

# Ligand Bond Energies in *cis*- and *trans*-[L-Pd(PH<sub>3</sub>)<sub>2</sub>Cl]<sup>+</sup> Complexes from Coupled Cluster Theory (CCSD(T)) and Density Functional Theory

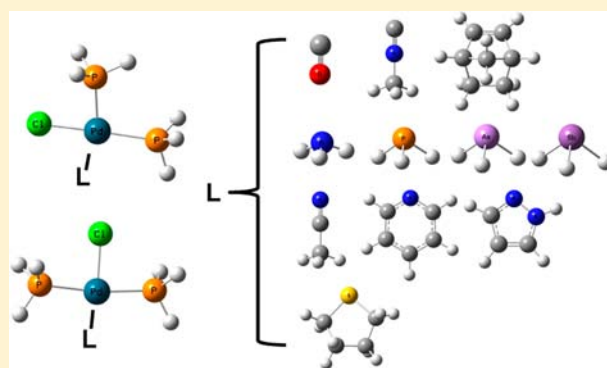
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## Supporting Information

**ABSTRACT:** The Pd–L ligand bond dissociation energies (BDEs) of *cis*- and *trans*-[L-Pd(PH<sub>3</sub>)<sub>2</sub>Cl]<sup>+</sup> were predicted using coupled cluster CCSD(T) theory and a variety of density functional theory (DFT) functionals at the B3LYP optimized geometries. *trans*-[L-Pd(PH<sub>3</sub>)<sub>2</sub>Cl]<sup>+</sup> is the more stable isomer when Pd forms a donor–acceptor bond with a C atom of the ligand, including the  $\pi$ -bond in norbornene; for the remaining complexes, the *cis*-[L-Pd(PH<sub>3</sub>)<sub>2</sub>Cl]<sup>+</sup> isomer is substantially lower in energy. For *cis*-[L-Pd(PH<sub>3</sub>)<sub>2</sub>Cl]<sup>+</sup> complexes, the Pd–L bond energies are 28 kcal/mol for CO; ~40 kcal/mol for AH<sub>3</sub> (A = N, P, As, and Sb), norbornene, and CH<sub>3</sub>CN; and ~53 kcal/mol for CH<sub>3</sub>NC, pyrazole, pyridine, and tetrahydrothiophene at the CCSD(T) level. When Pd forms a donor–acceptor bond with the C atom in the ligand (i.e., CO, CH<sub>3</sub>NC, and the  $\pi$ -bond in norbornene), the Pd–L bond energies for *trans*-[L-Pd(PH<sub>3</sub>)<sub>2</sub>Cl]<sup>+</sup> are generally ~10 kcal/mol greater than those for *cis*-[L-Pd(PH<sub>3</sub>)<sub>2</sub>Cl]<sup>+</sup> with the same L; for the remaining ligands, the ligand bond energy increases are ~3–5 kcal/mol from the *cis*-isomer to the *trans*-isomer. The benchmarks show that the dispersion-corrected hybrid, generalized gradient approximation, DFT functional  $\omega$ -B97X-D is the best one to use for this system. Use of the  $\omega$ -B97X-D/aD functional gives predicted BDEs within 1 kcal/mol of the CCSD(T)/aug-cc-pVTZ BDEs for *cis*-[L-Pd(PH<sub>3</sub>)<sub>2</sub>Cl]<sup>+</sup> and 1.5 kcal/mol for *trans*-[L-Pd(PH<sub>3</sub>)<sub>2</sub>Cl]<sup>+</sup>.



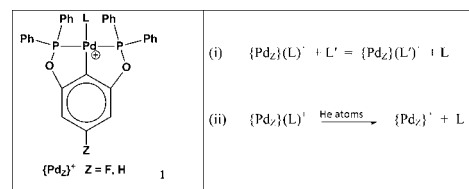
## INTRODUCTION

Palladium complexes,<sup>1</sup> often employing phosphorus-based ligands, function as homogeneous catalysts for many important organic reactions and display potentially useful photophysical properties.<sup>2,3</sup> An example of an important application of Pd-based catalysts is the Suzuki–Miyaura cross-coupling reaction.<sup>4</sup> As part of our studies on how ligand structure and energetics affect Pd cross-coupling catalysts,<sup>5</sup> we have previously calculated the binding energies of PH<sub>3</sub> to simple M(0) and M(II) model complexes, where M = Ni, Pd, and Pt, using correlated molecular orbital theory at the coupled cluster CCSD(T) level<sup>6</sup> with the correlation-consistent basis sets<sup>7</sup> extrapolated to the complete basis set (CBS) basis set limit.<sup>8</sup> For example, the respective CCSD(T)/CBS PH<sub>3</sub> BDEs in kilocalories per mole for *trans*-M(PH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> are 24.5 for Ni, 32.1 for Pd, and 40.3 kcal/mol for Pt. The commonly used B3LYP exchange-correlation functional had an average error of 6 kcal/mol for this BDE.

An ongoing project to model Pd–L bonding in a more complex system is using the computational results reported here to develop an appropriate computational approach to explain a variety of experimental results for the Pd(II) arylbis(phosphinite) pincer-ligand complexes shown in Scheme

I. Together with our collaborators, we are studying (i) laboratory solution-phase ligand-substitution equilibria moni-

### Scheme I



tored by <sup>31</sup>P (and <sup>19</sup>F for Z = F in Scheme I) NMR spectroscopy and (ii) gas-phase dissociation of L using mass spectrometry-collision induced dissociation (MS-CID).<sup>9</sup> A goal is to calculate BDE values to correlate with differences in (i) equilibrium constants for {Pd<sub>F</sub>}(L)<sup>+</sup> and {Pd<sub>H</sub>}(L)<sup>+</sup> when mixed with the same L' and for (ii) activation energies for Pd–L bond breaking determined via collision-induced decom-

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Table 1. Benchmarked DFT Exchange-Correlation Functionals

functional	exchange	correlation	type	refs
B1B95	Becke 96	Becke 95	HGGA	27, 23
B1LYP	Becke 96	Lee–Yang–Parr	HGGA	27, 21
B3LYP	Becke 93	Lee–Yang–Parr	HGGA	28, 21
B3P86	Becke 93	Perdew 86	HGGA	28, 22
B3PW91	Becke 93	Perdew–Wang 91	HGGA	28, 16
B971	Handy–Tozer’s modified B97	Handy–Tozer’s modified B97	HGGA	30
B972	Wilson–Bradley–Tozer’s modified B97	Wilson–Bradley–Tozer’s modified B97	HGGA	31
B98	Becke 98	Becke’s 1998 revisions to B97	HGGA	29
BB95	Becke 88	Becke 95	GGA	15, 23
BLYP	Becke 88	Lee–Yang–Parr	GGA	15, 21
BMK	Boese–Martin	Boese–Martin	HGGA	35
BP86	Becke 88	Perdew 86	GGA	15, 22
BPW91	Becke 88	Perdew–Wang 91	GGA	15, 16
CAM-B3LYP <sup>a</sup>	Becke 93	Lee–Yang–Parr	LR-HGGA	28, 21, 39
G96LYP	Gill 96	Lee–Yang–Parr	GGA	17, 21
HCTH147	Handy	Handy	GGA	24
HCTH407	Handy	Handy	GGA	24
HCTH93	Handy	Handy	GGA	24
HSEh1PBE	Heyd–Scuseria–Ernzerhof functional	Perdew–Burke–Ernzerhof	HGGA	33, 18
M06	Zhao and Thruhlar	Zhao and Thruhlar	HGGA	34
mPW1LYP	Adamo and Barone’s modified PW91	Lee–Yang–Parr	HGGA	25, 21
mPW1PBE	Adamo and Barone’s modified PW91	Perdew–Burke–Ernzerhof	HGGA	25, 18
mPW1PW91	Adamo and Barone’s modified PW91	Perdew–Wang 91	HGGA	25, 16
mPW3PBE	Adamo and Barone’s modified PW91	Perdew–Burke–Ernzerhof	HGGA	25, 18
mPWLYP	Adamo and Barone’s modified PW91	Lee–Yang–Parr	GGA	25, 21
mPWPBE	Adamo and Barone’s modified PW91	Perdew–Burke–Ernzerhof	GGA	25, 18
mPWPW91	Adamo and Barone’s modified PW91	Perdew–Wang 91	GGA	25, 16
O3LYP	Handy’s OPTX	Lee–Yang–Parr	HGGA	38, 21
OLYP	Cohen and Handy	Lee–Yang–Parr	GGA	19, 21
PBE	Perdew–Burke–Ernzerhof	Perdew–Burke–Ernzerhof	GGA	18
PBE1PBE	Adamo’s hybrid and Perdew–Burke–Ernzerhof	Perdew–Burke–Ernzerhof	HGGA	32, 18
PW91	Perdew–Wang 91	Perdew–Wang 91	GGA	16
SV5LYP	Slater	Lee–Yang–Parr and Vosko–Wilk–Nusair V	GGA	13, 21, 14
SVP86	Slater	Perdew 86 and Vosko–Wilk–Nusair V	GGA	13, 22, 14
SVWN5	Slater	Vosko–Wilk–Nusair V	LDA	13, 14
TPSSH	Tao–Perdew–Staroverov–Scuseria	Tao–Perdew–Staroverov–Scuseria	HGGA	20
TPSS	Tao–Perdew–Staroverov–Scuseria	Tao–Perdew–Staroverov–Scuseria	GGA	20
V5XC	van Voorhis–Scuseria	van Voorhis–Scuseria	GGA	26
$\omega$ -B97X-D <sup>a</sup>	Head-Gordon and co-workers based on Grimme’s B97-D	Head-Gordon and co-workers based on Grimme’s B97-D	LR-HGGA	40
$\omega$ -B97X	Head-Gordon and co-workers based on Becke’s B97	Head-Gordon and co-workers based on Becke’s B97	LR-HGGA	40
X3LYP	Xu and Goddard	Lee–Yang–Parr	HGGA	37, 21

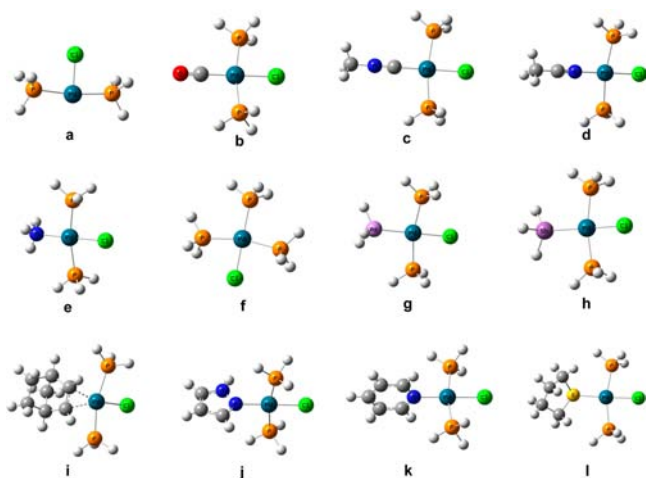
<sup>a</sup>Long range.

**CCSD(T) BDEs.** Table 3 lists the BDEs calculated at the CCSD(T)/aD and CCSD(T)/aT levels. For the *cis*-[L-Pd(PH<sub>3</sub>)<sub>2</sub>Cl]<sup>+</sup> complexes, the ligand BDEs can be grouped as follows: 28 kcal/mol for CO; ~40 kcal/mol for AH<sub>3</sub> (A = N, P, As, and Sb), norbornene, and CH<sub>3</sub>CN; and ~53 kcal/mol for CH<sub>3</sub>NC, pyrazole, pyridine, and THT at the CCSD(T)/aD level. The CCSD(T)/aT BDEs for the *cis* complexes do not change much from the CCSD(T)/aD values, with a mean deviation of 0.6 kcal/mol and a standard deviation of 0.8 kcal/mol. The largest differences (above the average deviations) between the CCSD(T)/aD and aT BDEs are -2.1 kcal/mol for norbornene, 1.1 kcal/mol for pyridine, and 1.0 kcal/mol for THT. The effect of increasing the basis set size on the BDEs at the CCSD(T) level for the *trans* complexes are larger than for the *cis* complexes, as the mean deviation between the aT and aD BDEs increases to 0.9 kcal/mol and the standard deviation increases to 1.1 kcal/mol. For *trans*-[L-Pd(PH<sub>3</sub>)<sub>2</sub>Cl]<sup>+</sup>, the aD–

aT differences for the BDEs greater than the mean deviation and the standard deviation are 1.5 kcal/mol for SbH<sub>3</sub>, 2.2 kcal/mol for PH<sub>3</sub>, and 1.4 kcal/mol for AsH<sub>3</sub>. At the CCSD(T)/aT level, the ligand BDEs for *cis*-[L-Pd(PH<sub>3</sub>)<sub>2</sub>Cl]<sup>+</sup> have the following order: pyrazole > CH<sub>3</sub>NC > pyridine > THT > NH<sub>3</sub> > CH<sub>3</sub>CN > PH<sub>3</sub> > norbornene > SbH<sub>3</sub> > AsH<sub>3</sub> > CO. The corresponding ligand BDEs for *trans*-[L-Pd(PH<sub>3</sub>)<sub>2</sub>Cl]<sup>+</sup> have the following order: CH<sub>3</sub>NC > pyridine > pyrazole > THT > norbornene > PH<sub>3</sub> > CH<sub>3</sub>CN > NH<sub>3</sub> > AsH<sub>3</sub> ≈ SbH<sub>3</sub> > CO.

**CCSD(T) *cis*–*trans* Differences.** The BDEs of the ligands for the *trans*-[L-Pd(PH<sub>3</sub>)<sub>2</sub>Cl]<sup>+</sup> complexes are generally larger than the BDEs of the *cis*-[L-Pd(PH<sub>3</sub>)<sub>2</sub>Cl]<sup>+</sup> complexes, consistent with the shorter Pd–L bond distances in the *trans*-complexes as compared with the *cis*-complexes. The differences in the BDEs between the *cis*- and *trans*-complexes at the CCSD(T)/aD level are up to 3 kcal/mol for NH<sub>3</sub>, pyrazole,





**Figure 2.** Calculated structures for (a)  $\text{trans-}[\text{Pd}(\text{PH}_3)_2\text{Cl}]^+$  with (b) CO, (c)  $\text{CH}_3\text{NC}$ , (d)  $\text{CH}_3\text{CN}$ , (e)  $\text{PH}_3$ , (f)  $\text{PH}_3$ , (g)  $\text{AsH}_3$ , (h)  $\text{SbH}_3$ , (i) norbornene, (j) pyrazole, (k) pyridine, and (l) tetrahydrothiophene ligands.

**Table 2. Important Geometry Parameters for  $\text{cis-}$  and  $\text{trans-}[\text{Pd}(\text{PH}_3)_2\text{Cl}]^+$**

ligand	$r(\text{Pd}-\text{PH}_3)^b$	$r(\text{Pd}-\text{Cl})$	$r(\text{Pd}-\text{L})$
	$\text{cis-}[\text{L-Pd}(\text{PH}_3)_2\text{Cl}]^+$		
$\text{cisoid-}[\text{Pd}(\text{PH}_3)_2\text{Cl}]^+{}^a$	2.348, 2.245	2.264	
CO	2.349, 2.346	2.317	1.990 (C)
$\text{CH}_3\text{NC}$	2.328, 2.345	2.323	2.003 (C)
$\text{CH}_3\text{CN}$	2.329, 2.280	2.320	2.072 (N)
$\text{NH}_3$	2.326, 2.299	2.318	2.135 (N)
$\text{PH}_3$	2.320, 2.360	2.326	2.360 (P)
$\text{AsH}_3$	2.320, 2.345	2.325	2.464 (As)
$\text{SbH}_3$	2.315, 2.352	2.332	2.636 (Sb)
norbornene	2.321, 2.326	2.337	2.347 (C), 2.536 (C)
pyrazole	2.317, 2.294	2.343	2.107 (N)
pyridine	2.323, 2.299	2.321	2.108 (N)
THT	2.321, 2.325	2.328	2.420 (S)
	$\text{trans-}[\text{L-Pd}(\text{PH}_3)_2\text{Cl}]^+$		
$\text{transoid-}[\text{Pd}(\text{PH}_3)_2\text{Cl}]^+{}^a$	2.369	2.266	
CO	2.375	2.301	1.926 (C)
$\text{CH}_3\text{NC}$	2.359	2.315	1.961 (C)
$\text{CH}_3\text{CN}$	2.359	2.291	2.024 (N)
$\text{NH}_3$	2.361	2.300	2.126 (N)
$\text{PH}_3$	2.360	2.326	2.320 (P)
$\text{AsH}_3$	2.355	2.323	2.433 (As)
$\text{SbH}_3$	2.353	2.329	2.608 (Sb)
norbornene	2.360	2.330	2.326 (C $\times$ 2)
pyrazole	2.359	2.298	2.073 (N)
pyridine	2.358	2.305	2.082 (N)
THT	2.357	2.270	2.290 (S)

<sup>a</sup>No ligand. <sup>b</sup>For the  $\text{cis-}$  complexes, the first value of  $r(\text{Pd}-\text{PH}_3)$  is the bond distance between Pd and the  $\text{PH}_3$  ligand  $\text{trans}$  to  $\text{F}^-$ , and the second value is the bond distance between Pd and the  $\text{PH}_3$  ligand  $\text{trans}$  to L.

and THT;  $\sim 5$  kcal/mol for  $\text{CH}_3\text{CN}$ ,  $\text{PH}_3$ ,  $\text{AsH}_3$ ,  $\text{SbH}_3$ , and pyridine; and  $\sim 10$  kcal/mol for CO,  $\text{CH}_3\text{NC}$ , and norbornene. For the ligands CO,  $\text{CH}_3\text{NC}$ , and norbornene, Pd forms a donor–acceptor bond with a C atom including the  $\pi$ -bond in norbornene in the ligand.

The  $\text{cisoid-}[\text{Pd}(\text{PH}_3)_2\text{Cl}]^+$  isomer without a ligand L is 6.9 kcal/mol more stable than the  $\text{transoid}$  isomer at the CCSD(T)/aD level, and 8.4 kcal/mol lower at the CCSD(T)/aT level. Although the  $\text{trans-}[\text{L-Pd}(\text{PH}_3)_2\text{Cl}]^+$  complexes generally exhibit higher ligand BDEs than the  $\text{cis-}[\text{L-Pd}(\text{PH}_3)_2\text{Cl}]^+$  complexes,  $\text{cis-}[\text{L-Pd}(\text{PH}_3)_2\text{Cl}]^+$  can still be the more stable isomer if the difference in the ligand BDE between the  $\text{trans-}$  and  $\text{cis-}[\text{L-Pd}(\text{PH}_3)_2\text{Cl}]^+$  complexes is smaller than 6.9 kcal/mol at the CCSD(T)/aD level or 8.4 kcal/mol at the CCSD(T)/aT level. For L = CO,  $\text{CH}_3\text{NC}$ , and norbornene, the  $\text{trans-}[\text{L-Pd}(\text{PH}_3)_2\text{Cl}]^+$  isomers are more stable than the  $\text{cis-}$  isomers (Table 3); for the remaining ligands, the  $\text{cis-}[\text{L-Pd}(\text{PH}_3)_2\text{Cl}]^+$  isomer is more stable. The  $\text{trans-}[\text{AsH}_3\text{-PdCl}(\text{PH}_3)_2]^+$  isomer is calculated to be only  $\sim 0.5$  kcal/mol higher in energy than the  $\text{cis-}$  isomer complex. For L =  $\text{CH}_3\text{CN}$ , the CCSD(T)/aD calculations predict the  $\text{trans-}$  isomer to be slightly lower than the  $\text{cis-}$  isomer by 0.2 kcal/mol, and the aT calculations predict  $\text{cis-}[\text{L-PdCl}(\text{PH}_3)_2]^+$  to be lower in energy by  $\sim 1$  kcal/mol. To summarize, the  $\text{trans-}[\text{L-Pd}(\text{PH}_3)_2\text{Cl}]^+$  complex is the more stable isomer when Pd forms a donor–acceptor bond with a C atom of the ligand, and for the remainder, the  $\text{cis-}[\text{L-Pd}(\text{PH}_3)_2\text{Cl}]^+$  complex is substantially lower in energy.

The  $\text{cisoid-}[\text{Pd}(\text{PH}_3)_2\text{Cl}]^+$  complex is more stable than  $\text{transoid-}[\text{Pd}(\text{PH}_3)_2\text{Cl}]^+$  because the weak-field ligand  $\text{Cl}^-$ , which is also as  $\pi$ -donor ligand, and the strong-field ligand  $\text{PH}_3$ , a  $\pi$ -acceptor ligand, at the  $\text{trans}$  position in  $\text{cisoid-}[\text{Pd}(\text{PH}_3)_2\text{Cl}]^+$  is better able to stabilize the structure as compared to the structure with two  $\text{PH}_3$  groups  $\text{trans}$  to each other in  $\text{transoid-}[\text{Pd}(\text{PH}_3)_2\text{Cl}]^+$ .<sup>43,44</sup> For the  $\text{cis-}[\text{L-Pd}(\text{PH}_3)_2\text{Cl}]^+$  and  $\text{trans-}[\text{L-Pd}(\text{PH}_3)_2\text{Cl}]^+$  complexes, the situation is more complicated, and only the interactions between the ligand pairs in which ligands are  $\text{trans}$  to each other are considered. Therefore, the total stabilization effect is the sum of the  $\text{trans-Cl-Pd-PH}_3$  and  $\text{trans-PH}_3\text{-Pd-L}$  effects in the  $\text{cis-}$  complexes and is the sum of the  $\text{trans-Cl-Pd-L}$  and  $\text{trans-PH}_3\text{-Pd-PH}_3$  effects in the  $\text{trans-}$  complexes. In the current work, the ligands L are  $\pi$ -acceptors. From the spectrochemical series, the ordering from weak-field to strong-field for the ligands is as follows:  $\text{Cl}^- < \text{CH}_3\text{CN} < \text{pyridine} < \text{NH}_3 < \text{PPh}_3 < \text{CO}$ . The stabilization effect when Cl is  $\text{trans}$  to the L or to  $\text{PH}_3$  is more important than when  $\text{PH}_3$  is  $\text{trans}$  to the L or to  $\text{PH}_3$ . For most cases in the current study, if L is a stronger-field ligand than  $\text{PH}_3$ , L prefers to be  $\text{trans}$  to the Cl in the more stable complex.

**CCSD(T) BDE Trends and Correlations.** The ligand BDEs exhibit some interesting trends. The ligand BDEs of the  $\text{trans-}$  isomer are larger than those of the  $\text{cis-}$  isomer due to the increased stability of  $\text{cisoid-}[\text{Pd}(\text{PH}_3)_2\text{Cl}]^+$  as compared to  $\text{transoid-}[\text{Pd}(\text{PH}_3)_2\text{Cl}]^+$ . For the pnictogen trihydrides,  $\text{AH}_3$ , the BDE values are comparable within  $\sim 5$  kcal/mol for the  $\text{cis-}$  and  $\text{trans-}$  structures. The BDEs of the  $\text{cis-}$  complexes with L = AH<sub>3</sub> decrease from A = N to A = As and then slightly increase for A = Sb. The corresponding BDEs of the  $\text{trans-}$  complexes increase from A = N to A = P and then decrease with the BDEs for A = As and Sb being comparable. The weakest BDE is for L = CO for both  $\text{cis-}$  and  $\text{trans-}$  isomers. The strongest ligand BDEs of the  $\text{cis-}$  isomer are for L =  $\text{CH}_3\text{NC}$ , pyridine, and pyrazole, with that for THT being slightly lower. The ligand BDEs for  $\text{CH}_3\text{CN}$  and norbornene are comparable to those for  $\text{AH}_3$  for the  $\text{cis-}$  isomer. For the  $\text{trans-}$  isomer,  $\text{CH}_3\text{NC}$  has the strongest ligand BDE followed by that for pyridine. Those for pyrazole and THT are slightly lower. It is noteworthy that the norbornene ligand BDE for the  $\text{trans-}$  isomer is greater than

Table 3. CCSD(T)/aD and CCSD(T)/aT BDEs (kcal/mol) for *cis*- and *trans*-[L-Pd(PH<sub>3</sub>)<sub>2</sub>Cl]<sup>+</sup>

method	CO	CH <sub>3</sub> NC	CH <sub>3</sub> CN	NH <sub>3</sub>	PH <sub>3</sub>	AsH <sub>3</sub>	SbH <sub>3</sub>	norbornene	pyrazole	pyridine	THT	md	sd
<i>cis</i>													
CCSD(T)/aD	28.2	52.9	41.6	43.2	41.3	37.3	37.9	40.8	53.6	53.6	51.8		
CCSD(T)/aT	27.9	52.7	42.0	42.9	41.9	37.3	38.0	38.7	53.5	52.5	50.8		
ΔBDE(aT – aD)	–0.3	–0.2	0.4	–0.3	0.6	0.0	0.1	–2.1	–0.1	–1.1	–1.0	0.6	0.8
<i>trans</i>													
CCSD(T)/aD	39.7	63.2	48.7	46.2	48.2	43.7	43.5	51.7	56.0	59.9	53.8		
CCSD(T)/aT	40.7	64.2	49.5	46.6	50.4	45.1	45.0	50.9	55.9	59.5	54.1		
ΔBDE(aT – aD)	1.0	1.0	0.8	0.4	2.2	1.4	1.5	–0.8	–0.1	–0.4	0.3	0.9	1.1
ΔE <sub>iso</sub> <sup>a</sup>													
CCSD(T)/aD	–4.6	–3.4	–0.2	3.9	0	0.5	1.3	–4.0	4.5	0.6	4.9		
CCSD(T)/aT	–4.4	–3.1	0.9	4.7	0	0.6	1.3	–3.8	6.0	1.4	5.1		
E <sub>iso</sub> (aT–aD)	0.2	0.3	1.1	0.8	0	0.1	0.0	0.2	1.5	0.8	0.2	0.5	0.7
ligand proton affinity													
PA(L) <sup>42</sup>	142.0	200.5	186.2	204.0	187.6	178.8		199.9	213.7	222.3	202.9		

<sup>a</sup>E<sub>iso</sub>: isomerization energy between the *trans*- and the *cis*-[L-Pd(PH<sub>3</sub>)<sub>2</sub>Cl]<sup>+</sup> conformers given by E<sub>iso</sub> = E(*trans*) – E(*cis*).

those for the AH<sub>3</sub> ligands. A final comparison that can be made is with the ligand Pd–PH<sub>3</sub> BDE for the neutral PdCl<sub>2</sub>(PH<sub>3</sub>)<sub>2</sub> complex for which a CCSD(T)/complete basis set limit value of 32.1 kcal/mol is available.<sup>8</sup> The Pd–PH<sub>3</sub> ligand BDE of cationic *cis*-[PH<sub>3</sub>-Pd(PH<sub>3</sub>)<sub>2</sub>Cl]<sup>+</sup> is 10 kcal/mol larger than for neutral PdCl<sub>2</sub>(PH<sub>3</sub>)<sub>2</sub> and the BDE for *trans*-[PH<sub>3</sub>-Pd(PH<sub>3</sub>)<sub>2</sub>Cl]<sup>+</sup> is 18 kcal/mol larger than the neutral complex. Thus the BDEs of the cationic complexes are larger than they are for the neutral metal complex, consistent with the qualitative expectation that binding a lone pair to a cation should be larger than binding to a neutral.

As the ligands are binding to a cationic metal center, it is possible that the ligand BDE could correlate with the basicity of the ligand as described by its proton affinity (PA). The ligand PAs except for that for SbH<sub>3</sub> are available from experiment<sup>45</sup> and are given in Table 3. It is clear that there are some qualitative correlations with the PAs in terms of high PAs correlating with larger ligand BDEs, but one cannot use this correlation to directly estimate ligand BDEs. For example, PA(norbornene) is less than PA(NH<sub>3</sub>) by about 4 kcal/mol and the ligand BDE for the *cis*-isomer for norbornene is less than that of NH<sub>3</sub>, consistent with this simple model. However, the situation is reversed for the *trans*-isomer and the order of ligand BDEs does not match that of the PAs. As another example, the ligand BDE for CH<sub>3</sub>NC is comparable to that of pyridine for the *cis*-isomer yet PA(CH<sub>3</sub>NC) is >20 kcal/mol lower than PA(pyridine). For the *trans*-isomer, the ligand BDE for CH<sub>3</sub>NC is greater than that for pyridine.

**Benchmarks of DFT Functionals.** A key goal of this effort is to determine which DFT functionals with a moderate-sized basis set are able to predict BDEs of good quality for the larger systems of experimental interest. We benchmarked different DFT functionals with the aD basis set for the BDEs in comparison to the high level CCSD(T)/aT BDEs for the [L-Pd(PH<sub>3</sub>)<sub>2</sub>Cl]<sup>+</sup> models.

Table 4 gives the energy differences between the BDEs calculated at DFT/aD level and the BDEs calculated at CCSD(T)/aT level for the *cis*-[L-Pd(PH<sub>3</sub>)<sub>2</sub>Cl]<sup>+</sup> complexes. The dispersion-corrected hybrid, generalized gradient approximation (HGGA) functional ω-B97X-D has the best performance with a mean deviation of 0.6 kcal/mol and a standard deviation of 0.7 kcal/mol, followed by the HGGA functionals BMK, ω-B97X, M06, HSEH1PBE, and PBE1PBE, and the pure GGA functional PW91 and PBE with mean deviations of up to

2 kcal/mol and standard deviations of up to 2.7 kcal/mol. The DFT functionals with a deviation of ~3 kcal/mol include the long-range corrected HGGA functional CAM-B3LYP, the HGGA functionals B3P86, MPW1PBE, TPSSH, MPW1PW91, and MPW3PBE, and the pure GGA functionals TPSS and BP86. The HGGA functional B3LYP shows a fairly poor performance, with an average deviation of ~6 kcal/mol. The local density approximation (LDA) functional gives the worst results, with deviations greater than 10 kcal/mol, consistent with the overbinding expected from use of a local functional.

For the *trans*-[L-Pd(PH<sub>3</sub>)<sub>2</sub>Cl]<sup>+</sup> complexes, the deviations for the DFT functionals from the CCSD(T)/aT results increase by 1–2 kcal/mol as compared to the deviations obtained for the *cis*-complexes (Table 5). The performance ranking of the DFT functionals is almost the same as for those found for *cis*-[L-Pd(PH<sub>3</sub>)<sub>2</sub>Cl]<sup>+</sup>. The best functional for the *trans*-complexes is still ω-B97X-D, with a mean deviation of 1.4 kcal/mol and a standard deviation of 1.5 kcal/mol, which outperforms the 1.6 kcal/mol of mean deviation and 2.1 kcal/mol of standard deviation using the second best functional, ω-B97X. The M06 functional, which was the fourth best for the *cis*-complexes, is comparable to ω-B97X with a mean deviation of 1.7 kcal/mol and a standard deviation of 2.1 kcal/mol. The second best functional for the *cis*-complexes, BMK, however shows a much worse performance for the *trans*-complexes, with BDEs ~4 kcal/mol different from the CCSD(T) values. The pure GGA functional VSXC gives a mean deviation of 3.0 kcal/mol and a standard deviation of 3.8 kcal/mol for the *trans*-complexes, compared to the corresponding deviations of 3.9 and 5.6 kcal/mol for the *cis*-complexes. Other functionals with a deviation no greater than 4 kcal/mol include the HGGA functionals HSEH1PBE, PBE1PBE, B3P86, MPW1PBE, TPSSH, MPW3PBE, and MPW1PW91, pure GGA functionals PW91, PBE, and TPSS, and the long-range-corrected HGGA functional CAM-B3LYP. As expected, the LDA functionals perform the worst for the BDE predictions of the *trans*-complexes.

The benchmark results for the *cis* and *trans* palladium phosphorus complexes suggest that ω-B97X-D is the best functional for the system we studied and can predict BDEs within 1 kcal/mol with respect to CCSD(T)/aT. Other HGGA and pure GGA functionals such as ω-B97X, M06, HSEH1PBE, PW91, PBE, and B3P86 also predict fairly reliable BDEs.

Table 4. Energy Differences between the BDEs by DFT/aD and the BDEs by CCSD(T)/aT for the *cis*-[L-Pd(PH<sub>3</sub>)<sub>2</sub>Cl]<sup>+</sup> Complexes<sup>a</sup>

functional	CO	CH <sub>3</sub> NC	CH <sub>3</sub> CN	NH <sub>3</sub>	PH <sub>3</sub>	AsH <sub>3</sub>	SbH <sub>3</sub>	norbornene	pyrazole	pyridine	THT	m. d.	s. d.
B1B95	-0.6	-2.3	-3.0	-2.2	-3.1	-3.5	-3.9	-4.2	-6.3	-6.1	-4.5	3.6	3.9
B1LYP	-2.6	-4.5	-4.4	-4.0	-6.0	-7.0	-7.9	-9.7	-8.3	-7.6	-7.9	6.4	6.7
B3LYP	-1.4	-3.8	-4.0	-3.6	-5.6	-6.7	-7.4	-8.8	-7.8	-7.0	-7.3	5.8	6.2
B3P86	2.6	0.3	-1.2	-0.5	-1.0	-2.0	-2.7	-3.8	-4.5	-3.9	-3.2	2.3	2.7
B3PW91	0.7	-1.6	-3.3	-2.6	-2.9	-3.8	-4.4	-6.5	-7.2	-6.3	-5.6	4.1	4.6
B971	0.3	-2.0	-2.8	-2.0	-2.8	-3.4	-4.1	-5.0	-6.1	-5.3	-4.2	3.5	3.8
B972	-1.7	-4.1	-5.3	-4.6	-4.6	-5.4	-6.1	-8.9	-9.6	-8.4	-7.6	6.0	6.4
B98	-0.2	-2.4	-3.1	-2.3	-3.4	-4.0	-4.8	-5.9	-6.5	-5.6	-4.8	3.9	4.3
BB95	1.2	-2.2	-4.4	-3.9	-5.1	-6.0	-6.3	-4.7	-8.2	-6.9	-5.0	4.9	5.3
BLYP	-1.0	-4.5	-5.7	-5.7	-7.9	-9.3	-10.2	-10.2	-10.1	-8.5	-8.6	7.4	7.9
BMK	1.0	0.5	1.9	2.7	-0.9	-0.2	-0.7	-0.9	-0.5	-0.3	-0.3	0.9	1.2
BP86	3.5	-0.2	-2.6	-2.0	-2.9	-4.3	-3.2	-2.4	-4.7	-3.2	-2.8	2.9	3.1
BPW91	2.0	-1.6	-4.5	-4.0	-4.4	-5.6	-6.1	-6.9	-8.9	-7.2	-6.2	5.2	5.6
CAM-B3LYP	0.7	-0.6	-0.3	0.1	-1.9	-2.8	-3.7	-5.9	-3.2	-3.2	-4.5	2.4	3.0
G96LYP	-2.4	-6.0	-7.6	-7.5	-9.5	-10.9	-11.7	-13.0	-12.8	-10.8	-11.3	9.4	9.9
HCTH147	-2.1	-5.8	-7.8	-7.4	-8.0	-9.1	-10.0	-12.1	-12.9	-10.8	-10.1	8.7	9.2
HCTH407	-3.7	-7.4	-9.4	-9.2	-9.6	-10.7	-11.6	-14.8	-15.1	-12.7	-12.1	10.6	11.0
HCTH93	-5.4	-9.3	-11.5	-11.2	-11.5	-12.4	-13.2	-17.4	-17.9	-15.1	-14.7	12.7	13.1
HSEH1PBE	2.8	0.7	-0.7	0.1	-0.2	-0.9	-1.5	-2.6	-3.8	-3.4	-2.3	1.7	2.1
M06	1.7	-0.5	0.0	-0.4	0.2	2.9	3.4	1.7	-2.8	-2.2	0.1	1.4	1.9
MPW1LYP	-1.4	-3.3	-3.0	-2.7	-4.8	-5.7	-6.7	-7.9	-6.6	-6.1	-6.3	5.0	5.3
MPW1PBE	1.6	-0.4	-2.0	-1.2	-1.2	-2.0	-2.6	-4.6	-5.6	-4.9	-4.0	2.7	3.2
MPW1PW91	1.4	-0.6	-2.1	-1.3	-1.4	-2.2	-2.8	-4.8	-5.6	-5.0	-4.1	2.8	3.3
MPW3PBE	2.0	-0.2	-1.9	-1.3	-1.6	-2.5	-3.1	-4.6	-5.5	-4.7	-3.9	2.8	3.3
MPWLYP	0.5	-2.9	-4.0	-4.0	-6.3	-7.7	-8.6	-7.8	-7.9	-6.5	-6.5	5.7	6.2
MPWPBE	3.7	0.2	-2.7	-2.2	-2.5	-3.7	-4.3	-4.3	-6.6	-5.1	-3.9	3.6	3.9
MPWPW91	3.5	0.0	-2.7	-2.3	-2.7	-3.9	-4.5	-4.5	-6.6	-5.1	-4.0	3.6	4.0
O3LYP	-5.1	-8.3	-9.9	-9.4	-10.0	-10.8	-11.6	-15.8	-15.8	-13.6	-13.5	11.3	11.7
OLYP	-5.7	-9.7	-11.9	-11.6	-12.1	-13.1	-13.8	-18.0	-18.6	-15.7	-15.4	13.2	13.7
PBE	4.7	1.3	-1.6	-1.0	-1.5	-2.8	-1.6	-0.6	-3.4	-2.1	-1.2	2.0	2.3
PBE1PBE	2.4	0.4	-1.2	-0.4	-0.5	-1.2	-1.8	-3.2	-4.4	-4.0	-2.9	2.0	2.5
PW91	5.2	1.9	-0.8	-0.3	-0.8	-2.2	-1.0	0.3	-2.4	-1.1	-0.3	1.5	2.0
SV5LYP	23.6	20.7	16.8	17.0	15.2	13.4	12.3	20.9	17.7	15.9	17.4	17.4	17.6
SVP86	28.6	25.7	20.4	21.0	20.5	18.8	17.7	27.6	22.0	19.9	22.5	22.2	22.5
SVWN5	17.2	14.3	10.5	10.6	9.4	7.8	6.8	12.0	9.6	9.0	10.1	10.7	11.0
TPSSH	2.5	-0.3	-1.5	-0.7	-1.8	-2.7	-3.4	-3.7	-5.0	-4.1	-3.7	2.7	3.0
TPSS	3.4	0.1	-1.5	-0.9	-2.2	-3.3	-4.0	-3.4	-5.1	-3.9	-3.5	2.8	3.2
VSXC	3.5	0.7	1.6	2.0	0.0	-1.4	-2.4	13.0	4.8	2.8	11.1	3.9	5.6
WB97X	1.1	0.9	0.7	1.9	1.8	1.4	0.5	-2.3	-1.0	-1.3	-1.2	1.3	1.4
WB97X-D	1.2	0.0	-0.3	0.6	0.3	-0.1	-0.8	0.1	-1.6	-0.8	-0.3	0.6	0.7
X3LYP	-0.8	-2.9	-3.1	-2.7	-4.6	-5.7	-6.6	-7.7	-6.7	-6.0	-6.3	4.8	5.2

<sup>a</sup>Negative values show that the DFT BDE is less than the CCSD(T) BDE.

We have previously calculated the PH<sub>3</sub> ligand BDE for the complex PdCl<sub>2</sub>(PH<sub>3</sub>)<sub>2</sub> at the CCSD(T)/complete basis set level and compared the BDE with many of the same functionals used in the current study.<sup>8</sup> As found here, all of the DFT functionals, except for the local SVWN5 which gives too large a BDE, predict a Pd-PH<sub>3</sub> BDE that is too small as compared to the CCSD(T) values. Of even more relevance is that the absolute magnitude of the error is essentially the same for the Pd-PH<sub>3</sub> BDEs in PdCl<sub>2</sub>(PH<sub>3</sub>)<sub>2</sub> and the *cis*- and *trans*-isomers. The best functionals determined for the neutral compound are the same as the ones found for the cation isomers.

**DFT Basis Set Effects.** To study the effect of increasing the basis set size for the DFT calculations on the ligand bond dissociation energies, we compared the BDEs at the DFT/aD and DFT/aT levels. The results are shown in the Supporting Information. The ligands can be grouped into two sets: a group

of small ligands containing 2–6 atoms—AsH<sub>3</sub>, CH<sub>3</sub>CN, CH<sub>3</sub>NC, CO, NH<sub>3</sub>, PH<sub>3</sub>, and SbH<sub>3</sub>—and a group of larger ligands—norbornene, pyrazole, pyridine, and tetrahydrothiophene (THT). For the *cis*-[L-Pd(PH<sub>3</sub>)<sub>2</sub>Cl]<sup>+</sup> complexes, the larger aT basis sets change most of the DFT BDEs by <1 kcal/mol for all of the small ligands and pyridine, and by 2 kcal/mol for the larger ligands norbornene, pyridine, and THT. For the *trans*-[L-Pd(PH<sub>3</sub>)<sub>2</sub>Cl]<sup>+</sup> complexes, the energy changes due to changing the basis set are smaller by ~0.5 kcal/mol. Thus using a larger basis set does not significantly impact the ligand BDEs at the DFT level. In general, the DFT/aT BDEs are smaller in magnitude than the DFT/aD BDEs, and Tables 4 and 5 show that most of the DFT/aD BDEs are smaller than the CCSD(T)/aT BDEs. Thus, increasing the basis set size does not improve the BDEs and, in fact, can make them further from the CCSD(T) results.

Table 5. Energy Differences between the BDEs by DFT/aD and the BDEs by CCSD(T)/aT for the *trans*-[L-Pd(PH<sub>3</sub>)<sub>2</sub>Cl]<sup>+</sup> Complexes<sup>a</sup>

functional	CO	CH <sub>3</sub> NC	CH <sub>3</sub> CN	NH <sub>3</sub>	PH <sub>3</sub>	AsH <sub>3</sub>	SbH <sub>3</sub>	norbornene	pyrazole	pyridine	THT	md	sd
B1B95	-0.6	-2.6	-2.9	-2.7	-4.3	-4.8	-5.2	-5.8	-5.7	-6.3	-5.6	4.2	4.6
B1LYP	-4.3	-6.4	-5.2	-5.5	-8.9	-9.7	-10.6	-14.1	-8.0	-8.8	-9.8	8.3	8.7
B3LYP	-2.5	-5.1	-4.6	-4.9	-7.9	-8.9	-9.8	-12.8	-7.3	-8.1	-8.8	7.3	7.8
B3P86	3.4	0.5	-0.7	-1.0	-2.0	-3.0	-3.7	-5.3	-3.5	-4.0	-3.7	2.8	3.2
B3PW91	1.2	-1.7	-3.0	-3.2	-4.1	-5.0	-5.7	-8.2	-5.9	-6.5	-6.2	4.6	5.1
B971	-0.4	-3.1	-3.2	-3.1	-5.0	-5.6	-6.3	-8.2	-5.7	-6.2	-5.7	4.8	5.2
B972	-1.6	-4.4	-5.4	-5.3	-6.0	-6.8	-7.6	-11.1	-8.3	-8.9	-8.4	6.7	7.1
B98	-1.0	-3.6	-3.5	-3.4	-5.6	-6.2	-7.0	-9.1	-5.9	-6.5	-6.4	5.3	5.7
BB95	3.1	-1.4	-3.4	-4.3	-5.5	-6.5	-6.9	-6.0	-6.8	-6.8	-5.4	5.1	5.4
BLYP	-1.0	-5.4	-5.9	-7.0	-10.0	-11.4	-12.2	-14.3	-9.1	-9.5	-9.9	8.7	9.4
BMK	-3.2	-3.2	0.7	0.9	-5.8	-4.7	-5.5	-7.3	-1.5	-1.8	-4.1	3.5	4.1
BP86	6.1	1.2	-1.2	-2.4	-3.0	-4.7	-5.7	-5.8	-5.0	-5.1	-4.5	4.1	4.4
BPW91	3.9	-0.8	-3.6	-4.4	-4.8	-6.2	-6.8	-8.2	-6.9	-7.1	-6.2	5.4	5.7
CAM-B3LYP	-0.5	-1.9	-0.7	-1.0	-4.1	-4.9	-5.7	-8.9	-3.1	-3.9	-5.8	3.7	4.5
G96LYP	-1.9	-6.5	-7.4	-8.5	-11.2	-12.6	-13.5	-16.5	-10.9	-11.4	-12.1	10.2	10.9
HCTH147	-0.7	-5.4	-7.4	-8.1	-8.8	-10.1	-11.1	-14.4	-10.8	-11.2	-10.4	9.0	9.6
HCTH407	-2.1	-6.9	-9.2	-9.9	-10.3	-11.7	-12.7	-17.0	-12.8	-13.3	-12.3	10.7	11.4
HCTH93	-4.1	-9.0	-11.3	-11.9	-12.4	-13.5	-14.5	-19.7	-15.1	-15.6	-15.0	12.9	13.5
HSEH1PBE	3.1	0.6	-0.5	-0.5	-1.4	-2.2	-2.9	-4.4	-3.2	-3.7	-3.0	2.3	2.7
M06	0.4	-2.1	-0.9	-1.8	-2.6	-0.1	0.2	-0.5	-3.7	-3.9	-2.1	1.7	2.1
MPW1LYP	-3.0	-5.1	-3.9	-4.2	-7.6	-8.4	-9.3	-12.2	-6.5	-7.3	-8.2	6.9	7.4
MPW1PBE	2.2	-0.3	-1.7	-1.7	-2.2	-3.0	-3.7	-5.8	-4.4	-5.0	-4.5	3.1	3.5
MPW1PW91	1.7	-0.7	-1.9	-1.9	-2.6	-3.4	-4.0	-6.3	-4.6	-5.2	-4.7	3.4	3.8
MPW3PBE	2.8	-0.1	-1.6	-1.8	-2.5	-3.5	-4.2	-6.0	-4.3	-4.9	-4.4	3.3	3.7
MPWLYP	0.6	-3.7	-4.1	-5.3	-8.4	-9.7	-10.6	-11.8	-7.2	-7.5	-7.8	7.0	7.7
MPWPBE	6.0	1.3	-1.6	-2.5	-2.8	-4.1	-4.7	-5.2	-4.8	-4.9	-3.7	3.8	4.1
MPWPW91	5.6	0.9	-1.8	-2.7	-3.1	-4.5	-5.1	-5.7	-5.0	-5.1	-4.0	4.0	4.2
O3LYP	-4.4	-8.3	-9.9	-10.2	-11.1	-12.1	-12.9	-17.8	-13.4	-14.1	-13.9	11.6	12.1
OLYP	-4.1	-9.2	-11.6	-12.3	-12.8	-14.0	-14.9	-19.7	-15.6	-16.1	-15.4	13.3	13.8
PBE	7.6	2.8	-0.3	-1.3	-1.3	-3.0	-3.9	-3.4	-3.9	-4.0	-2.7	3.1	3.6
PBE1PBE	3.1	0.5	-0.9	-0.8	-1.5	-2.2	-2.9	-4.5	-3.6	-4.1	-3.4	2.5	2.8
PW91	8.1	3.3	0.6	-0.6	-0.7	-2.5	-3.4	-2.7	-3.0	-3.0	-2.0	2.7	3.4
SV5LYP	30.8	26.1	21.3	18.7	18.5	16.4	15.3	25.2	18.4	18.9	20.1	20.9	21.3
SVP86	37.9	32.9	26.1	23.8	25.6	23.3	22.3	34.6	23.3	24.1	26.5	27.3	27.8
SVWN5	23.1	18.4	14.0	11.8	11.7	9.7	8.8	14.6	10.9	11.1	12.1	13.3	13.9
TPSSH	3.3	-0.2	-1.1	-1.3	-2.7	-3.6	-4.4	-5.2	-3.9	-4.3	-4.3	3.1	3.5
TPSS	4.9	0.6	-0.8	-1.4	-2.8	-3.9	-4.7	-4.8	-3.9	-4.1	-3.8	3.2	3.6
VSXC	2.6	-1.1	-0.4	-0.8	-3.4	-5.0	-5.9	7.2	-2.0	-0.5	4.3	3.0	3.8
WB97X	-1.2	0.0	-0.9	0.2	0.6	-1.0	-1.7	-5.1	-1.8	-2.4	3.0	1.6	2.1
WB97X-D	0.2	-1.2	-0.8	-0.2	-1.8	-2.0	-2.6	-1.9	-1.2	-1.6	-1.6	1.4	1.5
X3LYP	-1.9	-4.3	-3.7	-4.0	-7.1	-8.0	-8.9	-11.6	-6.3	-7.1	-7.8	6.4	7.0

<sup>a</sup>Negative values show that the DFT BDE is less than the CCSD(T) BDE.

**BDEs for Complex 1.** The various ligands discussed above were added to complex 1, {Pd<sub>Z</sub>}(L)<sup>+</sup> (Z = H, F) and the geometries were optimized at the B3LYP/DZVP2/aug-cc-pVDZ-PP level with the DZVP2 basis set<sup>46</sup> used for the atoms H, C, N, O, F, P, and S. The best BDEs at the DFT level for the model compounds were those obtained at the ωB97X-D level with the aD basis set so the ωB97X-D/aD method was used to calculate the BDEs for complex 1 as shown in Table 6. For all of the ligands we studied, the ligand BDE of {Pd<sub>F</sub>}(L)<sup>+</sup> is only ~0.5 kcal/mol greater than the ligand BDE of {Pd<sub>H</sub>}(L)<sup>+</sup> for the same L. The ligand BDEs for {Pd<sub>F</sub>}(L)<sup>+</sup> have the following order: CH<sub>3</sub>NC > pyridine > pyrazole > THT > norbornene > PH<sub>3</sub> > CH<sub>3</sub>CN > NH<sub>3</sub> > SbH<sub>3</sub> > AsH<sub>3</sub> > CO, which is basically same order as the ligand BDE ordering for *trans*-[L-Pd(PH<sub>3</sub>)<sub>2</sub>Cl]<sup>+</sup>. The ligand BDEs of {Pd<sub>F</sub>}(L)<sup>+</sup> are 10–14 kcal/mol smaller than the ligand BDEs of *trans*-[L-Pd-

Table 6. Ligand BDEs (kcal/mol) for {Pd<sub>Z</sub>}(L)<sup>+</sup>, Z = H, F

ligand	Pd-pincer-F	Pd-pincer-H
CO	32.8	32.4
CH <sub>3</sub> NC	48.3	47.6
CH <sub>3</sub> CN	36.2	36.0
NH <sub>3</sub>	35.4	35.0
PH <sub>3</sub>	37.2	36.8
AsH <sub>3</sub>	33.2	32.6
SbH <sub>3</sub>	33.5	32.9
norbornene	38.4	37.8
pyrazole	45.0	44.7
pyridine	45.6	45.4
THT	43.5	43.0



$(\text{PH}_3)_2\text{Cl}]^+$  for the same L, except that the CO BDE of  $\{\text{Pd}_P\}(\text{CO})^+$  is only 7.9 kcal/mol smaller than the CO BDE of  $\text{trans}[\text{CO-Pd}(\text{PH}_3)_2\text{Cl}]^+$ . This latter result is probably due to a smaller steric effect between CO and the two phosphinite moieties in complex **1** than in the other cases.

## CONCLUSIONS

The *trans*-isomers have stronger Pd-L bonds than the *cis*-complexes due to the stability of *cisoid*- $[\text{Pd}(\text{PH}_3)_2\text{Cl}]^+$ , but only the *trans*-complexes with Pd-C bonds are more stable than their *cis*-counterparts. The CCSD(T) values do not show a strong dependence on the basis set. The ligand BDEs correlate with the ligand proton affinity only very qualitatively. The DFT benchmarks show that the dispersion-corrected HGGA functional  $\omega$ -B97X-D is the best functional among all of the benchmarked DFT functionals for this system with  $\omega$ -B97X-D/aD predicting BDEs within 1 kcal/mol of the CCSD(T)/aT BDEs. It is difficult to determine if the HGGA functionals have a significant advantage over the GGA functionals for the palladium(II) phosphorus complexes. Increasing the basis set size for the DFT energy calculations does not improve the BDEs as compared to the BDEs calculated at the higher CCSD(T) level and, in fact, makes the agreement worse. The functionals except for the local one all give binding energies that are too small. The effect of charge on the complex is not important in terms of the errors at the DFT level for the Pd-PH<sub>3</sub> BDE where comparison with previous calculations is possible.<sup>8</sup> The corresponding ligand BDEs for the larger complex **1** are substantially smaller in magnitude than those for the model complexes  $[\text{L-Pd}(\text{PH}_3)_2\text{Cl}]^+$ .

## ASSOCIATED CONTENT

### Supporting Information

Complete author lists for refs 13 and 42. Energy differences between the BDEs at the DFT/aT and DFT/aD levels for the *cis*- and *trans*- $[\text{L-Pd}(\text{PH}_3)_2\text{Cl}]^+$  complexes. Optimized B3LYP Cartesian coordinates (Å) for *cis*- and *trans*- $[\text{L-Pd}(\text{PH}_3)_2\text{Cl}]^+$ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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