The Nature of the Platinum–Phosphine Bond. An *ab initio* Hartree–Fock and Density Functional Study*

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The electronic structure of model complexes [Pt(PX_3)$_2$] (X = H or F) has been investigated by *ab initio* calculations, carried out with several theoretical approaches, of different sophistication, based on the Hartree–Fock method and density functional theory. Density functional calculations including correlation and relativistic effects gave highly reliable theoretical values for the equilibrium geometries and stabilities of the complexes, more accurate than those previously reported. The best estimates of the Pt–P bond distances are 2.27 and 2.25 Å, for [Pt(PH_3)$_2$] and [Pt(PF_3)$_2$], respectively. The corresponding dissociation energies are 5.3 eV and 5.1 eV. The differences in chemical behaviour exhibited by PH_3 and PF_3 can be summarised as follows: the σ-donated charge from PX_3 to the metal is found to be 0.12 and 0.39 electron, for X = H and F· the π-back-donated charge is 0.48 and 0.59, respectively. Therefore the PF_3 ligand should be classified as a stronger σ donor and π acceptor than PH_3, but its platinum complex is not more stable than [Pt(PH_3)$_2$]. The role of the polarisation functions centred on the ligand atoms should be interpreted more generally than that of the conventional σ–π mechanism, due to the fact that σ- and π-orbital occupancies are related not only to metal–ligand charge exchange but also to a charge rearrangement internal to the ligands, which cannot be fully interpreted in terms of a simplified orbital picture. Indeed, the whole electronic structure of the platinum phosphine complexes is largely dominated by electron correlation and relativistic effects.

The nature of the metal–phosphine (M–P) bond in coordination chemistry has been a challenging subject for decades, due to the fact that some very peculiar structural and chemical features of transition-metal phosphine complexes cannot be explained assuming that this bond is dominated by phosphine to metal σ donation only. On the other hand, as the PX_3 ligand has no P–X π bonds, a classical π-back-bonding process involving empty molecular orbitals (MOs) on the ligands cannot take place.

Two different proposals have been put forward in the past in order to account for the existence of a π-back-bonding-like contribution to the M–P bond. The first[1] is based on the assumption that the phosphorus atom has low-lying vacant 3d orbitals which can overlap with the occupied d orbitals on the metal centre, leading to a conventional σ–π representation of the metal–ligand bonding. A second explanation has been proposed only recently[2] and is basically independent of the presence of d orbitals on the P atoms (d_P). The antibonding σ* MOs located on the P–X bonds have the appropriate symmetry to overlap with the d_π occupied orbitals on the metal, that is to form a subset of MOs with local (M–P) π symmetry. Xiao *et al.*[2a] carried out the first analysis based on MO calculations and concluded that the d_P orbitals do not play an essential role in determining the extent of the metal to phosphine back bonding. More recently, other theoretical calculations have been carried out, with various methodological schemes,[3,4] on model complexes such as [M(PX_3)$_2$] (X = H, F, Me or OMe) with the aim of obtaining a direct estimate of the role of the d_P orbitals in the formation of the metal–phosphine bond. An important π-back-bonding contribution to the M–P bond is expected to produce two main effects: an increase in the M–P dissociation energy and a decrease in the M–P bond equilibrium distance. The question to be answered is to what extent these facts, which are connected clearly to an increased stability of the M–P bond, have to be ascribed to the presence of polarisation functions on ligand centres, and in particular of d_P orbitals. Alternatively, the question can be raised as to whether back donation to the ligands has the effect of increasing substantially the electron population of d_P orbitals; only in the presence of a significant electron occupancy, one can infer that spd hybridisation occurs and that the d_P orbitals substantially participate in the formation of the M–P bond. Otherwise, the d_P orbitals have to be considered just as polarisation functions.

The detailed analysis of these aspects reported in refs. 3 and 4 was essentially based on the Hartree–Fock (HF) method and aimed at interpreting the formation of the platinum–phosphine bond in terms of a classical σ–π synergetic mechanism. However, there are other electronic factors, such as the electron correlation and relativistic effects, which have been almost completely neglected in previous investigations. Our study aims at obtaining a more complete description of the metal–phosphine bond, using theoretical approaches which explicitly include correlation and relativistic effects. The model complexes chosen are [Pt(PX_3)$_2$] (X = H or F) in which the presence of a Pt atom just enhances the importance of relativistic phenomena. In this sense, the results presented give a quite general overview of the electronic effects influencing Pt–P bond formation.

Computational Methods

The electronic and geometrical structures of free PX_3 (X = H or F) and the corresponding platinum(0) complexes [Pt(PX_3)$_2$]

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* *Non-SI unit employed:* eV ≈ 1.60 × 10^{-19} J.

have been investigated by means of the HF and density functional (DF) methods.

Within the HF scheme the Pt atom is described according to a relativistic effective core potential (RECP) model[5] as an 18 valence-electron atom (^3D: $5s^25p^65d^96s^1$). The basis set for Pt was derived from ref. 4 and augmented by diffuse s, p and d functions with exponents equal to 0.02, 0.03 and 0.04, respectively. The basis set (6s5p5d) was then contracted to (4s3p3d). An all-electron scheme was adopted for the ligand atoms H, F and P, described by double-zeta basis Gaussian functions.[6] The exponents of the d functions on F and P are equal to 0.90 and 0.37, respectively. The p orbitals on the H atoms have exponents equal to 1.00. The results of the Hartree–Fock calculations will be labelled as HF when not including and as HFp when including polarisation functions on ligand atoms. Similarly, the results of post-HF correlation treatments, carried out according to the second-order Moeller–Plesset perturbation method, will be denoted as MP2 and MP2p.

For the DF calculations the discrete variational method of Baerends and co-workers,[7] has been employed. The DF theory allows one to take into account, in an approximate but fully consistent way, the electron correlation effects, which in the framework of post-HF approaches (*e.g.* the configuration interaction method) can be obtained only at a much higher computational cost and, in general, in a non-size-consistent way. The DF calculations were carried out by considering also the non-local effects, both for the exchange and correlation contributions, which are known to be very important for a reliable prediction of binding energies. The local density function[8] has been modified by the non-local corrections proposed by Becke[9] for exchange and by Perdew[10] for correlation.

The DF approach of ref. 7 has been further developed to include the evaluation of the most important relativistic effects, like the mass-velocity and Darwin corrections, which are added to the non-relativistic Hamiltonian leading to the so-called quasi-relativistic (QR) scheme.[11] It is of interest to compare the QR results with those of the RECP approach, obtained by introducing effective one-electron operators.

In the present study, DF calculations on phosphine complexes have been carried out using a double-zeta basis set comprised of Slater-type orbitals. For atoms F, P and Pt the frozen-core approximation was assumed, the atomic cores being defined as (He) for F, (Ne) for P and (Xe, $4f^{14}$) for Pt. The results reported in the next section will be labelled as DF when not including and DFp when including polarisation functions on ligand atoms. The corresponding relativistic calculations will be denoted as RDF and RDFp.

For both HF and DF methods, the search for the best molecular structure has been performed assuming D_{3h} symmetry for $[Pt(PX_3)_2]$ complexes and C_{3v} symmetry for free PX_3. In the case of relativistic calculations, the geometry optimisation has been carried out in a fully numerical manner, due to the fact that analytical evaluation of the gradients of relativistic energy is not implemented in the available version of the ADF program.[12] The charge distribution will be discussed in terms of orbital and atomic contributions, according to the Mulliken analysis.[13] Such an approach, which has been subjected to criticisms due to its intrinsically arbitrary partition scheme,[14] still offers the advantage of being close to chemical intuition. On the other hand, all the interpretative models of transition-metal chemistry are still rich in concepts arising from the idea of partitioning the electronic charge into orbital and atom contributions. The theory of the σ–π synergic mechanism for the co-ordination bond is just one very illuminating example.

Results and Discussion

The computational procedures HF, MP2, DF and RDF mentioned above have been applied to the study of the structure, stability and charge distribution of the $[Pt(PX_3)_2]$ (X = H or F) complexes. The following discussion will address separately the effects induced by the presence of polarisation functions on ligand centres as well the relativistic and correlation effects.

Structure of the Complexes.—Table 1 contains equilibrium geometry parameters of free PH_3 and PF_3. Correlation corrections applied to the HF wavefunction (MP2 and MP2p calculations) always produce a small elongation of the P–H bond (0.01–0.02 Å) and a larger elongation of the P–F bond (0.04–0.05 Å). The inclusion of polarisation functions acts in the opposite direction, to a similar extent. Owing to cancellation of opposite contributions, the HF data are fairly close to the MP2p ones. The DF results confirm that the P–X bonds are shorter (by 0.02 and 0.11 Å, for X = H and F respectively) when polarisation functions are present (see DFp). The effect is considerably larger in the case of PF_3, which seems slightly affected also by relativistic effects (RDFp).

The HFp and MP2p results for P–H and P–F bond lengths are in a fairly good agreement with the experimental values (1.412[15] and 1.563[16] Å, respectively), while the DFp and RDFp results are less satisfactory, in particular for the PF_3 molecule for which the P–F equilibrium distance is overestimated by about 0.1 Å. Such a discrepancy is, however, not relevant for the forthcoming discussion, mainly aimed at pointing out variations in ligand geometries due to the formation of the co-ordination bond.

One can easily evaluate the extent to which the structural features of the complexes are influenced by the polarisation functions on the ligands by comparing the results in Tables 1 and 2. The P–H and P–F bond distances in the complexes are shorter than in the free phosphines: this seems to be quite a general result, independent of the specific features of the computational procedures, the only exception being the DF calculations on $[Pt(PF_3)_2]$.

The computed Pt–P distance in $[Pt(PH_3)_2]$ varies over a considerably large range, 2.25–2.46 Å depending on the specific assumptions of the theoretical models. This indicates that the metal–phosphorus bond length may be sensibly affected by

Table 1 Optimised geometry parameters for free PX_3 (X = H or F)

	P–X/Å		X–P–X/°	
Method	X = H	F	X = H	F
HF	1.421	1.657	96.5	95.9
MP2	1.438	1.708	95.6	96.7
DF	1.454	1.736	95.7	95.5
RDF	1.462	1.767	94.0	96.6
HFp	1.413	1.579	95.1	97.0
MP2p	1.415	1.620	93.7	97.3
DFp	1.447	1.681	95.7	98.1
RDFp	1.441	1.653	97.1	97.5

Table 2 Optimised geometry parameters for $[Pt(PX_3)_2]$ (X = H or F) complexes

	Pt–P/Å		P–X/Å		X–P–X/°	
Method	X = H	F	X = H	F	X = H	F
HF	2.359	2.330	1.410	1.640	99.3	97.0
MP2	2.326	2.301	1.427	1.692	99.1	97.8
DF	2.462	2.449	1.450	1.743	95.7	96.8
RDF	2.312	2.299	1.449	1.750	96.2	97.3
HFp	2.304	2.259	1.405	1.559	98.5	98.2
MP2p	2.253	2.212	1.409	1.607	97.8	96.7
DFp	2.460	2.380	1.446	1.669	95.8	96.4
RDFp	2.268	2.249	1.433	1.625	96.4	98.3

Table 3 Computed stabilities (eV)* for $[Pt(PX_3)_2]$ (X = H or F) complexes

	Method			
X	HF	MP2	DF	RDF
H	1.58	3.48	3.97	4.76
F	0.76	1.00	3.45	3.51
	HFp	MP2p	DFp	RDFp
H	2.06	3.98	4.25	5.32
F	2.00	2.71	4.41	5.08

* Expressed as the energies required for the dissociation $[Pt(PX_3)_2] \longrightarrow Pt + 2\ PX_3$.

several electronic factors, like those associated with polarisation, correlation and relativistic effects.

In HF-like calculations only the polarisation and correlation effects can be demonstrated, the relativistic ones being always automatically included in the form of the ECP adopted. The shortening of the Pt–P bond due to electron correlation only (compare MP2 with HF) is 0.03 Å, while it is much larger in the presence of polarisation functions (0.08 Å, compare MP2p with MP2). In contrast with the case of the free phosphines, polarisation and correlation act in the same sense, both contributing to the decrease in the metal–ligand distance. The smallest value for the Pt–P distance is obtained from MP2p calculations, *i.e.* 2.25 Å.

The non-relativistic DF calculations give a Pt–P bond length in $[Pt(PH_3)_2]$ equal to 2.46 Å, quite unaffected by polarisation functions, but considerably larger than the HF value determined with relativistic ECP. On the contrary, a contraction of the metal–ligand bond distance of 0.15 and 0.19 Å is produced by relativistic effects, in the absence or in the presence of polarisation functions, respectively.

It is natural to expect that polarisation, correlation and relativistic effects are equally, or even more, important for the equilibrium structure of the $[Pt(PF_3)_2]$ complex. All the computational methods listed in Table 2 give a Pt–P distance systematically shorter than the corresponding distance in $[Pt(PH_3)_2]$. As for the extent of the shortening of this distance, the effect of correlation (compare MP2 with HF and MP2p with HFp) is similar to that found for the PH_3 complex. The MP2p value is equal to 2.21 Å, about 0.04 Å shorter than in $[Pt(PH_3)_2]$. The DFp calculations predict a Pt–P distance 0.07 Å shorter than the DP ones, a variation much larger than that occurring in $[Pt(PH_3)_2]$, which indicates that the strong polarising effects caused by the presence of fluorine atoms can affect the electronic and geometric structure of $[Pt(PF_3)_2]$ substantially. The relativistic corrections produce an additional shortening of the Pt–P bond of about 0.13 Å.

Stability of the Complexes.—The stability of the complexes will be discussed in terms of the energy (ΔE) required to promote the dissociation $[Pt(PX_3)_2] \longrightarrow Pt + 2\ PX_3$, leading to fragments in their ground electronic state and equilibrium structure. As mentioned above, the RDFp calculations, performed with a density function including non-local and relativistic effects, are expected to give reliable values also for binding energies. For this reason and in the absence of experimental data, the RDFp ΔE values are assumed as a reference in order to discuss the reliability of all other methods.

As shown in Table 3, the ΔE values for $[Pt(PH_3)_2]$ vary in the range 1.58 (HF) to 5.32 eV (RDFp). The very low value given by the HF method is not unexpected due to the known tendency of this method to underestimate the heat of formation, especially in the case of transition-metal compounds. The inclusion of polarisation functions raises the ΔE value to 2.06 eV (HFp), that is by more than 25%. However, it cannot be concluded that polarisation functions are very important for the stability of the Pt–P bond in $[Pt(PH_3)_2]$, as the above result is biased by the inadequacies of the one-electron picture. In fact, when considering the correlation corrections (MP2), but still neglecting the polarisation ones, ΔE is about twice as large as the HF value. When polarisation effects are added (MP2p) the increase in ΔE is only about 9%. Even taking into account the approximate character of the MP2 approach, one can certainly conclude that the stability of $[Pt(PH_3)_2]$ is totally dominated by the correlation effects, which are hardly described by qualitative arguments based on the concerted σ–π mechanism.

The role played by electron correlation is fully confirmed by the results of the DF calculations. The DF value of ΔE is 3.97 eV, about 12% higher than the MP2 value, and the increase due to ligand polarisation (compare DFp and DF) is only about 7%. A much larger correction originates from relativistic effects, which contribute more than 20% to ΔE. When the best HF-like result for ΔE (MP2p, 3.98 eV) is compared with the best DF result (RDFp, 5.32 eV), it becomes apparent that the MP2 results are affected by an incomplete recovering of correlation energy.

The data of Table 3 confirm the conclusion drawn when discussing the best geometries of the platinum complexes that the presence of polarisation functions plays a determinant role in the case of $[Pt(PF_3)_2]$. The ΔE value increases from 0.76 to 2.00 eV, in passing from HF to HFp, and the increment is even larger when polarisation and correlation effects are considered simultaneously, leading to a value of ΔE equal to 1.00 and 2.71 eV in MP2 and MP2p, respectively. The polarisation contributions to the ΔE value, which are as large as 50% in the case of HF-like methods (HFp and MP2p), are smaller in the case of DF calculations, about 22 and 30% in the non-relativistic and relativistic case, respectively. The relativistic contribution to ΔE is equal to 0.7 eV, that is 14% of the total stability. The estimate of the relative importance of ligand polarisation is different in DF and HF-like calculations, but all the approaches qualitatively agree on the point that polarisation effects internal to the PF_3 ligand contribute to the binding energy much more than in the case of the PH_3 ligand. Qualitatively, the relative importance of relativistic and polarisation effects in $[Pt(PF_3)_2]$ is reversed with respect to the $[Pt(PH_3)_2]$ complex. However, the absolute values of ΔE confirm that, also in the presence of strong polarisation contributions, almost 70% of the stability of $[Pt(PF_3)_2]$ must be ascribed to correlation and relativistic effects.

Charge distribution in PX_3 *and in* $[Pt(PX_3)_2]$ *Complexes.*—The above discussion clearly indicates that the stability of the platinum-phosphine complexes may be largely influenced by electronic effects different from those representable by an independent-electron picture, like the Chatt–Dewar model[1] which was originally formulated using concepts of maximum overlap (or symmetry adaptation) applied to the metal and ligand orbitals. This suggests that interpretations of Pt–P bond strength based simply on electronic charge exchange *via* ligand-to-metal donation and metal-to-ligand back donation should be considered with caution. With this in mind, a Mulliken analysis obtained from HF, DF and RDF wavefunctions was made just to check how far the conventional σ–π description can be followed.

The charge distributions in the free phosphines PH_3 and PF_3 are reported in Table 4, those for platinum complexes in Table 5. In order to reduce the complexity of symmetry labelling we do not adopt the notation of the D_{3h} point group but the simpler classification into σ and π components. This is achieved by using for the free phosphines and complexes the molecular C_3 axis as reference. Some of the orbitals centred on Pt and P atoms should be labelled as δ orbitals with respect to the local Pt–P symmetry but, again for simplicity, the associated electron populations have been added to the π ones. Note, on the other hand, that the δ orbitals on platinum are always characterised

Table 4 Electron distribution on free PX_3 (X = H or F)*

		Method					
		HF	DF	RDF	HFp	DFp	RDFp
(*a*) PH_3							
σ_L	(P)	3.284	3.331	3.338	3.129	3.063	3.034
	(H)	0.239	0.233	0.221	0.290	0.312	0.322
π_L	(P)	1.623	1.699	1.733	1.934	2.144	2.166
	(H)	0.792	0.767	0.756	0.689	0.619	0.611
Q_P		0.093	−0.030	−0.072	−0.063	−0.207	−0.200
Q_H		−0.031	0.010	0.023	0.021	0.069	0.067
(*b*) PF_3							
σ_L	(P)	2.596	2.601	2.613	2.625	2.556	2.565
	(F)	2.468	2.466	2.462	2.458	2.481	2.478
π_L	(P)	0.703	0.966	0.992	1.161	1.139	1.150
	(F)	5.099	5.011	5.003	4.946	4.953	4.950
Q_P		1.701	1.423	1.395	1.214	1.302	1.285
Q_F		−0.567	−0.477	−0.465	−0.404	−0.434	−0.428

* The σ and π MOs are classified with respect to the C_3 molecular axis. Molecules PH_3 and PF_3 have 4 σ, 4 π and 10 σ, 16 π valence electrons, respectively; $\sigma_L(X)$ and $\pi_L(X)$ indicate σ and π electrons assigned to the atoms X.

Table 5 Electron distribution on $[Pt(PX_3)_2]$ (X = H or F) complexes*

		Method					
		HF	DF	RDF	HFp	DFp	RDFp
(*a*) $[Pt(PH_3)_2]$							
σ_{Pt}		2.550	2.573	2.248	2.594	2.638	2.121
π_{Pt}		7.837	7.754	7.652	7.741	7.675	7.519
σ_L	(P)	3.029	3.087	3.296	2.868	2.751	3.015
	(H)	0.232	0.204	0.193	0.278	0.310	0.308
	(total)	3.725	3.714	3.276	3.702	3.681	3.939
π_L	(P)	1.778	1.865	1.923	2.079	2.263	2.312
	(H)	0.768	0.753	0.750	0.684	0.633	0.643
	(total)	4.082	4.123	4.174	4.131	4.163	4.241
Q_{Pt}		−0.387	−0.327	0.100	−0.335	−0.312	0.360
Q_P		0.193	0.048	−0.219	0.053	−0.014	−0.327
Q_H		0.000	0.038	0.056	0.038	0.057	0.049
$\Delta\sigma_{L\to M}$		0.550	0.572	0.248	0.594	0.638	0.122
$\Delta\pi_{M\to L}$		0.164	0.246	0.348	0.262	0.326	0.482
(*b*) $[Pt(PF_3)_2]$							
σ_{Pt}		2.991	2.760	2.506	3.003	2.642	2.395
π_{Pt}		7.827	7.743	7.598	7.750	7.591	7.406
σ_L	(P)	2.219	2.261	2.499	2.127	2.452	2.425
	(F)	2.424	2.453	2.416	2.458	2.409	2.459
	(total)	9.505	9.620	9.747	9.500	9.679	9.803
π_L	(P)	0.819	1.039	1.152	1.344	1.727	1.439
	(F)	5.084	5.030	5.016	4.927	4.826	4.953
	(total)	16.087	16.129	16.201	16.125	16.205	16.297
Q_{Pt}		−0.818	−0.503	−0.104	−0.753	−0.233	0.199
Q_P		1.962	1.700	1.349	1.529	0.821	1.136
Q_F		−0.518	−0.483	−0.432	−0.385	−0.235	−0.412
$\Delta\sigma_{L\to M}$		0.991	0.760	0.506	1.003	0.642	0.394
$\Delta\pi_{M\to L}$		0.173	0.257	0.402	0.250	0.410	0.594

* The MOs are classified as σ or π with respect to the molecular C_3 axis. For simplicity, δ orbitals on Pt and P atoms are included in the π set. The parameters $\sigma_L(X)$ and $\pi_L(X)$ are the numbers of σ and π electrons assigned to atoms X, $\Delta\sigma_{L\to M}$ and $\Delta\pi_{M\to L}$ the total number of electrons transferred from the ligands to the metal and back donated from the metal to the ligands, respectively.

by an occupancy very close to 4.0, which is the value expected for a metal atom weakly polarised by ligands along an axial direction. This is equivalent to stating that the Pt–P bond formation can be qualitatively discussed by assuming a dominant rearrangement of σ and π electrons only.

The absolute values of the population in Tables 4 and 5 depend markedly on the specific computational procedure. In addition they are, as expected, quite sensitive to small changes in the orbital basis set adopted. For this reason, the present discussion serves only to identify trends and rules which may be derived from general features common to different theoretical models.

In the case of PH_3, where the ionicity is definitely small, the HF method gives a polarity of the P–H bond just reversed with respect to the HFp and DF predictions. The net atomic charge Q_P on the P atom has been computed to vary from 0.09 (HF) to −0.20 (RDFp) (see Table 4). Note that relativistic corrections are negligibly small for PH_3. All the theoretical models describe the P–F bond in PF_3 as characterised by a much more pronounced ionicity ($Q_P > 1.0$). Also in this case, the relativistic correction does not alter significantly the charge distribution.

In the case of the $[Pt(PH_3)_2]$ complex (see Table 5), HF, DF, HFp and DFp calculations indicate that the Pt atom carries a negative charge ($Q_{Pt} \approx -0.3$), a fact suggesting that the σ-donor ability of PH_3 prevails over the π acidity. By comparing the total σ and π populations on the co-ordinated PH_3 with those computed for the free molecules, the total number of σ-donated electrons ($\Delta\sigma_{L\rightarrow M}$) and the π-accepted electrons ($\Delta\pi_{M\rightarrow L}$) can easily be evaluated. According to the HF and DF results, $\Delta\sigma_{L\rightarrow M}$ and $\Delta\pi_{M\rightarrow L}$ are in the ranges 0.55–0.64 and 0.16–0.33, respectively. An enhanced π-accepting ability of the PH_3 is present in the HFp and DFp descriptions, which may be quantified as equal to 0.1 and 0.08 electron, that is about 38 and 25% of the total back-donated charge. Therefore, the polarisation functions appear to be very necessary to describe properly the π-acid character of the PH_3. Note, however, that also the $\Delta\sigma_{L\rightarrow M}$ values increase on going from HF to HFp (0.04) and from DF to DFp (0.07).

The population analysis carried out on relativistic wavefunctions obtained from DF calculations gives results quite different from those above. In $[Pt(PH_3)_2]$ the net charge on Pt is always positive ($Q_{Pt} = 0.10$ and 0.36 in RDF and RDFp) and, correspondingly, the PH_3 ligand appears to be a strong π acceptor and a weaker σ donor. The calculations on the free phosphines (in particular PH_3) have shown that the relativistic corrections to the charge distribution are negligibly small (see Table 4). As a consequence, the strong variations in the charge distribution within the complexes observed in relativistic calculations can be considered as originating just on the metal centre and then propagating also to the ligands. The high π acidity computed for PH_3 ($\Delta\pi_{M\rightarrow L} = 0.35$ and 0.48 in RDF and RDFp, respectively) is actually due to the loss of the σ acidity of the metal atom, which in turn may be qualitatively explained in terms of direct relativistic contraction of 6s and indirect relativistic expansion of 5d orbitals. On passing from DFp to RDFp, the major effect is observed for the 5d orbitals which decrease their occupancy by 0.45 (d_σ) and 0.14 (d_π) electron, while the 6s occupancy remains always close to 1.00. The $\Delta\sigma_{L\rightarrow M}$ quantity in RDFp (0.12) is much smaller than in RDF (0.64). Therefore, the relativistic effects drastically change the acid–base character of the platinum centre and, as a consequence, decrease also the σ-donor ability of the ligand, in contrast with the description obtained at the HF, HFp, DF or DFp level. The end result demonstrated by the RDFp description is a Pt–P bond dominated by the back-bonding mechanism ($\Delta\pi_{M\rightarrow L} = 0.48$, $\Delta\sigma_{L\rightarrow M} = 0.12$).

As for the $[Pt(PF_3)_2]$ complex, the HF and HFp results indicate a very strong σ-donor ability of the PF_3 ligands, $\Delta\sigma_{L\rightarrow M} = 0.99$ and 1.00, which is not compensated by back-bonding effects $\Delta\pi_{M\rightarrow L} = 0.17$ and 0.25. This leads to the description of a platinum centre carrying a large negative charge ($Q_{Pt} = -0.82$ and -0.75), in HF and HFp. Such a strong basic character of PF_3 is largely absent from the density functional results, which assign a net charge to Pt equal to -0.50 and -0.23 (DF and DFp, respectively). A further reduction of the σ-donor ability of PF_3 is obtained from relativistic calculations which describe a Pt atom with a small negative (-0.10) or small positive charge (0.20), in RDF and RDFp. From the data of Table 5, it is evident that only in the case of relativistic calculations, including polarisation effects, the $\Delta\sigma_{L\rightarrow M}$ and $\Delta\pi_{M\rightarrow L}$ quantities are nearly balanced, therefore fulfilling approximately the electroneutrality principle. The relativistic effects cause an increase in the platinum 6s population equal to 0.23 electron, while the d_σ and d_π orbitals decrease their occupancy by 0.38 and 0.20 electron, respectively. The global population of σ orbitals on Pt is smaller in relativistic than in non-relativistic results, which corresponds to a decreased σ basicity of PF_3. The PF_3 ligand exhibits a π acidity enhanced by the presence of polarisation functions (compare RDF and RDFp results: $\Delta\pi_{M\rightarrow L} = 0.40$ and 0.59).

Conclusion

The data described confirm that the description of the Pt–P bond in terms of the conventional σ–π Chatt–Dewar model might not be completely satisfactory as it does not account for important contributions which cannot be enforced in an independent-electron framework or a simplified orbital picture.

A very general consideration concerning the nature of the Pt–P bond is that its equilibrium length and its stability are severely affected by polarisation, correlation and relativistic effects. In the previous section we tried to show the relative importance of each contribution. However, in several cases the correlation effects (see MP2p and MP2 results) and the relativistic corrections (see RDFp and RDF results) are larger in the presence than in the absence of polarisation functions on ligand centres. Therefore, the separation of the three effects is only partially possible and of a qualitative nature only.

As for the Pt–P bond lengths, we have shown that electron correlation and relativistic corrections are essential constituents of a reliable prediction. The Pt–P bond contraction given by MP2 and MP2p procedures is much larger than one could expect on the basis of the relatively small amount of correlation energy recovered, which produces an evident underestimate of the dissociation energies. The incompletely satisfactory results obtained from HF-like calculations *via* the MP2 procedure are a strong indication that very sophisticated correlation treatments are needed in order to obtain reliable results. A study of the $[PtMe_2(PH_3)_2]$ complex[17] further confirms this view: the calculations performed with the generalised valence bond (GVB) method gave for the Pt–P distance a value of 2.46 Å. Such a prediction is about 0.2 Å larger than our RDFp estimate and is in disagreement with the experimental value obtained for the $[PtMe_2(PPh_2Me)_2]$ complex, to about the same extent. Similar values of the Pt–P bond distance result also from HF calculations on different platinum phosphine complexes,[3,18] independently of the oxidation state of the metal centre and its co-ordination sphere. The GVB method does not seem to be able to remove completely the inadequacies of the HF approach and, on the other hand, the MP2 treatment probably overestimates the contraction of the Pt–P bond while giving a relatively poor description of the co-ordination bond stability. In this sense, the DF approach including relativistic effects appears to be a good alternative to correlation treatments which, in order to reach a satisfactory accuracy, should be even more sophisticated than GVB or MP2 ones.

The Mulliken analysis has shown that the charge distribution on the platinum centre obtained from RDFp calculations is markedly different from those from HF or DF calculations. In particular, the RECP approach used in HF and HFp calculations gives Q_{Pt} values very close to those from DF or DFp, therefore it gives a wavefunction in which the s–d relativistic charge reorganisation is largely absent.

Our results can be used also to quantify the role of the d orbitals on the P atoms in the σ–π mechanism. To this end, it is useful to compare the $\Delta\pi_{M\rightarrow L}$ and $\Delta\sigma_{L\rightarrow M}$ quantities with the charge rearrangement undergone by the $d_P(\pi)$ and $d_P(\sigma)$ orbitals: this can be expressed by means of the quantities $\Delta d_P(\pi)$ and $\Delta d_P(\sigma)$ which indicate the variation in electron occupancies on going from free to co-ordinated compounds. In the case of the $[Pt(PH_3)_2]$ complex the variation $\Delta d_P(\sigma)$ on each P atom is 0.02, 0.05 and 0.13, from HFp, DFp and RDFp wavefunctions, respectively. The corresponding values for $\Delta d_P(\pi)$ are 0.05, 0.10 and 0.15. For $[Pt(PF_3)_2]$ the computed values are $\Delta d_P(\sigma) =$ 0.04, 0.13 and 0.16 and $\Delta d_P(\pi) = 0.08$, 0.15 and 0.19.

It is evident that for both complexes the accumulation of electronic charge on the $d_P(\pi)$ orbitals is equal to about 30% of the total $\Delta\pi_{M\rightarrow L}$ charge from HFp calculations and even higher (about 50–60%) from DFp and RDFp ones. This seems to support the hypothesis of an important participation of the d_P orbitals to the back-bonding mechanism. However, the values $\Delta d_P(\sigma)$ are also positive (a general trend common to all the computational approaches) and this is completely in contrast with results of the σ–π Chatt–Dewar method: in fact, the $d_P(\sigma)$ orbitals belong to the set of donor orbitals and their $\Delta d_P(\sigma)$ value should be, by definition, always negative. It can be concluded that d_P orbital populations cannot be related with the ligand–metal charge exchange only, but are determined largely by a charge rearrangement internal to the ligand itself, which must be classified just as a polarisation effect.

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References

1 M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, 1951, **18**, C71; J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 1953, 2939; F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley, New York, 1988.

2 (*a*) S.-X. Xiao, W. C. Trogler, D. E. Ellis and Z. Berkovitch-Yellin, *J. Am. Chem. Soc.*, 1983, **105**, 7033; (*b*) D. S. Marynick, *J. Am. Chem. Soc.*, 1984, **106**, 4064.

3 P. Fantucci, *Rend. Fis. Acc. Lincei*, 1981, **2**, 213; *Comments Inorg. Chem.*, 1991, **13**, 241.

4 G. Pacchioni and P. S. Bagus, *Inorg. Chem.*, 1992, **31**, 4391.

5 P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 299.

6 T. H. Dunning, jun., *J. Chem. Phys.*, 1970, **53**, 2883; T. H. Dunning, jun., and P. J. Hay, *Modern Theoretical Chemistry*, Plenum, New York, 1976.

7 E. J. Baerends, D. E. Ellis and P. Ros, *Chem. Phys.*, 1973, **2**, 42; E. J. Baerends and P. Ros, *Int. J. Quantum Chem.*, 1978, **S12**, 169.

8 R. G. Parr and W. Yang, *Density Functional Theory for Atoms and Molecules*, Oxford University Press, New York, 1989; T. Ziegler, *Chem. Rev.*, 1991, **91**, 651; S. H. Vosko, L. Wilk and N. Nusair, *Can. J. Phys.*, 1980, **58**, 1200.

9 A. D. Becke, *J. Chem. Phys.*, 1988, **88**, 2457; *Phys. Rev. A*, 1988, **38**, 3098.

10 J. P. Perdew, *Phys. Rev. B*, 1986, **33**, 8822.

11 J. G. Snijders and E. J. Baerends, *Mol. Phys.*, 1978, **36**, 1789; J. G. Snijders, E. J. Baerends and P. Ros, *Mol. Phys.*, 1979, **38**, 1909; T. Ziegler, J. G. Snijders and E. J. Baerends, *J. Chem. Phys.*, 1981, **74**, 1271.

12 ADF 1.1.3, Amsterdam Density Functional Program.

13 R. McWeeney, *J. Chem. Phys.*, 1951, **19**, 1614; 1952, **20**, 920; R. Mulliken, *J. Chem. Phys.*, 1955, **23**, 1833, 2343.

14 J. Cioslowski, P. J. Hay and J. P. Ritchie, *J. Phys. Chem.*, 1990, **94**, 148; I. N. Levine, *Quantum Chemistry*, Prentice-Hall, Englewood Cliffs, NJ, 1991.

15 F. Y. Chu and T. Oka, *J. Chem. Phys.*, 1974, **60**, 4612.

16 E. Hirota and Y. Morino, *J. Mol. Spectrosc.*, 1970, **33**, 460.

17 J. M. Wisner, T. J. Bartczak, J. A. Ibers, J. J. Low and W. A. Goddard III, *J. Am. Chem. Soc.*, 1986, **108**, 347.

18 P. Fantucci, M. Pizzotti and F. Porta, *Inorg. Chem.*, 1991, **30**, 2277; P. Fantucci, S. Lolli and M. Pizzotti, *Inorg. Chem.*, 1994, **33**, 2779.

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