six basis sets for $n$ = 2 and 6 and with five basis sets for $n$ = 10a and 10b. The results without counterpoise corrections are in Table 2. Ikeda et al.'s best estimates without counterpoise corrections for Pd were 21, 22, and 21 kcal/mol for $n$ = 2, 6, and 10a, whereas our best calculations without counterpoise corrections for these three cases would lead to best estimates of 17.6, 16.2, and 14.2 kcal/mol, respectively. Our finding that the (very expensive) Brueckner-orbital coupled cluster calculations with double excitations and quasiperturbative treatment of connected triple excitations (BCCD(T)) agree well (within 0.1–0.2 kcal/mol) with Hartree–Fock-orbital coupled cluster calculations with single and double excitations and quasiperturbative treatment of connected triple excitations (CCSD(T)) gives added confidence in the reliability of our best estimates. Furthermore, we see that BCCD(T) best estimates agree with fourth-order Møller–Plesset perturbation theory with single, double, and quadruple excitations (MP4(SQD)) within

1 kcal/mol but not with other levels of perturbation theory. The results, however, are slowly convergent with respect to basis set size, and our finding that binding energies calculated without counterpoise corrections are 3–7 kcal/mol lower than those of [15] is mostly a consequence of our using much larger basis sets. Ikeda et al. [15] used their BS1 basis (LANL + f for Pd and Pt and 6-31G(d) for P, C, and H) for optimization; and for single-point energy calculations (DFT and WFT) they used their BS2 basis, which is SDD + 2f (but without g; 311111/22111/411/11 contraction scheme) for Pd and Pt and 6-311G(d) for P, C, and H.

Two further issues can be addressed concerning basis sets. The first is that WFT calculations are more slowly convergent with respect to one-electron basis set than are DFT calculations. However, we can use the CCSD(T)-F12 method [60] to approach the complete basis set (CBS) limit. This is shown in Table 3 where we added correlating basis functions to calculations with two different one-electron basis sets. The comparison of the final two columns of this table reveals that mVQZ basis set practically corresponds to complete basis set. The improvement of the basis set convergence for a smaller basis wet can be seen in the BS3 columns of the table. This table shows a CBS limit of about 17.7 kcal/mol with $n = 2$ and 16.2 kcal/mol with $n = 6$.

The second issue is that WFT calculations are more sensitive to basis set superposition error than DFT calculations, so that binding energies calculated without counterpoise corrections for basis set superposition error might be too high. This is studied in Table 4, which first shows the CCC-corrected and BBCC-corrected results for Pd complexes with $n = 2$, 6, 10a, and 10b for the M06/BS3 and MP4(SDQ)/BS3 levels of theory. As expected, the BBCC corrections are about an order of magnitude larger than for DFT. Table 4 also gives a CCSD(T) calculation for $n = 2$, which shows that counterpoise corrections are about the same size for these two WFT methods. Table 5 gives counterpoise corrections for three different basis sets for CCSD(T), and this table shows that the CCC-corrected results agree within 1.3 kcal/mol, whereas the uncorrected results disagree by up to 5.6 kcal/mol, and the BBCC-corrected results differ by up to 3.5 kcal/mol. This confirms the expectation that BBCC overestimates the correction, whereas the CCC correction is reasonable. Using CCSD(T)-F12, the CCC correction is only 0.4 kcal/mol.

Using Tables 3 and 5, we can try to obtain an improved best estimate for $n = 2$. We begin with 17.6 kcal/mol in Table 2 and raise it to 0.1 kcal/mol to account for basis set incompleteness (as estimated from Table 3) and then lower it by 0.4 kcal/mol to correct for basis set superposition error (as estimated from Table 5), yielding 17.3 kcal/mol. We see that the corrections for basis set incompleteness and basis set superposition error partly cancel and are too small to be significant, so we will ignore these corrections in making our best estimates for Pd. Our best estimates are given in the last column of Table 6.

### 3.2. Basis set dependence of DFT results

First we tested two density functionals: B3PW91, which was the best performing functional in Ref. [15], and M06-L, which was the best functional for transition metals in Ref. [44]. The binding energies obtained with basis sets BS1–BS4 are presented in Table 6.

**Table 7**
Binding energies (kcal/mol) for BS3 for Pt complexes for various functionals with consistently optimized geometries.

| $n$ | M06-L | M06 | M06-2X | M05-2X | B3PW91 | BLYP | B1LYP |
|---|---|---|---|---|---|---|---|
| 2 | 19.0 | 15.5 | 18.0 | 21.1 | 19.2 | 10.2 | 11.0 |
| 4 | 16.6 | 13.9 | 16.4 | 19.6 | 16.0 | 6.7 | 7.7 |
| 6 | 12.6 | 11.2 | 13.8 | 17.0 | 11.6 | 1.8 | 3.4 |
| 8 | 11.0 | 10.2 | 12.3 | 15.6 | 8.8 | −1.1 | 0.6 |
| 10a | 7.6 | n.f.a | 9.2 | 12.3 | 4.0 | −6.1 | n.f.[a] |
| 10b | 10.6 | 11.3 | 13.6 | 17.3 | 7.6 | −3.6 | −1.3 |

[a] Not found.

This table shows that basis sets BS1, BS3, and BS4 give very similar results and that the local M06-L functional gives better performance than the hybrid B3PW91 functional. Since BS3 is slightly smaller than BS4, but still contains g functions on Pd and Pt, we chose it for the rest of the DFT calculations, which will be presented in Sections 3.3 and 3.4. Furthermore, we saw in Section 3.1 that counterpoise corrections for DFT are very small (0.3–0.6 kcal/mol) for DFT, so we will ignore them in what follows.

### 3.3. Comparison of Pd and Pt complexes

Ikeda et al. based their best estimates for Pt on MP4(SDQ) calculations without counterpoise corrections. They obtained 22.2, 22.5, 22.1, 22.6, and 21.1 for $n = 2$, 4, 6, 8, and 10a, respectively. We obtained improved best estimates for Pt by employing CCSD(T)-F12/BS3.

Our results for Pt complexes are shown in the last column of the lower half of Table 6. As for Pd, we obtain best estimates that are significantly lower for $n = 8$ than for $n = 2$, whereas they also estimated almost the same value for $n = 2$ and 8.

Tables 7 and 8 compare binding energies for Pt and Pd complexes, respectively, calculated for different functionals with basis set BS3. Tables 6–8 show very similar trends in all respects for Pd and Pt complexes. Therefore we will examine only the Pd complexes in the rest of this article.

### 3.4. Detailed study of Pd complexes

Unlike paper [15], where all binding energies for different functionals were calculated at the same geometries obtained from B3PW91 calculations, all data in Tables 6–8 correspond to optimized geometries for each functional, and we use the larger BS3 basis set. Note that some of the DFT binding energies in Tables 7 and 8 are negative, but in all these cases the binding energies correspond to local minima on the potential energy surface, that is, the structures have no imaginary frequencies. Some geometrical parameters of Pd complexes from Table 8 are given in Table 9. We see that for large $n$ ($n = 6$–10), B97-D, surprisingly, leads to the largest Pd–alkene distances, and ωB97 leads to the smallest, with a variation of 0.09–0.12 Å. The ωB97 and ωB97X-D functionals lead to the smallest variation in Pd–alkene distance over the set of four structures with $n = 2$–10, only 0.03 Å; and B97-2 gives by far the largest variation, 0.15 Å. The various functionals do not predict large differences in the central C=C bond length. The coordi-

**Table 8**
Binding energies (kcal/mol) for Pd complexes for various functionals with BS3 and consistently optimized geometries.

| $n$ | M06-L | M06 | M06-2X | M05-2X | B3PW91 | BLYP | B1LYP | B97-1 | B97-2 | B97-D | ωB97 | ωB97X | ωB97X-D |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2 | 17.1 | 13.4 | 10.7 | 14.8 | 15.6 | 9.7 | 9.0 | 15.1 | 13.0 | 15.4 | 19.7 | 16.2 | 16.4 |
| 4 | 15.9 | 12.9 | 10.1 | 14.0 | 13.2 | 7.0 | 6.5 | 12.9 | 10.6 | 14.8 | 16.6 | 14.8 | 15.6 |
| 6 | 13.4 | 11.5 | 8.8 | 12.6 | 9.7 | 3.2 | 3.2 | 9.9 | 7.2 | 13.2 | 14.9 | 12.8 | 14.3 |
| 8 | 12.8 | 11.2 | 8.2 | 11.8 | 7.5 | 1.0 | 0.9 | 8.0 | 5.0 | 13.1 | 13.3 | 11.0 | 13.3 |
| 10a | 10.2 | 9.1 | 5.3 | 8.8 | 3.2 | −3.4 | −3.4 | 4.0 | 0.6 | 11.2 | 10.1 | 7.5 | 10.5 |
| 10b | 11.8 | 11.5 | 8.4 | 12.4 | 5.3 | −2.5 | −1.9 | 6.0 | 2.6 | 13.5 | 13.9 | 11.0 | 14.1 |

**Table 9**
Selected geometrical parameters (bond lengths in Å and bond angels in deg) for $Pd(PH_3)_2C_nH_{n+2}$ ($n$ = 2, 6, 10) complexes from Table 4.

| $n$ | | M06-L | M06 | M06-2X | M05-2X | B3PW91 | BLYP | B1LYP | B97-1 | B97-2 | B97-D | ωB97 | ωB97X | ωB97X-D |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| – | Pd–P | 2.26 | 2.29 | 2.31 | 2.28 | 2.25 | 2.28 | 2.28 | 2.27 | 2.26 | 2.26 | 2.27 | 2.27 | 2.27 |
| 2 | Pd–P | 2.31 | 2.35 | 2.37 | 2.33 | 2.30 | 2.34 | 2.34 | 2.32 | 2.30 | 2.30 | 2.31 | 2.32 | 2.32 |
| | Pd–C | 2.16 | 2.19 | 2.20 | 2.19 | 2.16 | 2.21 | 2.20 | 2.18 | 2.17 | 2.20 | 2.15 | 2.16 | 2.17 |
| | Pd–X[a] | 2.05 | 2.08 | 2.09 | 2.08 | 2.05 | 2.10 | 2.09 | 2.06 | 2.05 | 2.08 | 2.03 | 2.05 | 2.05 |
| | C=C | 1.39 | 1.38 | 1.38 | 1.38 | 1.39 | 1.40 | 1.39 | 1.40 | 1.39 | 1.40 | 1.40 | 1.39 | 1.39 |
| | P–Pd–P | 110.4 | 111.2 | 113.4 | 114.4 | 111.4 | 110.5 | 112.0 | 111.4 | 111.6 | 112.1 | 112.3 | 112.4 | 112.6 |
| | P–Pd–C | 106.0 | 106.0 | 105.0 | 104.5 | 105.5 | 106.3 | 105.6 | 105.6 | 105.5 | 105.4 | 104.9 | 105.0 | 105.0 |
| 6 | Pd–P | 2.32 | 2.35 | 2.37 | 2.34 | 2.31 | 2.35 | 2.34 | 2.33 | 2.31 | 2.30 | 2.32 | 2.32 | 2.32 |
| | Pd–C | 2.21 | 2.23 | 2.24 | 2.21 | 2.18 | 2.25 | 2.23 | 2.20 | 2.19 | 2.24 | 2.16 | 2.18 | 2.19 |
| | Pd–X | 2.09 | 2.11 | 2.13 | 2.10 | 2.07 | 2.13 | 2.12 | 2.08 | 2.08 | 2.13 | 2.04 | 2.06 | 2.07 |
| | C=C | 1.41 | 1.39 | 1.39 | 1.39 | 1.41 | 1.42 | 1.40 | 1.41 | 1.41 | 1.41 | 1.40 | 1.40 | 1.40 |
| | P–Pd–P | 116.3 | 119.1 | 119.1 | 118.3 | 111.5 | 111.5 | 112.9 | 113.4 | 111.7 | 118.5 | 116.4 | 116.1 | 116.5 |
| | P–Pd–C | 103.3 | 102.2 | 102.4 | 102.6 | 105.5 | 105.9 | 105.2 | 104.6 | 105.5 | 102.4 | 102.8 | 103.2 | 103.1 |
| 10a | Pd–P | 2.31 | 2.36 | 2.37 | 2.33 | 2.31 | 2.35 | 2.34 | 2.33 | 2.31 | 2.30 | 2.32 | 2.32 | 2.32 |
| | Pd–C | 2.26 | 2.25 | 2.30 | 2.25 | 2.21 | 2.30 | 2.27 | 2.23 | 2.31 | 2.30 | 2.18 | 2.21 | 2.21 |
| | Pd–X | 2.14 | 2.13 | 2.19 | 2.14 | 2.09 | 2.18 | 2.16 | 2.11 | 2.20 | 2.18 | 2.06 | 2.09 | 2.10 |
| | C=C | 1.44 | 1.42 | 1.41 | 1.42 | 1.44 | 1.45 | 1.43 | 1.44 | 1.44 | 1.45 | 1.43 | 1.43 | 1.43 |
| | P–Pd–P | 116.9 | 115.4 | 119.5 | 118.2 | 111.0 | 111.3 | 112.5 | 112.0 | 110.4 | 119.8 | 115.8 | 115.2 | 115.7 |
| | P–Pd–C | 103.3 | 104.3 | 102.7 | 102.8 | 105.7 | 106.1 | 105.5 | 105.3 | 106.1 | 102.2 | 103.1 | 103.7 | 103.5 |
| 10b | Pd–P | 2.32 | 2.36 | 2.39 | 2.35 | 2.31 | 2.36 | 2.35 | 2.33 | 2.32 | 2.30 | 2.32 | 2.33 | 2.32 |
| | Pd–C | 2.21 | 2.22 | 2.23 | 2.20 | 2.18 | 2.24 | 2.22 | 2.19 | 2.18 | 2.25 | 2.15 | 2.17 | 2.18 |
| | Pd–X | 2.09 | 2.11 | 2.11 | 2.08 | 2.05 | 2.12 | 2.10 | 2.07 | 2.06 | 2.13 | 2.03 | 2.05 | 2.06 |
| | C=C | 1.44 | 1.43 | 1.42 | 1.42 | 1.44 | 1.46 | 1.44 | 1.45 | 1.44 | 1.45 | 1.44 | 1.43 | 1.43 |
| | P–Pd–P | 118.9 | 120.1 | 121.6 | 119.7 | 111.0 | 110.2 | 111.8 | 112.6 | 110.6 | 120.9 | 116.9 | 116.1 | 116.6 |
| | P–Pd–C | 101.6 | 101.3 | 100.6 | 101.3 | 105.2 | 106.0 | 105.3 | 104.4 | 105.5 | 100.8 | 102.1 | 102.7 | 102.6 |

[a] X is the center of the central C=C group. The first row of the table is for $Pd(PH_3)_2$ without an alkene.

nates for all optimized DFT/BS3 geometries are given in supporting information.

To compare the electronic energies without any variation in geometry, we also calculated binding energies at a single fixed geometry, in particular using geometries obtained with M06/BS3. The resulting binding energies are presented in Table 10, where they are compared with our best estimate of binding energy at these geometries from the WFT results in Table 6.

The first item to examine in Table 10 is the difference in binding energy for $n$ = 2 and 10b. Ikeda et al. [15] found that the $n$ = 2 and 10a structures have almost the same binding energy, whereas we find (primarily because of using larger basis sets) that the difference is 3.4 kcal/mol. However, for $n$ = 10 we also found a lower energy structure, $n$ = 10b, than the one they used, $n$ = 10a, and with this new structure we find that $n$ = 2 and $n$ = 10 have almost the same binding energy; the difference between them is only 0.3 kcal/mol. The deviation from this difference is indicated by Δ in Table 10. The two density functionals, B3LYP and B3PW91, examined for Pd complexes by Ikeda et al. have Δ ≅ 11 kcal/mol, in poor agreement with the best estimate. But seven of the other 15 functionals in Table 10 have Δ < 5 kcal/mol. The best functionals for this quantity are, in order of performance, M06-D, M06 and B97-D (tie), ωB97X-D, M06-L-D, ωB97, and M06-L.

We judge the quality of the density functional predictions in Table 10 on the basis of the mean unsigned deviation (MUD) from the best estimate, where the mean is an average over four absolute binding energies and six relative ones, including the difference between the binding energies for $n$ = 2 and 10b, which has already been discussed. Among the functionals that do not contain damped molecular mechanics empirical dispersion corrections, ωB97 and M06 are tied for best MUD, at 2.5 kcal/mol, and M06-L has the third best performance with an MUD of only 2.9 kcal/mol. Including functionals that have empirical damped dispersion corrections, the best methods become (in order, with MUD in kcal/mol in parentheses): M06-D (1.3), M06-L-D (1.5), and B97-D and ωB97X-D (tied at 1.8).

**Table 10**
Binding energies (kcal/mol) for $Pd(PH_3)_2C_nH_{n+2}$ ($n$ = 2,6,10) for different functionals at geometry M06/BS3 for basis set BS3.

| $n$ | B3PW91 | B3LYP | BLYP | BP86 | PBE0 | B98 | B97-1 | B97-2 | B97-D |
|---|---|---|---|---|---|---|---|---|---|
| 2 | 15.2 | 10.2 | 9.6 | 17.2 | 18.0 | 14.0 | 14.9 | 12.7 | 15.2 |
| 6 | 8.8 | 3.8 | 2.4 | 10.6 | 12.4 | 8.2 | 9.3 | 6.4 | 12.9 |
| 10a | 2.0 | −3.2 | −5.0 | 3.9 | 6.4 | 1.9 | 3.2 | −0.5 | 10.6 |
| 10b | 4.2 | −1.5 | −3.8 | 5.9 | 8.8 | 3.9 | 5.1 | 1.4 | 13.3 |
| Δ[a] | 10.8 | 11.4 | 13.1 | 11.0 | 8.9 | 9.9 | 9.4 | 10.9 | 1.6 |
| MUD[b] | 7.2 | 9.5 | 10.7 | 6.5 | 5.1 | 7.1 | 6.5 | 8.3 | 1.8 |

| $n$ | ωB97 | ωB97X | ωB97X-D | M05 | M06 | M06-L | M06-D[c] | M06-L-D[c] | B.E.[d] |
|---|---|---|---|---|---|---|---|---|---|
| 2 | 17.3 | 15.9 | 16.0 | 11.0 | 13.4 | 16.8 | 14.6 | 17.8 | 17.6 |
| 6 | 14.1 | 12.2 | 13.8 | 6.0 | 11.5 | 13.3 | 13.6 | 15.0 | 16.2 |
| 10a | 10.0 | 7.6 | 10.9 | 0.0 | 9.1 | 9.8 | 12.3 | 12.3 | 14.2 |
| 10b | 13.1 | 10.4 | 13.6 | 1.5 | 11.5 | 11.8 | 14.9 | 14.6 | 17.3 |
| Δ | 3.9 | 5.2 | 2.2 | 9.2 | 1.6 | 4.7 | 0.6 | 2.9 | 0.0[e] |
| MUD | 2.5 | 3.8 | 1.8 | 7.8 | 2.5 | 2.9 | 1.3 | 1.5 | 0.0[e] |

[a] Δ is mean unsigned error in the relative binding energy for $n$ = 2 and 10b.
[b] MUD denotes mean unsigned deviation from the best estimate for ten quantities, namely four absolute binding energies (2, 6, 10a, and 10b) and six relative binding energies (2 vs. 6, 2 vs. 10a, 2 vs. 10b, 6 vs. 10a, 6 vs. 10b, and 10a vs. 10b).
[c] In Ref. [57], the parameter $s_6$ was optimized to 0.20 and 0.25 for M06-L-D and M06-D, respectively.
[d] B.E. denotes the best estimate, obtained as explained in footnotes b and d of Table 6.
[e] zero by definition.

**Table 11**
Partial atomic charges on Pd, P, and C calculated by the NBO and Hirshfeld methods[a].

| *n* | Atom | B3PW91 | | B3LYP | | BLYP | | BP86 | | PBE0 | | B98 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | Pd | −0.36b | −0.22c | −0.36 | −0.22 | −0.36 | −0.36 | −0.23 | −0.21 | −0.36 | −0.23 | −0.36 | −0.22 |
| | P | 0.13 | 0.13 | 0.16 | 0.14 | 0.15 | 0.12 | 0.13 | 0.12 | 0.12 | 0.13 | 0.15 | 0.14 |
| 2 | Pd | −0.33 | −0.04 | −0.31 | −0.03 | −0.29 | −0.33 | −0.05 | −0.01 | −0.33 | −0.05 | −0.32 | −0.04 |
| | P | 0.20 | 0.11 | 0.22 | 0.13 | 0.20 | 0.19 | 0.11 | 0.10 | 0.19 | 0.11 | 0.22 | 0.13 |
| | C(Pd) | −0.49 | −0.12 | −0.48 | −0.11 | −0.48 | −0.49 | −0.12 | −0.12 | −0.49 | −0.12 | −0.48 | −0.11 |
| 6 | Pd | −0.26 | −0.02 | −0.25 | −0.02 | −0.23 | −0.27 | −0.03 | 0.01 | −0.27 | −0.03 | −0.26 | −0.02 |
| | P | 0.19 | 0.12 | 0.22 | 0.13 | 0.20 | 0.18 | 0.11 | 0.11 | 0.18 | 0.11 | 0.21 | 0.13 |
| | C(Pd) | −0.30 | −0.06 | −0.29 | −0.06 | −0.29 | −0.30 | −0.06 | −0.06 | −0.30 | −0.06 | −0.29 | −0.06 |
| 10a | Pd | −0.22 | 0.00 | −0.21 | 0.00 | −0.19 | −0.23 | −0.01 | 0.02 | −0.23 | −0.01 | −0.22 | 0.00 |
| | P | 0.18 | 0.12 | 0.21 | 0.14 | 0.19 | 0.17 | 0.12 | 0.11 | 0.17 | 0.12 | 0.20 | 0.13 |
| | C(Pd) | −0.14 | −0.02 | −0.14 | −0.02 | −0.14 | −0.14 | −0.02 | −0.02 | −0.14 | −0.02 | −0.14 | −0.02 |
| 10b | Pd | −0.26 | 0.01 | −0.24 | 0.02 | −0.23 | −0.27 | 0.00 | 0.04 | −0.27 | 0.00 | −0.25 | 0.01 |
| | P | 0.19 | 0.12 | 0.22 | 0.14 | 0.20 | 0.19 | 0.12 | 0.11 | 0.19 | 0.12 | 0.22 | 0.13 |
| | C(Pd) | −0.13 | −0.02 | −0.13 | −0.02 | −0.13 | −0.13 | −0.02 | −0.02 | −0.13 | −0.02 | −0.13 | −0.02 |

| *n* | Atom | B97-1 | | B97-2 | | B97-D | | ωB97 | | ωB97X | | ωB97X-D | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | Pd | −0.36 | −0.22 | −0.36 | −0.23 | −0.36 | −0.22 | −0.36 | −0.24 | −0.36 | −0.23 | −0.36 | −0.23 |
| | P | 0.14 | 0.14 | 0.14 | 0.14 | 0.14 | 0.14 | 0.15 | 0.14 | 0.15 | 0.14 | 0.14 | 0.13 |
| 2 | Pd | −0.32 | −0.03 | −0.32 | −0.05 | −0.31 | −0.03 | −0.32 | −0.05 | −0.32 | −0.05 | −0.32 | −0.04 |
| | P | 0.21 | 0.12 | 0.21 | 0.12 | 0.20 | 0.12 | 0.22 | 0.12 | 0.22 | 0.12 | 0.21 | 0.12 |
| | C(Pd) | −0.48 | −0.12 | −0.48 | −0.12 | −0.48 | −0.11 | −0.49 | −0.11 | −0.49 | −0.12 | −0.49 | −0.12 |
| 6 | Pd | −0.26 | −0.02 | −0.26 | −0.03 | −0.25 | −0.01 | −0.27 | −0.04 | −0.27 | −0.04 | −0.26 | −0.03 |
| | P | 0.21 | 0.13 | 0.20 | 0.12 | 0.19 | 0.12 | 0.22 | 0.12 | 0.21 | 0.12 | 0.20 | 0.12 |
| | C(Pd) | −0.29 | −0.06 | −0.29 | −0.06 | −0.29 | −0.06 | −0.30 | −0.06 | −0.30 | −0.06 | −0.30 | −0.06 |
| 10a | Pd | −0.21 | 0.00 | −0.22 | −0.01 | −0.20 | 0.01 | −0.23 | −0.02 | −0.22 | −0.02 | −0.22 | −0.01 |
| | P | 0.20 | 0.13 | 0.19 | 0.13 | 0.18 | 0.13 | 0.20 | 0.13 | 0.20 | 0.13 | 0.19 | 0.12 |
| | C(Pd) | −0.14 | −0.02 | −0.14 | −0.02 | −0.13 | −0.02 | −0.14 | −0.02 | −0.14 | −0.02 | −0.14 | −0.02 |
| 10b | Pd | −0.25 | 0.02 | −0.26 | 0.00 | −0.24 | 0.02 | −0.26 | −0.01 | −0.26 | 0.00 | −0.26 | 0.00 |
| | P | 0.21 | 0.13 | 0.20 | 0.13 | 0.20 | 0.13 | 0.22 | 0.13 | 0.21 | 0.13 | 0.21 | 0.12 |
| | C(Pd) | −0.13 | −0.02 | −0.13 | −0.02 | −0.13 | −0.02 | −0.14 | −0.02 | −0.14 | −0.02 | −0.14 | −0.02 |

| *n* | Atom | M05 | | M06 | | M06-L | | MP2 | | MP4(SDQ) | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | Pd | −0.33 | −0.21 | −0.32 | −0.19 | −0.36 | −0.22 | −0.38 | −0.23 | −0.35 | −0.22 |
| | P | 0.11 | 0.12 | 0.15 | 0.14 | 0.17 | 0.14 | 0.23 | 0.17 | 0.25 | 0.17 |
| 2 | Pd | −0.28 | −0.02 | −0.26 | 0.00 | −0.31 | −0.03 | −0.34 | −0.01 | −0.32 | 0.00 |
| | P | 0.18 | 0.10 | 0.22 | 0.12 | 0.23 | 0.13 | 0.31 | 0.15 | 0.32 | 0.15 |
| | C(Pd) | −0.50 | −0.12 | −0.47 | −0.11 | −0.47 | −0.11 | −0.47 | −0.12 | −0.45 | −0.11 |
| 6 | Pd | −0.22 | 0.00 | −0.20 | 0.02 | −0.26 | −0.02 | −0.27 | 0.01 | −0.24 | 0.02 |
| | P | 0.17 | 0.11 | 0.21 | 0.13 | 0.23 | 0.13 | 0.30 | 0.15 | 0.30 | 0.15 |
| | C(Pd) | −0.30 | −0.06 | −0.28 | −0.06 | −0.28 | −0.06 | −0.30 | −0.07 | −0.29 | −0.06 |
| 10a | Pd | −0.18 | 0.02 | −0.22 | 0.00 | −0.16 | 0.04 | −0.20 | 0.04 | | |
| | P | 0.16 | 0.11 | 0.22 | 0.13 | 0.20 | 0.13 | 0.28 | 0.15 | | |
| | C(Pd) | −0.14 | −0.02 | −0.13 | −0.02 | −0.14 | −0.02 | −0.16 | −0.03 | | |
| 10b | Pd | −0.21 | 0.03 | −0.20 | 0.05 | −0.26 | 0.02 | −0.23 | 0.05 | | |
| | P | 0.17 | 0.11 | 0.21 | 0.13 | 0.23 | 0.13 | 0.29 | 0.15 | | |
| | C(Pd) | −0.14 | −0.02 | −0.13 | −0.02 | −0.13 | −0.02 | −0.16 | −0.03 | | |

[a] In this table, all DFT calculations are made with the BS3 basis set, and all WFT calculations are made with the BS2 basis set. The geometry is obtained by M06/BS3. NBO charges are given in the left column, and Hirshfeld charges are given in the right column.

In light of recent calculations [89–91] and experiments [91,92] on organometallic complexes with large ligands that show the importance of attractive noncovalent interactions, it is interesting to ask what role the inclusion of such interactions plays in the improvement we see above in the trend of binding energy with *n*. The functionals M06-D, M06, B97-D, ωB97X-D, M06-L-D, and M06-L all provide a more realistic treatment of attractive noncovalent interactions than the functionals studied in Ref. [15]; however, that need not be the reason for their improved performance. At long range, dispersion interactions decay as $R^{-6}$ where $R$ is the distance between atoms or fragments. Without adding molecular mechanics terms, the density functional approximations studied here do not include long-range dispersion interactions, but some of them (e.g., the M06 family) do include a reasonably accurate description of medium-range interactions arising from the same type of correlation energy as long-range dispersion interactions. Since various functionals include different amounts of medium-range correlation energy, the damped dispersion terms in "–D" methods were separately parameterized for each functional by its developers to try to make up for the missing portion. When molecular mechanical damped dispersion was included in the B97-D and ωB97X-D functionals (when they were created [55,56]), other parameters in these functionals were re-optimized so the difference of the results obtained with these functionals and with the earlier B97-1, B97-2, ωB97, or ωB97X functionals cannot be attributed simply to damped dispersion. The M06-L-D and M06-D functionals do, however, differ from M06-L and M06 simply by the addition of damped dispersion, but the added damped dispersion is severely scaled back (see footnote a in Table 10) because M06-L and M06 already contain medium-range correlation energy that corresponds to medium-range damped dispersion. In this context, it is very interesting that M06-L-D and M06-D reduce the MUDs of M06-L and M06, respectively by a factor of about 2.

Table 11 presents calculated partial atomic charges for the Pd complexes. The last two columns in the table shows the charges calculated at MP2/BS2//M06/BS3 and MP4SDQ/BS2//M06/BS3 levels of theory; other results are from DFT. This table confirms that the methods that do poorly for binding energies do not do so because of spurious charge transfer contributions. In fact all the density functionals lead to remarkably similar partial atomic charges.

Examining the M06/BS3 structures, we find the shortest Pd–H(–C) distance (in Å, followed in parentheses by the position of the carbon) is 2.73 ($\alpha$), 2.73 ($\alpha$), 2.73 ($\alpha$), 2.70 ($\alpha$), 3.09 ($\beta$), and 2.78 ($\gamma$) for $n$ = 2, 4, 6, 8, 10a, and 10b. For the same interactions in the Pt complexes, we find 2.73, 2.73, 2.73, 2.70, and 2.91 Å for $n$ = 2, 4, 6, 8, and 10b. (In contrast, the Tr–H(–P) distances are in the range 3.19–3.40 Å in all cases.) Agostic and near-agostic interactions are common in alkyl groups attached to transition metals [93–95], and in light of the shorter H–Pd distances in structure 10b, the question arises of whether the favorable structure 10b is partly stabilized by an alkenyl agostic interaction. Although the transition metal center is formally a coordinatively unsaturated 16-electron species, there are no empty d orbitals on the $d^{10}$ metal, so we do not expect an agostic interaction. Furthermore, agostic interactions are associated with lengthened C–H bonds and lowered C–H stretching frequencies [95,96], but we do not find either of these (all calculated C–H bond lengths are in the range 1.080–1.090 Å). Furthermore, a rough rule of thumb for the border between agostic and anagostic is 2.3 Å [93]. Thus there do not appear to be any agostic interactions in these compounds.

## 4. Conclusions

By using improved density functionals we are able to calculate the absolute and relative interaction energies of $Pd(PH_3)_2$ with ethene and with $C_6$ and $C_{10}$ conjugated alkenes with a mean unsigned deviation as small as 2.5 kcal/mol; this good performance is obtained with the M06 and ωB97 density functionals, but small mean unsigned deviations can also be obtained with the local M06-L density functional (2.9 kcal/mol) or the ωB97X density functional (3.8 kcal/mol). These density functionals are all based on a single Slater determinant, showing that it is not necessary to use a multiconfigurational treatment to obtain reasonable accuracy for these systems. The new functionals also lead to improved accuracy for the analogous Pt complexes.

By adding damped molecular mechanical dispersion, the mean unsigned deviation from the best estimates can be reduced to 1.3 kcal/mol with the M06-D functional.

These calculations demonstrate the high quantitative accuracy that can be obtained even for previously troublesome catalytic systems by using recently developed density functionals.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2010.03.016.

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