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Metal–Phosphine Bonding Revisited. σ-Basicity, π-Acidity, and the Role of Phosphorus d Orbitals in Zerovalent Metal–Phosphine Complexes

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We have performed ab initio calculations to determine the degree of σ-basicity and π-acidity of a series of phosphorus ligands in model compounds of the type Pd–PX_3, *trans*-L–Pd–PX_3 and $(CO)_3Pd$–PX_3 with PX_3 = $P(CH_3)_3$, PH_3, $P(OCH_3)_3$, or PF_3 and L = CO or NH_3. We found that all the phosphine ligands considered are good σ-donors, with PF_3 being only a moderately weaker base than $P(CH_3)_3$. In this respect, we demonstrate the inadequacy of the proton affinity as a measure of the σ-basicity of a ligand in zerovalent metal complexes. Alkylphosphine ligands are also good π-acceptors, but different from the σ-basicity, the π-acidity increases markedly along the series $P(CH_3)_3 < PH_3 < P(OCH_3)_3 < PF_3$. We have analyzed the extent to which the phosphorus 3d orbitals are directly involved in the bonding, in particular in the π-back-donation from the metal to the ligand. The P d functions are essential for a correct description of the metal–phosphorus bond. However, their role is that of polarization functions which can combine with the PX_3 antibonding orbitals to form hybridized π-acceptor orbitals and not that of orbitals directly involved in the charge transfer from the metal. The π-acidity of $P(CH_3)_3$ and PH_3 is considerably reduced upon removal of the phosphorus d functions.

Introduction

The bonding in zerovalent transition metal–phosphine or –phosphite complexes is usually described[1,2] in terms of the Dewar–Chatt model of σ-donation and π-back-donation.[3,4] According to this picture, the PX_3 ligand donates charge to the metal through the P lone pair, and the metal d orbitals back-donate charge into the empty P 3d orbitals.[1,2] This description had been generally accepted until it was shown[5–7] that antibonding P–X orbitals of the PX_3 ligand can act as accepting orbitals without invoking a direct participation of the P 3d orbitals. This interpretation was suggested by ab initio calculations on the free PX_3 ligands[5] and on metal–PX_3 complexes[6] and later supported by a careful analysis of the experimental metal–P and P–X bond lengths in a series of molecules in which the molecular charge was varied.[7] This alternative view of a direct π-back-donation into the antibonding P–X orbitals has received considerable attention and has found its way into recent inorganic textbooks.[8,9] Thus, two opposite descriptions exist for the interpretation of the metal–phosphine bond.

Also the σ-basicity and the π-acidity of phosphine ligands is a controversial subject, despite the large number of techniques applied to study this problem, including IR,[10] UV/vis,[11] photoelectron,[12] Mössbauer,[13] and NMR[14] spectroscopies, X-ray analysis,[15] and electrochemistry.[16] Some authors[17–19] suggest that alkylphosphine ligands are pure σ- and even π-donors[19] with no π-accepting ability, while other authors[20] assume that alkyl- and in particular arylphosphines are good π-acceptors. The origin of this disagreement lies in the difficulty to clearly separate in an experiment the contributions of the two mechanisms.

In this work, we have determined the extent of the participation of the P d orbitals in the bonding in zerovalent metal–phosphine complexes and the relative σ-basicity and π-acidity of a series of phosphorus ligands. We have performed accurate ab initio Hartree–Fock calculations on Pd model compounds and analyzed the corresponding wave functions. Correlation effects have been introduced in few selected cases by means of configuration interaction, CI, calculations. The systems considered are of the type Pd–PX_3, *trans*-L–Pd–PX_3, and $(CO)_3Pd$–PX_3 where PX_3 stands for $P(CH_3)_3$, PH_3, PF_3, $P(OCH_3)_3$ and L is either CO or NH_3.

The calculations (see Appendix for details) have been performed by employing flexible basis sets with and without representation of 3d orbitals on phosphorus. The geometry of the complexes has been fully optimized. The molecular SCF wave functions have been analyzed by means of the constrained space orbital variation

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Table I. Results of the CSOV Analysis (See Text) for Pd–P$(CH_3)_3$, Where the Basis Set Used Includes d Basis Functions on Phosphorus[a]

	d functions on P			no d functions on P		
	D_e, kJ/mol	ΔE, kJ/mol	$\Delta\mu$, au	D_e, kJ/mol	ΔE, kJ/mol	$\Delta\mu$, au
	Variation of PR_3 First					
(1) frozen orbital	−83			−80		
(2) $P(CH_3)_3$ polarization	−81	+2	+0.11	−79	+1	+0.09
(3) $P(CH_3)_3 \rightarrow$ Pd donation	−34	+47	+0.33	−32	+47	+0.29
(4) Pd polarization	+12	+46	−0.32	+11	+43	−0.28
(5) Pd → $P(CH_3)_3$ back-donation	+52	+40	−0.29	+37	+26	−0.21
(6) full SCF	+64	+12	+0.13	+46	+9	+0.14
	Variation of Pd First					
(1) frozen orbital	−83					
(2) Pd polarization	−37	+46	−0.21			
(3) Pd → $P(CH_3)_3$ back donation	+1	+38	−0.36			
(4) $P(CH_3)_3$ polarization	+6	+5	+0.16			
(5) $P(CH_3)_3 \rightarrow$ Pd donation	+56	+50	+0.27			
(6) full SCF	+64	+8	+0.10			

[a] The analysis has been performed at the equilibrium geometry, r(Pd–P) = 2.36 Å. In the first part of the table, results are reported for the variation of the $P(CH_3)_3$ ligand first followed by the variation of the Pd atom; in the second part, the order of the variation has been changed. The dissociation energy, D_e in kJ/mol, has been computed as E[Pd] + E[P$(CH_3)_3$] − E[Pd–P$(CH_3)_3$]. ΔE gives the contributions of each CSOV step to the D_e; changes in the dipole moment, $\Delta\mu$ in au, are also given.

(CSOV)[21] technique which provides a measure of the relative importance of σ- versus π-bonding. We have determined the importance for the various substituents on P in PX_3 and for the contributions of the d orbitals on P. Details of the CSOV approach are given in the Appendix.

We will show that the d functions on P play a significant role in the description of the bonding with the metal center; their major effect is to produce a considerable shortening and strengthening of the metal–P bond. However, the role of the d's is essentially that of polarization functions, favoring the formation of hybridized π-orbitals on PX_3[5–7,22] and not that of acceptor orbitals. The antibonding P–X orbitals can form π bonds with the metal even in the absence of P d orbitals;[5,6] however, the presence of the d functions on P considerably reinforces the back bonding. The role of the d's in improving the description of the π-back-donation is particularly large for ligands like $P(CH_3)_3$ and PH_3 compared to PF_3, or phosphites.

We will also show that all the phosphine ligands considered act simultaneously as σ-donors and π-acceptors and that alkylphosphines also have an appreciable π-acidity. However, while the σ-donor ability is not very sensitive to the nature of the substituents on P, the π-acidity changes markedly going from alkylphosphines to PF_3.

Bonding in Pd–P$(CH_3)_3$: σ- versus π-Charge Transfer

First, we address the problem of how to measure the extent of σ- and π-charge transfer in a complex. To this end, we have determined the molecular wave function with some constraints, according to the CSOV procedure (see the Appendix).[21]

We will discuss briefly the complete results for Pd–P$(CH_3)_3$; the analysis has been performed with and without d orbitals on P (Table I). In both cases the geometry is that optimized with the P d functions. We have kept the geometry fixed in order to analyze the electronic effects induced by the removal of the d's on P without confusing these effects with geometric changes. The first step of the CSOV consists in superposing, for r(Pd–P) = r_e, the "frozen" charge densities of the Pd and $P(CH_3)_3$ fragments computed separately. This step measures the extent of the Pauli repulsion arising from the nonbonding overlap of the two fragments. In the following steps, the $P(CH_3)_3$ unit is allowed to vary while the Pd charge density is frozen. Then the $P(CH_3)_3$ density is fixed, and the Pd unit is allowed to vary. This order of the constrained variations is completely arbitrary.[21,23] Thus, we have performed the variation in two ways, varying first the $P(CH_3)_3$ unit and then the Pd atom and vice versa; see Table I. The results, however, are virtually independent of the order of the variation. Before we discuss the results, it is worth mentioning that the bonding mechanisms measured by the CSOV are virtually unaffected by basis set superposition errors, BSSE, which are on the order of few kilojoules per mole; see Appendix.

The polarization of $P(CH_3)_3$ is negligible, <5 kJ/mol, while that of Pd is large, ≃50 kJ/mol. A significant contribution to the polarization of Pd in response to the presence of the $P(CH_3)_3$ ligand is from the 4d hybridization, or promotion, to 5sp. In the unconstrained, full SCF, wave function for Pd–P$(CH_3)_3$, the Pd configuration is $4d^{10-x}\,5sp^{x}$, where x is small, ≃0.1–0.2 electrons. In particular, the projection of the free Pd atom 4d orbitals onto the Pd–P$(CH_3)_3$ wave function[24a] gives a 4d occupation of 9.9, which corresponds to $x \simeq 0.1$. The Mulliken population analysis gives a Pd configuration close to $4d^{8.7}\,5sp^{1.3}$; see Table II. However, the population analysis strongly overestimates the 5s and underestimates the 4d occupations. On the other hand, the projection gives an upper bound to the Pd 4d occupation, but this upper bond is a better estimate than that given by the Mulliken population.[24a–c]

The $P(CH_3)_3$ σ-donation to Pd is the most important interunit, or covalent, contribution to the bonding, ≃50 kJ/mol. This σ-donation and the Pd polarization are almost unaffected by the presence of the d's on P. The Pd to $P(CH_3)_3$ back-donation is only slightly smaller than the σ-donation; its contribution to the interaction energy is ≃40 kJ/mol, with the d's on P. This result is of considerable importance because it shows that even trialkylphosphine ligands have a remarkable π-acidity. Upon removal of the d's, the π stabilization is still large but reduced to 26 kJ/mol (Table I).

An additional measure of the intermolecular charge transfer is given by the changes in the molecular dipole moment, μ. Since the nuclei are fixed and oriented along the z axis, with the P atom at positive z, changes in the dipole moment, $\Delta\mu$, reflect the charge rearrangement for the particular CSOV steps. The $\Delta\mu$ values for the donation and back-donation steps indicate the charge transfer between the fragments. The sign of $\Delta\mu$ is such that $\Delta\mu > 0$ represents charge flow from $P(CH_3)_3$ toward Pd and vice versa. This is because the C_{3v} axis of Pd–P$(CH_3)_3$ has been chosen as the z axis with Pd at $z = 0$ and P at $z > 0$. The charge flow for the σ-donation, $\Delta\mu \simeq 0.3$ au, is similar but opposite to that associated with the π-back-donation, $\Delta\mu \simeq -0.3$ au; see Table I. In the absence of the d's on P, $\Delta\mu$ at the π-back-donation step is ≃30% smaller than with the d's, Table I.

The dipole moment analysis further supports the view of a significant π-back-donation for trialkylphosphine ligands. The difference in dissociation energy, D_e, determined with and without d's on P, 64 and 46 kJ/mol, respectively, is almost entirely due to the change in π-back-bonding, 40 vs 26 kJ/mol (Table I).

The dependence of the various bonding mechanisms on the Pd–P distance has been examined by performing the CSOV analysis at six points around r_e(Pd–P) with and without d functions

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Table II. Mulliken Population Analysis for $P(CH_3)_3$ and $Pd–P(CH_3)_3$ Molecules Computed with and without d Functions on P

		P				Pd[a]			
		s	p	d	charge	s	p	d	charge
$P(CH_3)_3$	with no d's	5.70	8.75		+0.55				
	with d's	5.75	8.95	0.07	+0.24				
$Pd–P(CH_3)_3$	with no d's	5.65	8.86		+0.50	3.29	6.06	8.74	–0.10
	with d's	5.67	8.91	0.11	+0.31	3.35	6.08	8.67	–0.10

[a] An 18-electron ECP is used for Pd; the ground-state atomic configuration is $4s^2\ 4p^6\ 4d^{10}$.

on P; see Figures 1 and 2. The Pauli repulsion contribution grows nearly exponentially as the Pd–P distance decreases. The dominant attractive contributions, σ-donation, π-back-donation, and Pd polarization, on the other hand, increase their importance more or less linearly as the bond distance decreases. However, while the Pauli repulsion, the σ-donation, and the Pd polarization curves are virtually identical when computed with and without d's on P (the differences are always less than 2–3 kJ/mol), the π-back-donation is considerably smaller without d's on P for the entire range of Pd–P distances considered; see Figures 1 and 2. The final potential energy curve results from the sum of all the bonding terms and the elongated minimum computed without d's originates from the reduced π-back-bonding. Clearly, the d's on P play an important role in the bonding. This is the subject of the next section.

The Role of Phosphorus 3d Orbitals

The importance the P d basis functions in the description of the bonding with Pd is shown by the Pd–P equilibrium bond distances, r_e, and the D_e's, see Table III. Upon inclusion of d's on P, the bond distances decrease by ≃0.11–0.14 Å, corresponding to a ≃5% shrinkage of the Pd–P bond, and the D_e's increase by ≃30–60%, depending on the nature of X. As a consequence, the inclusion of d basis functions on P changes the order of the stability of the $Pd–PX_3$ compounds. When d functions on P are included, the order of the $Pd–PX_3$ bonding is $Pd–PF_3 \simeq Pd–P(CH_3)_3 \simeq Pd–P(OCH_3)_3 > Pd–PH_3$; when d functions are not included, it is $Pd–P(CH_3)_3 > Pd–P(OCH_3)_3 \simeq Pd–PF_3 \simeq Pd–PH_3$; see Table III.

The difference between the bonding with and without d basis functions on P may arise from two possible ways in which these functions could affect the chemical bonding. When d functions are included in the basis set, it becomes possible to represent P 3d atomic orbitals, and the changes that occur could be a consequence of the direct involvement of P 3d orbitals in the bond with Pd. In fact, it is often assumed that this is the role of P d basis functions. However, another possibility is that the d functions are polarization functions. That is, they allow a representation of the polarization of the P 3p orbitals due to the nonspherical potential of the PX_3 ligand. This possibility can be explored by adding a p function to the $Pd–PX_3$ basis set at the bond midpoint between Pd and P. A bond midpoint p function can describe the polarization of the P 3p orbitals; however, it cannot describe the P 3d orbital!

We have studied $Pd–P(CH_3)_3$ adding a single p function ($\alpha_p = 0.5$) at the bond midpoint but without P d functions. The $P(CH_3)_3$ bond distances and angles were fixed as those obtained without P d functions. $r_e(Pd–P) = 2.37$ Å is essentially the same as $r_e(Pd–P) = 2.36$ Å obtained with P d functions. Even with the fixed $P(CH_3)_3$ geometry, the D_e is lowered by 9 kJ/mol. This is strong evidence that the P d functions allow the polarization of PX_3. The 3d orbitals are not involved in the Pd–P bond!

The role of the d orbitals, or even of a p polarization function at the bond midpoint, is to change the properties of the isolated PX_3 ligand. A careful analysis of the energy and spatial extent of the PX_3 π virtual orbitals clearly shows that in the presence of the d functions the π* orbitals of the $P(CH_3)_3$ fragment become stabilized and move away from CH_3 and toward Pd. The overall effect is to enhance the Pd to PX_3 π-back-donation.

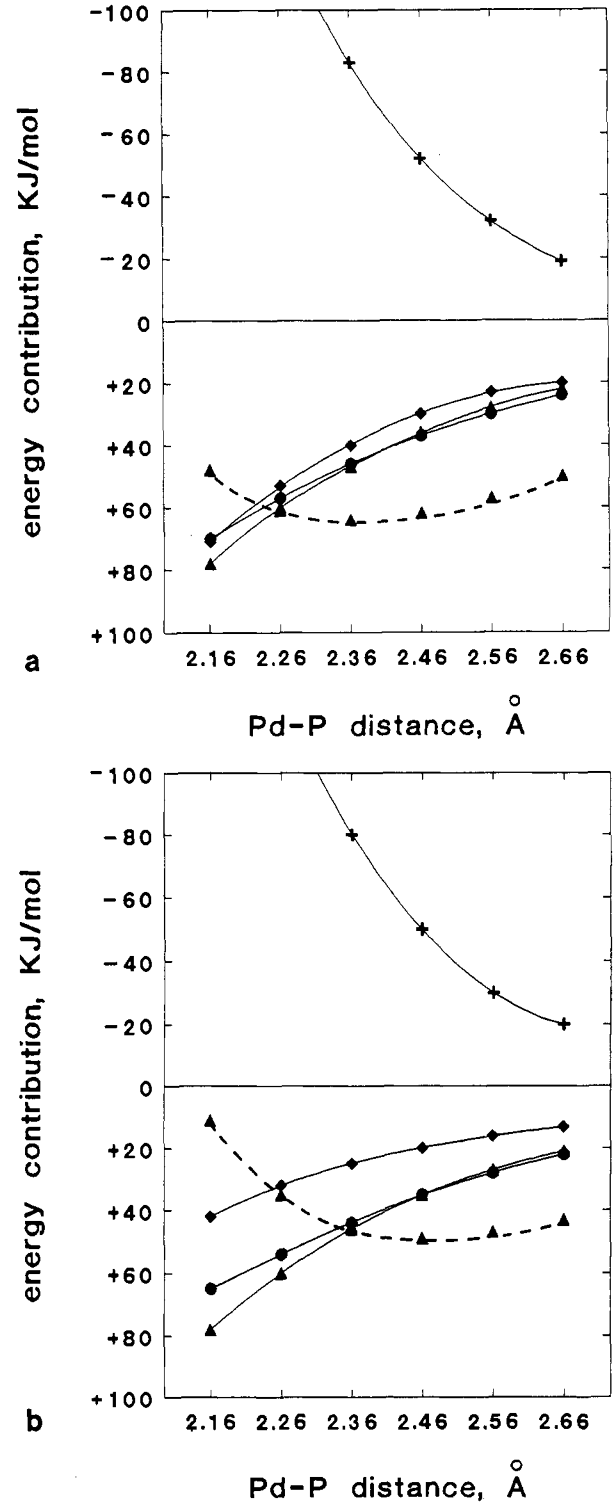

Figure 1. Bonding contributions in $Pd–P(CH_3)_3$ as function of r(Pd–P) determined according to the CSOV procedure (see text): (a) d functions are included in the P basis set; (b) no d functions on P. Key: (+—+) Pauli repulsion; (▲—▲) σ-donation; (●—●) Pd polarization; (◆—◆) π-back-donation; (▲- -▲) full SCF curve.

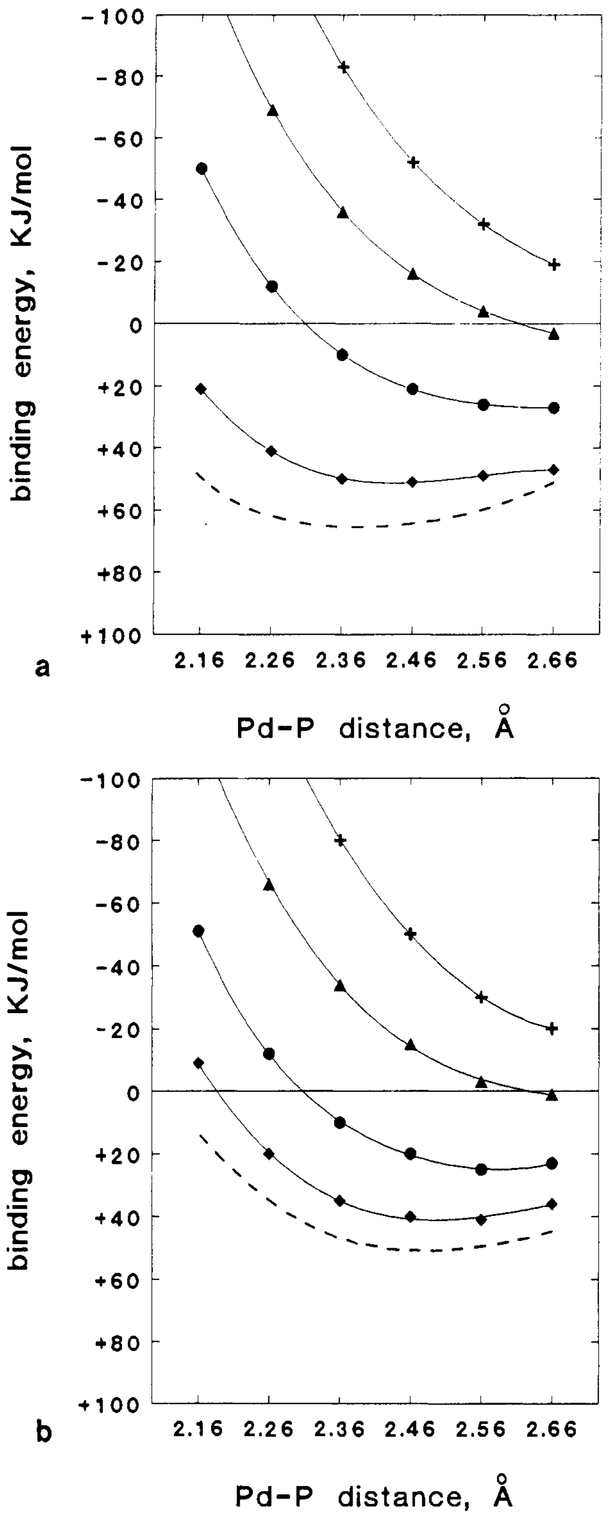

Figure 2. Potential energy curves in Pd–P(CH$_3$)$_3$ determined by adding the various bonding mechanisms: (a) d functions are included in the P basis set; (b) no d functions on P. Key: (+—+) Pauli repulsion; (▲—▲) Pauli repulsion + σ-donation; (●—●) Pauli repulsion + σ-donation + Pd polarization; (◆—◆) Pauli repulsion + σ-donation + Pd polarization + π-back-donation; (- -) full SCF curve.

A widely used[5,6,22,25] measure of the participation of the P d functions in the π-back-donation is given by the Mulliken gross population analysis.[26] It is well known that this analysis has no physical meaning;[27] nevertheless, the Mulliken population is useful for qualitative purposes. The inspection of the Mulliken charges for Pd–P(CH$_3$)$_3$ indicates that the population of the P d orbitals increases upon coordination to the Pd atom by 0.04 electrons only, see Table II; the removal of the P d's has only modest consequences on the d population of Pd.

Table III. Optimal Geometrical Parameters, r_e and α_e, and Dissociation Energies, D_e, for Pd–PX$_3$ Complexes Computed with and without d Functions on Phosphorus

	P basis set	r_e(Pd–P), Å	r_e(P–X), Å	α_e(Pd–P–X), deg	D_e, kJ/mol
P(CH$_3$)$_3$	with no d's		1.90	118	
	with d's		1.85	118	
Pd–P(CH$_3$)$_3$	with no d's	2.47	1.89	117	48
	with d's	2.36	1.85	117	64
	no d's; 1 p^a	2.37			57
PH$_3$	with no d's		1.41	120	
	with d's		1.41	121	
Pd–PH$_3$	with no d's	2.48	1.40	120	37
	with d's	2.34	1.40	120	54
P(OCH$_3$)$_3$	with no d's		1.68	116	
	with d's		1.61	116	
Pd–P(OCH$_3$)$_3$	with no d's	2.41	1.67	116	42
	with d's	2.30	1.61	116	63
PF$_3$	with no d's		1.65	121	
	with d's		1.58	120	
Pd–PF$_3$	with no d's	2.36	1.65	121	40
	with d's	2.24	1.57	121	65

^{a} One p polarization function (α_p = 0.5) was placed at the bond midpoint.

The conclusions described above are based on the use of SCF wave functions. Electron correlation effects have been taken into account by computing the CI potential energy curves for the Pd–P(CH$_3$)$_3$ stretching with and without d basis functions. The 10 4d electrons of Pd and the two P(CH$_3$)$_3$ lone pair electrons have been correlated (see Appendix). Correlation effects induce a considerable shortening, $\simeq$0.07 Å, of the Pd–P bond length; this decrease in r_e is the same when basis sets with and without d's on P are used. With P d functions, the correlated CI D_e is larger by 24 kJ/mol than without P d functions; this is similar to the P d function increase of the SCF D_e of 16 kJ/mol. Further, the CI value of ω_e for the Pd–P stretch is $\simeq$20% larger than the SCF value but the increase in ω_e is very similar for the basis sets with and without P d functions. Thus, the CI change in r_e, D_e, and ω_e indicate that correlation effects, although important to determine accurate values of some properties, do not change the picture obtained at the SCF level. This is consistent with the fact that the Hartree–Fock wave function has a large weight in the CI expansion, $c^2 \simeq 0.93$.

σ and π Contributions in Different Phosphorus Ligands

The energy and dipole moment contributions, ΔE and $\Delta\mu$,[21] from σ-donation and π-back-donation steps of the CSOV were computed with P d functions at r(Pd–P) = r_e for all the PX$_3$ ligands, Table IV. It turns out that the amount of σ-donation is not too different for the four ligands considered; even the PF$_3$ ligand, despite the electronegative substituents, acts as a moderate σ-donor. On the contrary, the π-accepting ability changes dramatically as function of X. The π-back-donation is not too different from the σ-donation in Pd–P(CH$_3$)$_3$, it becomes larger than the σ-donation in Pd–PH$_3$ and Pd–P(OCH$_3$)$_3$, and it clearly dominates in Pd–PF$_3$; see top of Table IV. It is well-known that PF$_3$ is a π-acceptor of comparable strength to CO in metal complexes[28] as well as on metal surfaces.[21b]

The CSOV analysis was repeated by removing the P d functions. It turns out that the σ-donor capability is moderately affected by

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Table IV. σ-Donation and π-Back-Donation Contributions in Pd–PX$_3$ Complexes (X = CH$_3$, H, OCH$_3$, F) As Determined by the CSOV Analysis for Wave Functions with and without d Functions on Phosphorus (See Also Table I)[a]

	r_e(Pd–P)	D_e	σ-donation ΔE	σ-donation $\Delta\mu$	π-back-donation ΔE	π-back-donation $\Delta\mu$
d Functions on P, Equilibrium Geometry						
Pd–P(CH$_3$)$_3$	2.36	64	47	+0.33	40	–0.29
Pd–PH$_3$	2.34	51	38	+0.26	47	–0.36
Pd–P(OCH$_3$)$_3$	2.30	63	53	+0.23	59	–0.49
Pd–PF$_3$	2.24	66	44	+0.20	85	–0.56
No d Functions on P, Equilibrium Geometry						
Pd–P(CH$_3$)$_3$	2.47	49	33	+0.25	20	–0.17
Pd–PH$_3$	2.48	37	27	+0.18	13	–0.11
Pd–P(OCH$_3$)$_3$	2.41	43	43	+0.15	35	–0.32
Pd–PF$_3$	2.36	40	34	+0.17	51	–0.44

[a] The dissociation energy, D_e, and the σ- and π-interaction energy contributions, ΔE, are in kJ/mol, the dipole moment changes, $\Delta\mu$, in au, and the bond distances, r_e(Pd–P), in Å.

Table V. Results of the CSOV Analysis (See Text) for (CO)$_3$Pd–PH$_3$ and (CO)$_3$Pd–PF$_3$ Complexes[a]

	(CO)$_3$Pd–PH$_3$ ΔE, kJ/mol	(CO)$_3$Pd–PH$_3$ $\Delta\mu$, au	(CO)$_3$Pd–PF$_3$ ΔE, kJ/mol	(CO)$_3$Pd–PF$_3$ $\Delta\mu$, au
PX$_3$ polarization	18	+0.10	5	+0.13
PX$_3$$\rightarrow$Pd(CO)$_3$ donation	65	+0.58	54	+0.35
Pd(CO)$_3$ polarization	41	–0.23	45	–0.40
Pd(CO)$_3$$\rightarrow$PX$_3$ back-donation	66	–0.39	72	–0.48

[a] The analysis has been performed for r[(CO)$_3$Pd–PH$_3$] = 2.34 Å and r[(CO)$_3$Pd–PF$_3$] = 2.24 Å; d functions on P were included in the basis set. ΔE gives the energetic contribution of each CSOV step; changes in the dipole moment, $\Delta\mu$, in au, are also given.

the removal of the P d orbitals; there is only a small change, $\simeq$10–30%, in ΔE and $\Delta\mu$, Table IV. The change of the π-back-donation on the contrary is significant, with a loss of $\simeq$50–70% of the π-back-bonding stabilization in Pd–P(CH$_3$)$_3$ and in Pd–PH$_3$, and of $\simeq$40% in Pd–P(OCH$_3$)$_3$ and Pd–PF$_3$. (A similar effect was observed on the Ni(PF$_3$)$_4$ complex.[28a])

The change in Pd–P distance, and the related change in the π-acidity, are by far the main consequences, although not the only ones, of the removal of the P d functions. In fact, the d's on P also help the description of the P–X bond[26] and alter the P–X bond distance as well, Table III.

It is worth noting that the complexes which are more affected by the absence of the d's are Pd–PH$_3$ and Pd–P(CH$_3$)$_3$. In Pd–PH$_3$, in particular, the extent of π-back-donation in absence of P d orbitals is very small, and the ligand acts more as a σ-donor than as a π-acceptor. This is reversed with respect to the case where the d's are present, see Table IV. Thus, the use of PH$_3$ to model more complex phosphine ligands in theoretical calculations is justified only for qualitative purposes.

These results have been obtained on simplified model complexes of the type Pd–PX$_3$; to prove that the results are also valid for real complexes, we have repeated the CSOV analysis on more realistic molecules of the type (CO)$_3$Pd–PX$_3$, with X = H and F; see Table V. A pseudotetrahedral geometry was assumed for the (CO)$_3$Pd–PX$_3$ complexes, and the Pd–PX$_3$ and Pd–CO distances were taken from the optimal values found for the *trans*-L–Pd–PX$_3$ molecules; see below and Table VII. In this case, we also found that PF$_3$ is only a moderately weaker σ-base than PH$_3$, as shown by both the ΔE_{int} and $\Delta\mu$ values at the PX$_3$$\rightarrow$Pd(CO)$_3$ donation step, while it is a somewhat stronger π-acid. Therefore, the results obtained with the simplified Pd–PX$_3$ models are fully supported by the CSOV analysis performed on a coordinatively saturated complex.

Table VI. Proton Affinity of PX$_3$ Molecules (X = CH$_3$, H, OCH$_3$, F) Computed as the Energy Difference of the [H–PX$_3$]$^+$ Complex with Respect to the Deprotonated Molecule Where the Stabilization Energy Has Been Decomposed into the Sum of Electrostatic, PX$_3$ Polarization, and σ-Donation Contributions[a]

		protonation energy, kJ/mol				
	r_e(P–H),[b] Å	electrost	polarizn of PX$_3$	σ-donation	total[c]	gas-phase expt
P(CH$_3$)$_3$	1.39	517	29	391	937 (999)	934[d]
PH$_3$	1.39	375	27	377	779 (832)	783[d]
P(OCH$_3$)$_3$	1.39	362	28	376	766 (901)	912[e]
PF$_3$	1.39	156	28	351	535 (633)	669[f]

[a] See text for a description of the decomposition of the PA into these three terms. [b] The distance of the proton from the P atom has been optimized by keeping fixed the PX$_3$ unit. [c] In parentheses are given the values for the fully optimized [H–PX$_3$]$^+$ structure. [d] Reference 32. [e] Reference 33. [f] Reference 34.

Table VII. Optimal Distances, in Å, and Bond Dissociation Energies, in kJ/mol, for L–Pd–PX$_3$ Complexes (L = CO, NH$_3$; X = CH$_3$, H, OCH$_3$, F) Computed with and without d Functions on Phosphorus

complex	phosphorus basis set	r(Pd–P), Å (Δr,[a] Å)	r(P–X), Å	r(Pd–L), Å	D_e, kJ/mol Pd–P	D_e, kJ/mol Pd–L
CO–Pd–P(CH$_3$)$_3$	with no d's	2.49 (+0.02)	1.88	1.99	80	83
	with d's	2.43 (+0.07)	1.84	2.01	91	79
NH$_3$–Pd–P(CH$_3$)$_3$	with no d's	2.39 (–0.08)	1.89	2.23	86	92
	with d's	2.30 (–0.07)	1.85	2.25	112	102
CO–Pd–PH$_3$	with no d's	2.50 (+0.02)	1.40	2.00	61	76
	with d's	2.41 (+0.07)	1.40	2.03	69	70
NH$_3$–Pd–PH$_3$	with no d's	2.39 (–0.09)	1.40	2.23	72	90
	with d's	2.27 (–0.07)	1.40	2.26	97	101
CO–Pd–P(OCH$_3$)$_3$	with no d's	2.42 (+0.01)	1.66	2.04	59	68
	with d's	2.36 (+0.06)	1.60	2.05	81	70
NH$_3$–Pd–P(OCH$_3$)$_3$	with no d's	2.30 (–0.11)	1.67	2.24	87	99
	with d's	2.22 (–0.08)	1.61	2.27	117	109
CO–Pd–PF$_3$	with no d's	2.35 (–0.01)	1.65	2.09	45	57
	with d's	2.27 (+0.03)	1.58	2.13	67	53
NH$_3$–Pd–PF$_3$	with no d's	2.26 (–0.10)	1.66	2.24	97	112
	with d's	2.18 (–0.06)	1.58	2.25	130	119

[a] Δr is computed with respect to the Pd–PX$_3$ complex (see Table III); it measures the change in r_e(Pd–P) due to the addition of the CO or NH$_3$ ligands trans to PX$_3$.

Proton Affinity and σ-Basicity of Phosphine Ligands

We have shown that all the ligands considered act at the same time as σ-donors and π-acceptors; we have no evidence of a phosphine ligand which is a pure σ-donor or a pure π-acceptor. Furthermore while the π-accepting ability changes considerably as function of the PX$_3$ ligand, the σ-donation is only slightly smaller in PF$_3$ than in P(CH$_3$)$_3$. Apparently, this conclusion contradicts the general belief that the trend in σ-basicity is, as measured by pK_a values, PF$_3$ < P(OCH$_3$)$_3$ < P(CH$_3$)$_3$.[9,29] However, the pK_a values are not appropriate measures of basicity. For instance, they are sensitive to the solvation energies of the phosphorus compound; the order of basicity is often reversed in solution with respect to the gas phase.[30,31] Moreover, the pK_a values refer to the interaction of the PX$_3$ molecule with the hard acid H$^+$, rather than a soft acid such as a transition metal atom. In other words, the large electric field created by the proton is not present in a zerovalent complex.

The proton affinity, PA, of PX$_3$ depends on three terms: (1) the purely electrostatic interaction between the electric field associated with the proton, H$^+$, and the PX$_3$ charge distribution (permanent dipole, quadrupole, and higher moments), (2) the induced polarization of PX$_3$, and (3) the σ-donation from PX$_3$

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(29) For a discussion of various measures of phosphine basicity, see: Busch, R. C.; Angelici, R. J. *Inorg. Chem.* **1988**, *27*, 681.

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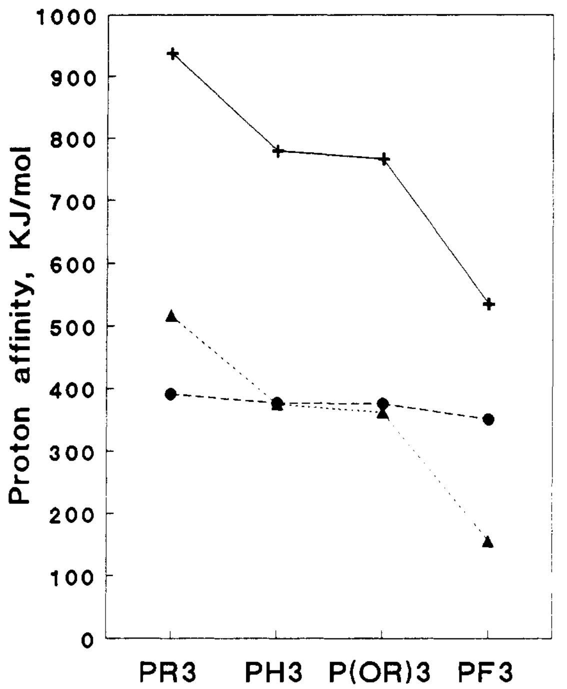

Figure 3. Electrostatic (···) and σ-donation (- -) contributions to the proton affinities (—) of phosphorus ligands. See also Table VI.

to the unoccupied orbitals of the proton. Of these three terms, the first two are absent or practically negligible in zerovalent metal–phosphine complexes; see steps 1 and 2 of the CSOV (Table I). We have decomposed the PA of PX_3 into the contributions from these three terms. For the electrostatic and PX_3 polarization contributions, we have used a model of a point charge, PC, of +1 denoted $[PC-PX_3]^+$. The electrostatic contribution is given by the energy lowering of the charge distribution of the PX_3 in the presence of the PC. The PX_3 polarization contribution is given by the energy lowering of the full SCF energy of $[PC-PX_3]^+$. For the PX_3 σ-donation to the proton, the PC is replaced by a proton to form $[H-PX_3]^+$; the only difference between $[PC-PX_3]^+$ and $[H-PX_3]^+$ is that the latter model has basis functions which can accept charge from PX_3. The $[PC-PX_3]^+$ model does not include these functions, and the PC cannot accept charge. Thus, the σ-donation is given by $E_{SCF}([H-PX_3]^+) - E_{SCF}([PC-PX_3]^+)$. This decomposition is given in Table VI and Figure 3.

The computed trend in PA (Table VI) is that usually expected, with $P(CH_3)_3$ which has a PA about 300 kJ/mol larger than PF_3, in satisfactory agreement with the gas-phase data.[32-34] However, the differences in the PA are almost entirely due to the electrostatic term and not to the σ-donation which is nearly constant along the series, see Figure 3; $P(CH_3)_3$ is only a $\simeq$10% stronger base than PF_3. This is fully consistent with the fact that the σ-donor ability varies only moderately as function of X in $Pd-PX_3$ complexes. The σ-donation in $[H-PX_3]^+$ is much larger than that in $Pd-PX_3$. This is because it is energetically more favorable to add charge to the positively charged H^+ than to an almost neutral Pd atom.

Structural Changes Induced by a Ligand Trans to PX_3

The structural changes induced by trans ligands on the metal–PX_3 bonding have been the subject of several experimental studies.[20,35] We have investigated the structural changes induced by the addition of a ligand trans to $Pd-PX_3$; the two ligands considered are CO and NH_3 (Table VII). It is generally accepted that CO is a good π acceptor and NH_3 is a good σ donor. For the interaction of CO with metal surfaces[21] and with metal atoms,[21c] CSOV analyses have confirmed that CO is, indeed, a good π acceptor. For the interaction of NH_3 with Cu surfaces[21b] and Al surfaces[21a,b] the CSOV analyses indicate that electrostatic effects arising from the large dipole moment of NH_3 make much important contributions to the metal–NH_3 bond than does the NH_3 σ-donation. The geometry of the $L-Pd-PX_3$ complex (L = CO, NH_3) has been fully optimized and considerable changes in the Pd–P bond occur. These changes, however, are not the same for basis sets with and without d functions on P; see Table VII.

The CO ligand should be expected to reduce the extent of the π-back-donation from Pd to PX_3 because CO, a good π acceptor, competes with PX_3 to form dative covalent bonds with Pd. The elongation of the Pd–P bond is consistent with a reduced Pd to PX_3 π-back-donation. The magnitude of this elongation is large, $\simeq$0.06–0.07 Å, when P d functions are present, negligible otherwise. This is an additional indication that, in the absence of P d basis functions, the Pd–P π-back-bonding is poorly represented; the system is not very sensitive to the addition of a strong π-acceptor like CO. The effect is not the same for all the PX_3 ligands; PF_3 is the strongest π acceptor, and the elongation of the Pd–P bond length in $Pd-PF_3$ is small, 0.03 Å; it is 0.06 Å for the intermediate π-acid $P(OCH_3)_3$ and 0.07 Å in the other cases. Hence, the change in metal–P distance induced by CO closely follows the scale of π-acidity of PX_3. It is also worth noting that there is a direct correlation between the importance of the π-back-donation for the $Pd-PX_3$ bond and the bond strength and bond length for Pd–CO. For the best π-acceptor, PF_3, the Pd–CO bond length is longer than those in any of the other $CO-Pd-PX_3$ systems; it is longer by 0.12 Å than that for $P(CH_3)_3$ which is the poorest π-acceptor. The Pd–CO bond strength is strongest for $CO-Pd-P(CH_3)_3$ and weakest for $CO-Pd-PF_3$. Because PF_3 is a good π-acceptor, there is less Pd dπ charge available to form a π bond with CO; the Pd–CO bond is weak and the bond length is long. The opposite is true for $P(CH_3)_3$ which is a poor π-acceptor leaving more Pd dπ charge available to form a strong Pd–CO bond. The r(Pd–CO) and D_e(Pd–CO) for the other phosphines, PH_3 and $P(OCH_3)_3$, are intermediate between those for $P(CH_3)_3$ and PF_3.

The effect of σ-donation from NH_3 to Pd is to increase the electron density on the metal and, as a consequence, to lead to increased π-back-donation from Pd to PX_3; this will strengthen the $Pd-PX_3$ bond and reduce the Pd–P bond length. However, we note that the electric field associated with the NH_3 dipole moment,[21b] which has the direction H^+N^-, could have a similar effect on the Pd to PX_3 π-back-donation. This electric field should make it energetically favorable to move charge on Pd away from the N atom and toward PX_3; thus, it could act to increase the $Pd-PX_3$ π-back-donation. The Pd–P bond shrinkage is rather large, $\simeq$0.06–0.11 Å, no matter which basis set is used, Table VII. As a result of the increased Pd to PX_3 π-back-donation, the D_e for the $Pd-PX_3$ bond in $NH_3-Pd-PX_3$ is significantly larger than for $Pd-PX_3$ alone; compare Tables III and VII. The increase of the $D_e(Pd-PX_3)$ is larger when d functions are included on P; this is completely consistent with our interpretation that the $Pd-PX_3$ dative π bond is stronger when these polarization functions are included. However, the change (reduction) in the Pd–P bond length is larger when the P basis set does not include d functions than when it does. This would appear to be inconsistent with the fact that the P d functions lead to stronger Pd–P π bond, but a

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Table VIII. C–O Equilibrium Bond Distances, r_e, and Vibrational Frequencies, ω_e, in *trans*-CO–Pd–PX_3 Computed with and without d Functions on P with Experimental Values for the $Ni(CO)_3PX_3$ Complex Also Given

	with P d's		without P d's		exptl[38]
	r_e, Å	ω_e, cm^{-1} ($\Delta\omega$,[a] cm^{-1})	r_e, Å	ω_e, cm^{-1} ($\Delta\omega$,[a] cm^{-1})	ω_e, cm^{-1} ($\Delta\omega$,[b] cm^{-1})
CO–Pd–$P(CH_3)_3$	1.134	2235 (–55)	1.135	2228 (–62)	2064 (–79)
CO–Pd–PH_3	1.132	2247 (–43)	1.133	2236 (–54)	
CO–Pd–$P(OCH_3)_3$	1.131	2254 (–36)	1.131	2257 (–33)	2085 (–58)
CO–Pd–PF_3	1.127	2292 (+2)	1.127	2292 (+2)	2111 (–32)

[a] $\Delta\omega$ is determined with respect to the computed CO ω_e, 2290 cm^{-1}.
[b] $\Delta\omega$ is determined with respect to the experimental CO ω_e, 2143 cm^{-1}.

careful analysis of the contributions to the bond length show that this behavior is not at all inconsistent with a shortening of the Pd–P π bond. The Pd–P distance computed with the d's on P is already 5% shorter than that computed without; the further reduction of the distance caused by the NH_3 ligand competes with the increase of the Pauli repulsion, which grows nearly exponentially as the metal–ligand distance decreases.[36] Although the π-back-donation is considerably reinforced in the presence of NH_3, the decrease in bond length is limited by the increase in Pauli repulsion. This effect should always be taken into account in the correlation of bond distances with, for instance, the π-acidity of a ligand. The equilibrium bond distance, see Figures 1 and 2, results from the balance of several mechanisms and not from a single bonding contribution.[36]

Finally, it is worth noting that the presence of a second ligand increases the stability of the Pd–PX_3 bond (cf. Tables III and VII), an effect which has been observed also for other linear complexes[37] and which can arise from both electrostatic and rehybridization mechanisms.

Correlation of the CO ω_e with the Phosphine Acidity

The position of the CO IR absorption band in molecular complexes of the type $M(CO)_n(PX_3)_m$ varies as function of the nature and the number of phosphines coordinated to the metal center.[38] The corresponding CO vibrational frequencies are often used as an indirect measure of the relative basic or acid strength of the PX_3 ligand. We have computed the CO ω_e for the *trans*-CO–Pd–PX_3 model complexes (Table VIII), and we found a direct relationship between the CO ω shift of coordinated CO with respect to free CO and the PX_3 π-acidity; see also Table IV. $P(CH_3)_3$ is the poorest π-acceptor and CO exhibits the largest negative ω shift; PF_3 is such a good π-acceptor that the CO ω shift is virtually zero (Table VIII). The computed red shifts of the CO ω_e closely follow the experimental trend, $P(CH_3)_3 >$ (PH_3, not measured) $> P(OCH_3)_3 > PF_3$. This indicates that the observed CO ω shifts[38] can be explained on the basis of the π-acidity only, without the necessity to assume also a significant difference in the amount of σ-charge transfer.

Because we have not included electron correlation effects, the absolute values of the CO ω_e are too large by $\simeq 170$ cm^{-1}.[39] However, the trend of the ω_e for different PX_3 groups is expected to remain the same if a more accurate treatment of the CO ω_e is made.

Conclusions

Largely on the basis of experimental data, the properties of phosphorus ligands have been roughly parametrized into electronic and steric components.[38,40] The further separation of the electronic term into σ and π components is, however, not easy to determine from experimental measurements. This has led to some disagreement about the more or less basic or acid nature of a given PX_3 ligand.

The present calculations show that all the PX_3 ligands considered, including PF_3, are good σ-donors. This may seem to be in contrast with the usual assumption that the σ-donor ability decreases as $P(CH_3)_3 \gg P(OCH_3)_3 \gg PF_3$;[9,29] these assumptions are based, for instance, on the pK_a values of phosphonium ions, $[H–PX_3]^+$, or on the measurement of the stretching frequencies of CO in $(CO)_nM–PX_3$ complexes as a function of X.[38] We have shown that the proton affinities are not good measures of the σ-donor ability of a phosphine ligand in a complex. This is because the difference in PA arises mainly from the electrostatic interaction between the electric field generated by the proton and the PX_3 charge distribution; the σ-donation contribution to the PA is only 10% larger in $P(CH_3)_3$ than in PF_3. On the other hand, our results show that the major consequences induced by the nature of the substituent X are in the π-acidity, which follows the trend $P(CH_3)_3 < P(OCH_3)_3 < PF_3$.

We have shown that the PX_3 ligands are potential σ-donors and π-acceptors. However, it is clear that the σ-basicity and the π-acidity of a phosphorus ligand varies as function of the metal to which is bound as well as of the other ligands in the complex; the actual degree of basicity or acidity can vary dramatically as the chemical environment changes.

The P d basis functions are essential for a correct description of both the length and the strength of the metal–P bond. Their role, however, is that of polarization functions rather than of orbitals directly accepting charge from the metal. The vacant antibonding P–X orbitals of PX_3 act as π-acceptors even in the absence of the P d's but their π-acidity increases considerably when the d orbitals are present. This is because the d polarization functions help the formation of hybrid π-acceptor orbitals.[7] For alkylphosphine ligands, in particular, the π-acidity is appreciable in the presence of P d's, but is modest otherwise.

The present work is based essentially on the analysis of Hartree–Fock wave functions. Electron correlation effects are important for some properties of the systems that we have considered, in particular to obtain accurate values for the D_e's and r_e's. However, the main purpose of this work is not to determine accurate values of these properties but to identify the relative importance of the various bonding mechanisms in different phosphorus ligands. We believe that our qualitative analysis based on ab initio SCF wave functions will not change in a major way when correlation effects are included.

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Appendix. Computational Details

Self consistent field (SCF) molecular orbital (MO) calculations were carried out within the Hartree–Fock computational scheme employing a relativistic effective core potential (ECP)[41] to replace the $1s^2$ to $3d^{10}$ core electrons of the Pd atom. The Pd $4s^2\,4p^6\,4d^{10}$ electrons were explicitly included in the valence. The Gaussian basis set for Pd, [5s,5p,4d/5s,4p,3d],[41] is of triple-ζ plus polarization type (TZP). Six components of the d functions were used. With this basis set, the energy of the ground state of the Pd atom (^1S, $4d^{10}$) is –125.869 014 au.

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The remaining atoms were treated at the all electron level. The basis set for P is that of Dunning,[42] [13s10p/6s5p]; the 3d orbitals of P have been represented by two Gaussian functions of exponents $\alpha = 0.537$ and $\alpha' = 0.153$.[43] The final basis sets for P are thus of TZ (no d functions) or TZP (with d functions) quality. The basis sets for the substituent groups in PX_3 (X = CH_3, F, OCH_3, H) are of double-ζ, DZ, quality;[39] only the methyl group in $P(OCH_3)_3$ was treated at single-ζ level with a MINI-1 basis set.[44] The CO and NH_3 ligands were described by a split-valence MIDI basis set.[44] The H basis set used to compute the proton affinities is of TZP type.[42]

These basis sets are sufficiently flexible to avoid the occurrence of a large basis set superposition error (BSSE). The BSSE of the computed stabilities has been determined for the case of Pd–$P(CH_3)_3$ adopting the method proposed by Boys and Bernardi,[45] which gives an upper bound to the BSSE. For the case with d functions on P, the BSSE correction on the dissociation energy is 7 kJ/mol; when the P d functions are removed, the BSSE error is only slightly larger, 8 kJ/mol.

The molecular geometry optimization, based on analytical gradient techniques, has been carried out by means of the HONDO-8 program.[46] Our interpretation for the bonding, based on the CSOV procedure,[21] has been performed by means of the MOLECULE-ALCHEMY program package.[47]

Correlation effects have been introduced for Pd–$P(CH_3)_3$ through single–double configuration interaction, SD-CI, calculations. The 10 4d electrons of Pd and the two lone pair electrons of $P(CH_3)_3$ have been correlated. This gives a CI expansion of $\simeq$23 000 configurations with d's on P and $\simeq$19 500 configurations without P d functions. The dissociation limit has been computed by performing a SD-CI calculation on a supermolecule where the two fragments, Pd and $P(CH_3)_3$, are separated by 1000 au. Thus, the CI D_e's are affected by a size-consistency error which slightly overestimates the stability of the complex.

The CSOV procedure is described in detail in ref 21; we present here a brief summary of its essential features. The CSOV approach has been used to determine the character of the bonding for several atomic and molecular adsorbates to surfaces.[48a–e] It has also been used for the analysis of the bonding in metal complexes[23b,48f] and of hydrogen bonding in the water dimer.[48g] (1) The analysis starts from the interaction of fixed densities, or frozen orbitals, FO, of the separated units, Table I; for the Pd atom, the FO starting point is for the ground state $4d^{10}$ configuration. (2) $V(PX_3;PX_3)$: here, the Pd orbitals are fixed as the free atom orbitals; polarization of the PX_3 orbitals within the PX_3 centered basis set is allowed. (3) $V(PX_3;\text{full basis})$: the virtual linear combinations of the Pd centered basis functions are included in the PX_3 variational space and PX_3 to Pd donation is possible. (4) $V(Pd;Pd)$: the PX_3-occupied orbitals, as changed by polarization and charge transfer, are fixed as determined in step 3 and intraunit polarization of Pd is allowed. (5) $V(Pd;\text{full basis})$: Pd to PX_3 donation is possible since the PX_3 virtual orbitals are included in the variational space. The results of CSOV step 5 are compared to a full, unconstrained calculation. If they are similar, as in Table I, the CSOV has included all important bonding effects.

When both σ-donation and π-back-donation are important, there may be a synergistic coupling between them, and the results of the CSOV at step 5 will be different from the unconstrained full SCF result. For example, in $Fe(CO)_5$, the binding energy in CSOV step 5 is $\simeq$100 kJ/mol smaller than the SCF value.[48f] This is because of the coupling of large contributions from the σ- and π-donations with each other and with the intraunit polarizations. This synergistic coupling is taken into account by making another cycle of constrained variations. When this is done for $Fe(CO)_5$, the CSOV interaction is different from the full SCF value by less than 10 kJ/mol.[48f] The small differences for the D_e of Pd–$P(CH_3)_3$ between CSOV step 5 and the full SCF result (Table I) show that the synergistic coupling is small and that a second cycle of constrained is not needed.

Furthermore, the results of Table I show that the changes in the bonding contributions due to the different order of variation are minor.

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