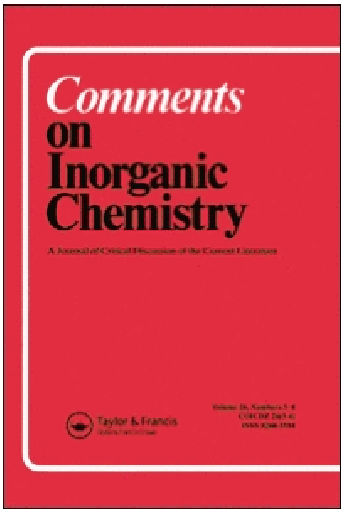

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The Role of the d Orbitals of the Phosphorus Atom in the Metal-Phosphine Coordination Bond

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The Role of the d Orbitals of the Phosphorus Atom in the Metal–Phosphine Coordination Bond

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Ab initio calculations carried out on PX_3 ($X = CH_3$, H and F) ligands and on the $(PX_3)_2Pt$ complexes have shown that the d orbitals of the phosphorus atom may be important for an improved description of the molecular geometry and stability, since they produce a sizeable shortening of the M–P bond. However, the occupancy of the d orbitals is small, both in free and coordinated ligands, a fact which excludes a significant spd hybridization.

The analysis of the electronic wavefunctions determined with and without d functions on the P atoms reveals that the π back-bonding mechanism has an increasing importance along the series CH_3, H, F, in agreement with the common chemical expectation. However, the results definitely show that the d functions on P atoms are unimportant in determining the extent of the metal-to-phosphine back-bonding.

Key Words: *theory of coordination bond, metal–phosphine coordination bond, electronic structure of transition metal complexes, ab initio calculations*

1. INTRODUCTION

The Dewar–Chatt model[1] of sinergic σ-donation and π back-donation in the metal–phosphorus bond (M–P) has been widely accepted, since it can qualitatively account for several spectroscopic[2]

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and structural[3] observations. In the conventional description,[4] the π-acidity of the PX_3 ligands is ascribed to the presence of the 3d orbitals on the phosphorus atom (d_P) which are assumed to lie not too high in energy with respect to the occupied d orbitals of the metal atom (d_M) and to possess a proper symmetry to give relevant d_P–d_M overlap.

Recent theoretical studies of PX_3 ligands[5] and related metal complexes[6] have shown that the π-acidity of PX_3 can be described in a substantially correct way without invoking the contributions of d_P's, the major role being played by the (locally) antibonding σ^* orbitals of the PX_3 group. A careful reinterpretation of X-ray data concerning MP and PX equilibrium distances[7] seems to converge to the same basic conclusions.

Very recently, the role of the d_P functions in stabilizing the M–P bond has been theoretically analyzed in a very direct way on the basis of results of Hartree–Fock (HF) ab initio calculations on $(PH_3)_2Pt$ and $(PH_3)_2Pt(\eta^2O_2)$ complexes, carried out with basis sets including and not including d orbitals on P atoms.[8] The exact nature of the d_P functions used in HF calculations will be discussed in the following sections. Here, the results of Ref. 8 can be summarized briefly as follows. (i) The d_P functions induce a shortening of the theoretically computed PtP distance of about 0.07 Å. (ii) The complex stability (ΔE) evaluated at HF level increases by about 40% when d_P functions are used. It must be noted however that the HF ΔE values are usually largely underestimated because the HF method ignores the interelectron correlation effects. As shown in Ref. 8, such effects can be much more important than those due to the participation of the d_P's. In fact, at a correlated level, the increase of ΔE due to the d_P's is only about 20%. Therefore, the claim that the d_P orbitals are essentially important to stabilize the M–P bond can be misleading when based on results of the HF method only, due to its inherent approximations: the worse is the HF description, the larger might result the stabilizing effect due to the d_P functions. (iii) The population analysis has shown that the d_P occupancy is always small and very similar in free and coordinated phosphine ligands. Therefore, if an important π back-donation effect occurs, this cannot be ascribed to the presence of the d_P orbitals.

The present note is an extension of the work of Ref. 8: the model complexes $(PX_3)_2Pt$ ($X = CH_3$, H and F) have been studied with and without d_P functions, at the HF level. The corresponding wavefunctions have been analyzed in terms of the occupation numbers of the MO's belonging to the fragments forming the complex. Such an analysis generates a quantitative representation of the M–P coordination bond in terms of σ and π contributions or, equivalently, in terms of basicity and acidity of the ligands.

2. THE ONE-ELECTRON APPROXIMATION, THE ORBITAL PICTURE AND THE ELECTRON DISTRIBUTION IN THE M–P COORDINATION BOND

When discussing the σ-π theory of the metal–ligand (M–L) bond, it is of basic importance to realize that the model is essentially based on the one-electron orbital picture. The molecular orbitals (MO) located on various ligands forming the complex are considered either fully occupied (in closed shell systems) or completely empty. Their mutual interaction and their interaction with the atomic orbitals (AO) of the metal center are mainly determined by the nodal and symmetry properties and by the relative energy position.

However, the basic concepts on which the σ-π theory is based (the one-electron orbitals and the associated one-electron energies) have a quite poor physical meaning and become ill defined when correlated wavefunctions are considered, that is, when the many-electron system is studied with rigorous theoretical approaches. In this sense, the Dewar–Chatt model must be considered as derived from a low-level quantum chemical picture: its validity is limited to a qualitative rationalization of the bonding properties of ligands and to a pictorial representation of the charge transfer which accompanies the formation of the coordination bond. Attempts at translating the σ-π model into a more quantitative scheme can be misleading if the underlying simplifications from which the model is built are ignored. All these observations aim to point out that our analysis of the σ-π contributions and the role of the d_P's in the M–P bond has validity if and only if the one-electron approximation is *a priori* considered as acceptable.

In the following, the theoretical basis of the analysis of the electron distribution within a complex, in terms of occupancies of MO's of the constituent fragments, will be reviewed.

Let us consider the wavefunction of the complex ψ^c to be an antisymmetrized product of MO's φ_i^c ($i = 1, \ldots, m_c$), which are expanded in a set $\{\chi_i^c\}$ of fixed functions, according to $|\varphi^c\rangle = |\chi^c\rangle$ $\mathbf{T}^c$. The aim is to decompose the electron density associated with ψ^c in terms of contributions assigned to the MO's on fragments f (f will denote the metal M and the various ligands $L_1, L_2, \ldots$). We suppose that the basis set $\{\chi_i^c\}$ of the complex includes all the sets $\{\chi_i^f\}$ of the individual fragments. The MO's of the fragment f are defined as $|\varphi^f\rangle = |\chi^f\rangle\mathbf{T}^f = |\chi^f\rangle(\mathbf{T}_o^f\mathbf{T}_v^f)$, where the coefficient matrix $\mathbf{T}^f$ is considered as partitioned into occupied $\mathbf{T}_o^f$ and virtual $\mathbf{T}_v^f$ parts, respectively, which enter the definition of the one-electron density matrix $\mathbf{R}_o^f = \mathbf{T}_o^f\tilde{\mathbf{T}}_o^f$ and the corresponding "empty" density matrix $\mathbf{R}_v^f = \mathbf{T}_v^f\tilde{\mathbf{T}}_v^f$. Also, $\mathbf{R}_o^f$ and $\mathbf{R}_v^f$ are representations of the projectors onto the space of occupied and unoccupied orbitals, respectively. For $\alpha = o$ or v, one has

$$\hat{\rho}_\alpha^f = |\chi^f\rangle\mathbf{R}_\alpha^f\langle\chi^f| = \sum_i |\chi^f\rangle T_{i\alpha}^f \tilde{T}_{i\alpha}^f\langle\chi^f| = \sum_i \hat{\rho}_{i\alpha}^f.$$

If $\mathbf{S}^f = \langle\chi^f|\chi^f\rangle$ indicates the overlap matrix for the fragment f, then the two following basic relations hold for the projector $\hat{\rho}_\alpha^f$:

$$\mathrm{Tr}\hat{\rho}_\alpha^f = \mathrm{Tr}\mathbf{S}^f\mathbf{R}_\alpha^f = m_\alpha^f; \quad \mathrm{Tr}\hat{\rho}_{i\alpha}^f = 1, \tag{1}$$

$$\hat{\rho}_\alpha^{f2} = \hat{\rho}_\alpha^f\hat{\rho}_\alpha^f = |\chi^f\rangle\mathbf{R}_\alpha^f\mathbf{S}^f\mathbf{R}_\alpha^f\langle\chi^f| = |\chi^f\rangle\mathbf{R}_\alpha^f\langle\chi^f| = \hat{\rho}_\alpha^f, \tag{2}$$

where m_α^f is the number of occupied ($\alpha = o$) or unoccupied ($\alpha = v$) MO's of the fragment f.

Equation (1) (closure property) and Eq. (2) (idempotency property) are satisfied only by a set of orthogonal elementary projectors, or, in other words, only orthogonal projectors lead to a *correct count* of the electrons. Clearly, Eqs. (1) and (2) are automatically fulfilled by the orthogonal sets $\{\varphi_i^f\}$ of each fragment ($\tilde{\mathbf{T}}_i^f\mathbf{S}^f\mathbf{T}_j^f = \delta_{ij}$). Different considerations must be done when several fragments are present and characterized by a non-zero overlap $\langle\varphi^f|\varphi^{f'}\rangle \neq 0$. In this case the operator $\hat{P} = \Sigma_f|\varphi^f\rangle\langle\varphi^f|$ is not a projector on the full space because $\hat{P}^2 \neq \hat{P}$. This is due to the fact that $\bar{\mathbf{S}} = (\tilde{\mathbf{T}}^{f_1}\tilde{\mathbf{T}}^{f_2}\ldots)\mathbf{S}(\mathbf{T}^{f_1}\mathbf{T}^{f_2}\ldots) \neq 1$.

The only possible correct definition of projectors for a composite system must be based on re-orthogonalized MO's, that is,

$$\hat{\rho} = \sum_f |\varphi^f\rangle \mathbf{S}^{-1} \langle\varphi^f| = \sum_f |\bar{\varphi}^f\rangle\langle\bar{\varphi}^f|,$$

with $|\bar{\varphi}^f\rangle = |\chi\rangle\bar{\mathbf{T}}^f = |\chi\rangle\mathbf{T}^f(\bar{\mathbf{S}})^{-1/2}$.

Of course, the $|\bar{\varphi}^f\rangle$ MO's are now supposed to be expanded in the common set $\{\chi_i^c\}$.

Clearly, the re-orthogonalization process can produce *distortion* of the original free ligand MO's. This is however an unavoidable point; the use of the $(\bar{\mathbf{S}})^{-1/2}$ matrix, on the other hand, guarantees that the distortion is the smallest one possible (in the least-squares sense[9]), compatible with the orthogonality constraints.

A given orbital $\bar{\varphi}_i^f$ can now be used as a projector acting on the full set of the occupied orbitals of the complex φ_j^c. The quantity

$$\omega_i^f = \sum_j \langle\varphi_j^c|\bar{\varphi}_i^f\rangle\langle\bar{\varphi}_i^f|\varphi_j^c\rangle$$

has the meaning of occupation number of the fragment orbital $\bar{\varphi}_i^f$ within the complex. The condition that the quantity $2\Sigma_{i,f}\omega_i^f$ is equal to the total number of electrons in a (closed-shell) complex is now automatically satisfied. If $\bar{\varphi}_i^f$ belongs to the set of occupied orbitals of f, then $\omega_i^f \leq 2$, while if $\bar{\varphi}_i^f$ is unoccupied in the free fragment f, ω_i^f is different from zero, but usually quite small. The difference $2 - \omega_i^f$ is the measure of *basicity* of $\bar{\varphi}_i^f$ being equal to the number of the *donated* electrons. For MO's which are virtual in free fragments, the quantity ω_i^f measures the number of *accepted* electrons, or the acidity of $\bar{\varphi}_i^f$.

Rigorously, in order to project exactly all the electrons of the complex, one should use all the possible projectors of all the fragments. We have verified, however, that in the case of Pt-phosphine complexes the number of electrons projected onto the subspaces spanned by core and valence orbitals of the metal atom and phosphine ligands plus the $6p_M$ and the first e and a_1 (C_{3v} symmetry notation) MO's unoccupied in the free phosphine ligand is already extremely close to the exact value. This simplifies the discussion since the *chemical* meaning of the first empty orbitals is evident.

The long digression on the properties of the projectors was motivated by the need to clearly establish the limits and validity of such an analysis. The first application of projectors defined with the help of MO's of the free ligands to the study of σ and π contributions to the M–CO bond in $Ni_x(CO)_y$ clusters has been made[10] within the framework of the Neglect of Diatomic Overlap (NDO) approximation. In this case the condition $\bar{S} = 1$ is satisfied by definition and the above formulation is exactly valid. Later studies[11] were done, on the contrary, within computational schemes characterized by $\bar{S} \neq 1$, but using an incorrect definition of the projectors because the overlap among fragments was neglected. As shown above, this inconsistency can be easily removed by simple theoretical considerations. In spite of this, projectors wrongly defined have been widely employed by Pacchioni *et al.*[12] in a series of papers devoted to the study of the ionic/covalent character of the M–L bond. In order to show how large can be the error caused by an inconsistent definition of the projectors, one can consider the simple case of the H_2 molecule. The occupied bonding orbital, expressed in terms of 1s orbitals on the two atoms, say χ_1 and χ_2, has the form $\varphi = (2 + 2S)^{-1/2}(\chi_1 + \chi_2)$, $S = \langle\chi_1|\chi_2\rangle$. The application of the operator $\hat{P} = |\chi_1\rangle\langle\chi_1| + |\chi_2\rangle\langle\chi_2|$ (which neglects the non-orthogonality terms) leads to the quantity $\langle\varphi|\hat{P}|\varphi\rangle = 1 + S$. The corresponding number of projected electrons $(2 + 2S)$ is even larger than 3 for a HH distance of 0.7 Å, at which $S \approx 0.66$.

The role of the d_P orbitals in the M–P bond can be analyzed, in principle, also in terms of orbital occupancies computed according to the standard definition of McWeeny[13] or Mulliken,[14] or one of the several variants.[15] It is not uncommon to find in the quantum chemical literature strong criticisms against the population analysis,[16] often defined as an unphysical approach. It is certainly true that orbital populations are not physical observables since AO's lose their significance within a molecule and the partition of the total charge among basis functions is, to some extent, arbitrary. In spite of these limitations, many chemical concepts developed in the past and used for decades are just based on the Mulliken analysis. For instance, the use of ideas associated with the formal atomic charge (oxidation number) or acid–base behaviour of ligands in complexes is implicitly based on Mulliken-type analysis, since it represents an attempt at partitioning the total molecular charge over fragments and orbitals centered on fragments. Under the condition that only *variations* in populations are considered, along a series of analogous molecules described with similar basis sets, the Mulliken analysis remains a powerful tool to interpret the electronic wavefunction in terms of traditional (and useful) chemical concepts.

3. THE 3d ORBITALS OF THE PHOSPHORUS ATOM AND THE d_P FUNCTIONS OF THE PHOSPHINE LIGANDS

The free P atom has a ^4S (. . . $3s^23p^3$) electronic ground state. Experimental data[17] concerning energies of various excited states are reported in Table I. The lowest state with d orbitals in the leading configuration is the ^2F state (. . . $3s^23p^23d^1$), lying at 8.747

TABLE I

Experimental and theoretical data for the phosphorus atom[a]

State[b]		Energy Level
(. . .) $3s^23p^3$	^4S	0.000
$3s^23p^24s^1$	^4P	6.967
$3s^13p^4$	^4P	7.395
$3s^23p^24p^1$	^4D	8.136
$3s^23p^23d^1$	^2F	8.749
$3s^23p^2(P^+)$	^3P	10.980

Atomic HF results:
Ground state ^4S, E_T = -340.71214

^2F state (. . . $3s^23p^2sd^1$)[c]

E_T	$\Delta E(^2F \leftarrow {}^2S)$	ζ_d	C_d
−340.37581	9.15	0.19749	0.06989
		0.03762	0.40927
		0.01137	0.69746
−340.36994	9.31	0.01611	1.00000

[a] Energy levels and excitation energies (ΔE) in eV. Total energies (E_T) in au.

[b] Only the lowest state for a given electron configuration is reported. The state energies are averaged over the J multiplets.

[c] ζ_d and C_d are the optimized exponents of the 3d orbitals and the associated expansion coefficients.

eV above the ground state and less than 2 eV below the ionization limit (10.486 eV). Note that several other states exist which are more stable than the ^2F state and correspond to excitations to 4s and 4p orbitals.

We have derived an optimal description of the 3d orbitals for the ^2F state by means of variational calculations carried out with three d Gaussian functions, with optimized exponents. The exponents of s and p functions are those of Ref. 18 for the ^4S state, while have been reoptimized for the ^2F one. Atomic energies equal to −340.71214 and −340.37467 au (1 au of energy = 27.21 eV) for ^4S and ^2F states, respectively, correspond to an excitation energy $^2F \leftarrow {}^4S$ of 9.182 eV, which is in acceptable agreement (in the absence of all correlation effects) with the experimental value. Qualitatively correct results can be obtained even with a single (optimized) d function (see Table I). As can be seen from the data of Table I, the d Gaussian functions mainly involved in the description of the ^2F state are the most diffuse ones. The plot of the 3s, 3p and 3d orbitals of the ^2F state (see Fig. 1) clearly shows the relative radial expansion of valence orbitals. The outermost max-

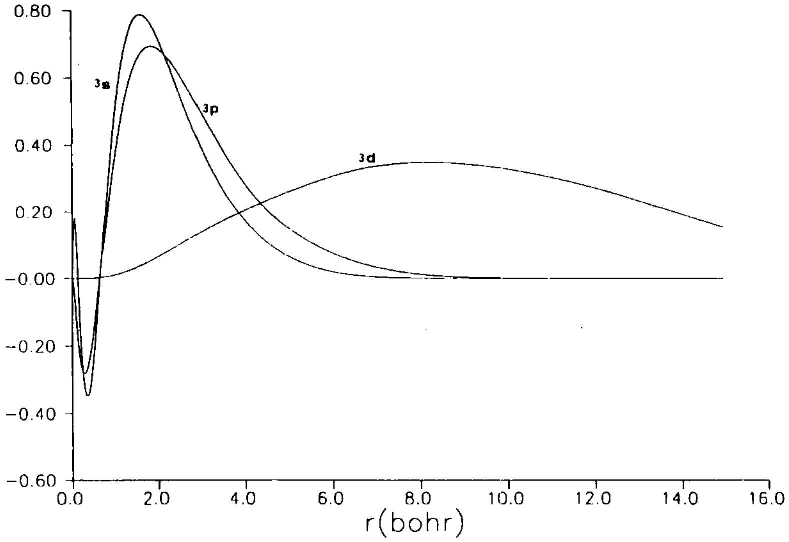

FIGURE 1 3s, 3p and 3d orbital radial functions of the P atom (^2F, . . . $3s^23p^23d^1$).

imum occurs at about 2 bohr (1 bohr = 0.529 Å) for 3s and 3p and about 9 bohr for 3d.[19] The following conclusion is obvious: the 3d orbitals lying high in energy and characterized by large spatial diffusion cannot be useful to form hybrid orbitals (which, by definition, must possess pronounced directionality) with the s and p orbitals. As a consequence, pure atomic 3d orbitals are of little importance in the description of the bond within the PX_3 ligands.

This is demonstrated in a more direct way by the results of our ab initio HF calculations on $P(CH_3)_3$, PH_3 and PF_3 molecules. The adopted basis sets is of STO 4-31G type[20] on all the atoms, with (or without) an additional d_P function on the P atom. The exponents of the d orbitals (ζ_d) for the three ligands have been derived from a simultaneous optimization of the molecular structure and the exponent itself. The ζ_d values so obtained are, by definition, the best possible values, compatible with the HF approach and the structure of the 4-31G basis. In addition, in the case of the PH_3 ligand, calculations have been carried out centering on the P atom and function with $\zeta_d = 0.016$ which is very close the optimum (single-zeta) value for the ^2F atomic state.

The results of the HF calculations concerning the PX_3 ligands are reported in Table II. The optimized ζ_d values are equal to 0.546, 0.495 and 0.572 for X = CH_3, H and F, respectively. All are much higher than the values characteristic for the 3d orbital of the free atom. This means that the best d_P functions in PX_3 are spatially much more contracted than the 3d atomic orbitals, thus having radial expansion similar to that of the 3s and 3p orbitals. This is exactly the requirement which the *polarization functions* should obey. In quantum chemical calculations, the polarization functions are necessary to properly account for the variation in shape of the electron distribution around an atom when this is involved in chemical bonds, that is, subjected to an electric field no longer spherical. In the total wavefunction the polarization functions usually have an amplitude much smaller than that of the true valence orbitals but can play a determinant role in the energetics of the chemical bond.

This is just what occurs in the case of the PX_3 molecules. The total d_P occupancies, computed according to the Mulliken approach, are equal to 0.141, 0.157 and 0.353, for X = CH_3, H and

TABLE II

Optimum geometry and charge distribution for PX_3
($X = CH_3$, H and F) ligands[a]

	$X = CH_3$	$X = H$	$X = F$
best ζ_d[b]	0.546	0.495(0.016)	0.572
PX[cd]	1.926	1.433	1.639
	1.873	1.410(1.433)	1.572
XPX[cd]	100.4	95.0	99.6
	101.1	94.0 (95.0)	96.9

Mulliken population data[f]

	$X = C$		$X = H$		$X = F$	
	no d_P	d_P	no d_P	d_P	no d_P	d_P
P s	5.734	5.599	5.774	5.678(5.776)	5.621	5.542
p_σ	3.450	3.463	3.492	3.477(3.492)	2.917	2.922
p_π	5.347	5.413	5.670	5.716(5.668)	4.672	4.716
d_σ		0.007		0.010(0.000)		0.062
d_π		0.068		0.092(0.000)		0.139
d_δ		0.066		0.055(0.000)		0.152
X[g]s	3.406	3.380	1.021	0.992(1.021)	4.008	3.983
p	3.304	3.268			5.589	5.506

[a] XZ bond distances, Å; XZY valence angles, deg.

[b] ζ_d indicates the optimized exponent for d functions on P atom (see text).

[c] The results obtained without and with d_P's are reported in the first and second entry, respectively. The results obtained with ζ_d set to the best atomic value (0.016) are reported in parenthesis.

[d] HC = 1.080 and 1.082 Å, without and with d_P's, respectively.

[e] HCP = 110.07 and 110.96°, without and with d_P's, respectively.

[f] The σ, π and δ orbitals are defined with respect to the C_3 symmetry axis. The results obtained with ζ_d equal to 0.016 are reported in parenthesis.

[g] The average population on s_H orbital is 0.815 and 0.827, without and with d_P's, respectively.

F, respectively, which must be considered, in general, as relatively small. The net atomic charges on the P atom, for $X = CH_3$, H and F, are equal to 0.469, 0.064, 1.790 and 0.384, -0.028, 1.467 without and with d_P's, respectively (see Table II). These data allow an important observation: the best ζ_d values do not correlate with the net charge on the P atom nor with the inductive effects of the X groups. In particular, the d orbital exponent for PH_3 is much higher than the best free-atom value despite the fact that the net charge on P is almost zero. Several attempts have been made in the past to explain the shrinking of the 3d orbitals in molecules as due to inductive effects or, equivalently, to a positive charge located on the P atom. Such speculations have been pushed so far that even "experimental" evidence for d orbital contraction has been proposed.[21] However, the hypothesis that a positive charge on P would produce a stabilization of the 3d level (and a consequent contraction of the 3d orbitals) is clearly contradicted by simple analysis of the experimental data for the P^+ ion.[17] The first state with occupied d orbitals (. . . $3s^23p^13d^1$, ^3P) lies at 12.86 eV above the ground state (. . . $3s^23p^2$, ^3P). Therefore the excitation energy required to produce the lowest (. . . $3d^1$) state in P^+ is about 4 eV higher than that necessary for the corresponding excitation of the neutral P atom.

According to the present ab initio results, the fact that in the PX_3 derivatives the d orbitals on P are much more contracted than in the free atom is simply a need to effectively polarize the true valence 3s and 3p orbitals.

In the PX_3 ligands, the d_P functions cause a shortening of the computed PX bond distances of 0.06, 0.02 and 0.06 Å, for X = CH_3, H and F, respectively. The corresponding variations of the XPX angles are in general smaller than 1° (see Table II). When the ζ_d value is fixed to 0.016 (the best atomic value) the computed molecular geometry for PX_3 is almost coincident with that obtained without d functions. The effect of very diffuse d orbitals is therefore negligible, a fact which is confirmed also by the s and p orbital populations which, in this case, are almost unchanged with respect to the values computed without d_P's.

4. THE ELECTRONIC AND GEOMETRICAL STRUCTURE OF THE $(PX_3)_2Pt$ COMPLEXES

In the case of the platinum–phosphine complexes, the Pt atom has been described according to the Effective Core Potential method (ECP) as an 18 valence electron atom ($5s^25p^65d^96s^1$). The expression of the ECP operator (which includes also some relativistic effects) and the associated contracted 3s3p2d basis have been taken from Ref. 22. The basis set used for all other atoms is the same used for the free ligands.

The three complexes $(PX_3)_2Pt$ (X = CH_3, H and F) have been studied at the HF level only. This certainly would represent a severe approximation if the aim would be to compute suitable values of the complex stabiliy, but one might expect that the HF description can be acceptable for qualitative discussion of the charge distribution.

The best geometry of the complexes obtained under the constraint of D_{3h} symmetry are reported in Table III. It is apparent that the effect of the d_P's is mainly a shortening of the PtP bond distance (−0.076, −0.068, −0.088 Å, for X = CH_3, H and F, respectively), which is almost constant for the three complexes. The geometry parameters internal to the coordinated PX_3 groups show a decrease of the PX distance (0.01–0.02 Å) and an increase of the XPX angle (1–4°). Both effects, however, seem to be essentially due to the coordination process and cannot be clearly correlated with the absence or presence of the d_P's. The d_P functions do not substantially change both the XPX and the XPPt angle.

TABLE III

Optimum geometry of $(PX_3)_2Pt$ (X = CH_3, H and F) complexes[a]

	X = C	X = H	X = F
PtP	2.396 2.320	2.366 2.298 2.367	2.357 2.269
PX[b]	1.911(−0.015) 1.854(−0.019)	1.416(−0.017) 1.399(−0.011) 1.417(−0.016)	1.618(−0.021) 1.550(−0.022)
XPX[c]	101.6(1.2) 103.3(2.1)	98.9 (3.9) 98.0 (4.0) 98.93(3.95)	97.9(1.3) 98.4(1.5)

[a] XZ bond distances, Å; XZY valence angles, deg. The results obtained without and with d_P's are reported in first and second entries, respectively. For X = H, the third entry reports results obtained with ζ_{d_P} = 0.016 (the best single-zeta atomic value, see text). The variation with respect to the best geometries of the free ligands are reported in parenthesis.

[b] CH = 1.078 and 1.079 Å, without and with d_P's, respectively.

[c] HCH = 112.32 and 111.31°, without and with d_P's, respectively.

According to Bethe's rule,[23] this is an indication that the composition of the hybrid orbitals around the P atom are basically unaltered by the d_P's.

The composition of the wavefunction of the complexes in terms of the orbitals centered on the metal atom and MO's on the ligands is reported in Table IV, while Table V presents data concerning the global σ and π effects.

The analysis carried out according to the method outlined in Section 2 gives evidence that for all the PX_3 ligands considered the fragment MO's mostly involved in the coordination process are the highest occupied a_1 and the lowest unoccupied e orbitals, which are associated with the P lone pair and the π-accepting site, respectively. The two MO's are characterized by maximum values $(2 - \omega_i^f)$ among occupied MO's and maximum value ω_i^f among virtual MO's, respectively. Such a description is, however, only qualitatively correct. Other a_1 MO's low lying in energy give non-negligible contributions to the L → M σ donation, especially in the case of the $P(CH_3)_3$ ligand.

The data of Table V show that the basicity of PX_3 with respect to the Pt(0) center decreases in the series $X = CH_3$, H and F (0.520, 0.430, 0.383 and 0.555, 0.459, 0.425 are the σ-donated electrons, computed without and with d_P's, respectively), while the π-acidity has an opposite trend (0.073, 0.092, 0.144 and 0.076, 0.118, 0.177 are the π-back-donated electrons, computed without and with d_P's, respectively). Contributions from the π L → M donation and the σ M → L back-donation are always small, but not negligible.

Both the computed trends of σ-basicity and π-acidity are in close agreement with the expectation based on the chemical characteristics of the three ligands. In this sense, our theoretical results do not contradict the common experimental evidence concerning the possible role of the M → L π back-bonding, but does not agree with the view which assigns great importance to the d_P functions.

The projection of the wavefunction of the complexes onto the space of the atomic orbitals on the Pt atom gives the following evidence. The orbitals of δ symmetry are unaffected by the coordination bond; the decrease in the occupancy of the π orbitals (with respect to the value 4.0 of the free atom) is always very close to the number of electrons back-donated to the ligands (apart from

TABLE IV

Electron distribution in $(PX_3)_2Pt$ complexes expressed as occupation of AO's on Pt and MO's on ligands[a]

$[P(CH_3)_3]_2Pt$ complex	no d_P	d_P
Pt (core)	7.995	7.995
6s	0.964	1.011
$6p_\sigma$	0.410	0.428
$6p_\pi$	0.135	0.153
$5d_\sigma$	1.644	1.654
$5d_\pi$	3.854	3.833
$5d_\delta$	3.999	3.997
total	19.001	19.071
$P(CH_3)_3$ (core)	15.998	16.000
$5a_1$	1.805	1.787
3e	3.962	3.956
$6a_1$	1.964	1.966
4e	4.000	4.000
$7a_1$	1.972	1.972
5e	3.978	3.979
$1a_2$	2.000	2.000
6e	4.000	4.000
$8a_1$	1.741	1.720
$9a_1^*$	0.006	0.008
$7e^*$	0.073	0.076
total	41.499	41.464

$(PH_3)_2Pt$ complex	no d_P	d_P	$3d_P$
Pt (core)	7.988	7.988	8.000
6s	0.896	0.922	0.887
$6p_\sigma$	0.275	0.279	0.256
$6p_\pi$	0.086	0.085	0.087
$5d_\sigma$	1.672	1.697	1.676
$5d_\pi$	3.825	3.766	3.957
$5d_\delta$	4.000	4.000	3.997
total	18.742	18.737	18.860
PH_3 (core)	9.998	10.000	10.000
$3a_1$	1.811	1.799	1.824
2e	3.957	3.961	3.958
$4a_1$	1.761	1.742	1.756
$3e^*$	0.092	0.118	0.007
$5a_1^*$	0.009	0.012	0.025
total	17.629	17.631	17.570

TABLE IV (*Continued*)

$Pt(PF_3)_2$ complex	no d_P	d_P
Pt (core)	7.981	7.970
6s	0.727	0.838
$6p_\sigma$	0.241	0.245
$6p_\pi$	0.048	0.053
$5d_\sigma$	1.764	1.733
$5d_\pi$	3.718	3.646
$5d_\delta$	3.999	3.999
total	18.479	18.485
PF_3 (core)	16.000	16.000
$5a_1$	1.926	1.918
3e	3.991	3.996
$6a_1$	1.975	1.984
4e	4.000	4.000
$7a_1$	1.965	1.972
5e	4.000	4.000
6e	3.993	3.992
$1a_2$	2.000	2.000
$8a_1$	1.751	1.701
$9e^*$	0.144	0.177
$9a_1^*$	0.015	0.018
total	41.760	41.758

[a] The occupation numbers of the fragment orbitals are determined by means of orthogonal projectors (see text). The σ, π and δ notations refer to the local symmetry of the Pt–P axis. The a_1^* and e^* MO's are empty orbitals in free ligands, with σ and π symmetry, respectively.

a small contribution due to the $6p_\pi$ orbitals). The σ atomic orbitals of Pt are interesting for a quite important charge reorganization. This latter point deserves an additional comment. In analogy with what was found in theoretical studies on the carbonyl complexes of transition metals,[24] the electrons occupying the 6s Pt orbital are subjected to a strong Coulomb repulsion with the σ lone pair on the P atoms. Therefore, in order that a strong coordination bond takes place, the Pt atom needs to be promoted to the valence state $5d^{10}$. In this case, the σ acid site on Pt would be completely associated with the empty 6s orbital. On the contrary, if the promotion $5d^9 6s^1 \rightarrow 5d^{10}$ does not occur, the σ-acid site would be associated with the unfilled $5d_\sigma$ AO. In all the examined cases, the occupancy of the 6s orbital is close to 1.0 and is always larger in

TABLE V

σ donation and π back-donation in $(PX_3)_2Pt$ complexes

	$[P(CH_3)_3]_2Pt$		$(PH_3)_2Pt$		$(PF_3)_2Pt$	
	no d_P	d_P	no d_P	d_P	no d_P	d_P
L → M donation σ	0.520	0.555	0.430	0.459 0.420	0.383	0.425
donation π	0.060	0.065	0.043	0.039 0.042	0.016	0.012
M → L donation σ	0.006	0.008	0.009	0.012 0.025	0.015	0.018
donation π	0.073	0.076	0.092	0.118 0.007	0.144	0.177
total L → M	0.580	0.620	0.473	0.498 0.462	0.399	0.437
total M → L	0.079	0.084	0.101	0.130 0.032	0.159	0.195
total (L → M) − (M → L)	0.501	0.536	0.372	0.368 0.430	0.240	0.242

the presence of the d_P's. This shows that the promotion to the $5d^{10}$ configuration of the Pt atom does not occur, a fact confirming that the σ donor ability of PX_3 is much higher than the π-acceptor with respect to the CO ligand. In addition, our results show that the d functions on the phosphorus atom can also enhance the σ-basicity and not only the π-acidity. Indeed, the global L → M donation is larger with d_P's than without. Therefore, on average, the donor–acceptor ability of each PX_3 ligand is about the same, when described with or without d_p's.

A second set of calculations on PH_3 and $Pt(PH_3)_2$ molecules has been carried out in order to prove that the chemical meaning of the results reported above is basically independent of the details of the employed theoretical method.

The results of the previous calculations will be referred to now as "Calculation A." The new ones (Calculation B) have been obtained using for P and H atoms a basis set of triple-zeta quality,[18] more flexible than that used in Calculation A. In addition, also the ECP operator and basis set for Pt has been deliberately changed, using the data of Ref. 25: the Pt atoms is considered in this case as a 10 valence electron atom, described by a contracted basis of type 3s2p3d, which is again more extended than that of Calculation A.

As in previous cases, the exponent of the d functions on P has been obtained from an optimization of the PH_3 molecule, ζ_d = 0.4774.

The correlation contribution has been taken into account according to the CAS-SCF method[26] for PH_3 (8 valence electrons distributed in all possible ways among 7 valence MO's) and the CI method for the $(PH_3)_2Pt$ complex (single and double excitations allowed from the occupied valence space to all virtual MO's with valence character).

For the PH_3 ligand (see Table VI) the more flexible basis set and the inclusion of the correlation effects cause variations in optimum PH distance and HPH angle as large as 0.04 Å and 5°, respectively. However, the electron distribution remains virtually unchanged. In particular even the CAS-SCF results exclude a large participation of the d_P's and confirm the results of the more approximate HF treatment.

Similar considerations hold for the complex $(PH_3)_2Pt$. The geometry optimization carried out at the HF-ECP level gives results in very close agreement with those of the Calculation A (see Table VII). The Mulliken population analysis carried out on the HF and HF-CI wavefunctions shows that, in general, the correlation effects have very little influence. In particular the d_π orbitals of the P

TABLE VI

Effect of the basis set and correlation treatment on structure and electron distribution in PH_3[a]

	Calculation A		Calculation B			
			HF		CAS-SCF	
	no d_P	d_P	no d_P	d_P	no d_P	d_P
PH	1.433	1.410	1.427	1.410	1.464	1.440
HPH	95.0	94.0	98.9	97.6	94.6	93.9
s	5.734	5.599	5.728	5.686	5.764	5.711
p_σ	3.450	3.463	3.559	3.531	3.492	3.488
p_π	5.347	5.413	5.663	5.687	5.712	5.728
d_σ		0.007		0.000		0.000
d_π		0.068		0.092		0.081
d_δ		0.066		0.055		0.043

[a]See text for specification of the basis sets. PH distance, Å; HPH angle, deg. The orbital populations are reported for the P atoms only.

TABLE VII

Effect of the basis set and correlation treatment on structure and electron distribution in $Pt(PH_3)_2$[a]

		Calculation A	Calculation B	
PtP		2.298	2.273	
PH		1.399	1.402	
HPPt		98.0	98.4	
Orbital populations		(HF)	(HF)	(HF-CI)
Pt	s	2.989	0.762	0.740
	p_σ	2.190	0.329	0.313
	p_π	4.007	0.006	0.068
	d_σ	1.604	1.615	1.601
	d_π	3.764	3.774	3.729
	d_δ	3.995	3.992	3.969
P	s	5.513	5.537	5.536
	p_σ	3.378	3.364	3.384
	p_π	5.872	5.877	5.841
	d_σ	0.059	0.017	0.018
	d_π	0.127	0.128	0.130
	d_δ	0.015	0.065	0.064

[a]See text for specification of the basis sets and details concerning the CI treatment. PtP and PH distances, Å; HPPt angle, deg. The orbital populations are reported for Pt and P atoms only.

atom have occupancy equal to 0.128 and 0.130, at the HF and HF-CI levels, respectively. The corresponding values for the total d contribution are 0.190 and 0.202.

For the sake of completeness, Tables VI and VII also report the comparison between the results of Calculations A and B. This definitely shows that the main features concerning the M–P bond are essentially independent of the computational details and therefore have general validity.

5. CONCLUSIONS

The present study has confirmed the results of other ab initio investigations[5,6,8,27] concerning the role of the d orbitals of the phosphorus atom in stabilizing the M–P coordinative bond.

In particular, the following two points have been proved on the basis of rigorus theoretical results. (i) The d_P functions necessary for an improved description of the PX_3 ligands and the related complexes are completely different from the 3d orbitals of the free P atom in its valence configuration . . . $3s^2 3p^2 3d^1$. The radial extension of such orbitals is too large and their energy too high to be considered as chemically relevant. The d_P functions in PX_3 ligands act as polarization functions, characterized by low occupancy but able to induce important shortening of the M–P bond distance. (ii) The change in d_P occupancy going from free to coordinated PX_3 ligands is modest and, in any case, involves both the σ and π components. No evidence has been obtained of an important contribution of the d_P's to the π back-bonding mechanism. On the contrary, d_P functions seem to be very important also in the description of the ligand-to-metal σ donation.

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