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Electronic Structure and Reactivity of Dioxygen–Platinum Complexes: An ab Initio MO-LCAO Study

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Ab initio Hartree Fock calculations have been carried out on the complex $L_2Pt(\eta^2\text{-}O_2)$ and its derivatives $L_2Pt(OOH)X$ and $L_2Pt(OOH)(XY)$ obtained by reaction with HX (HX = H_2O, HCl, HOOCH, NH_3) and HXYH (HXYH = oxalic acid, *o*-catechol, hydrazine, hydroxylamine, ethylendiamine, *o*-phenylendiamine). In addition also the reaction $L_2Pt(OOH)X + HX \rightarrow H_2O_2 + L_2PtX_2$ leading to the formation of hydrogen peroxide has been studied. The theoretical investigation gave, for all considered species, optimum complex geometry, charge distribution and reaction energies being evaluated by means of a correlation energy density functional. The ability of the HX reagents to form hydrogen peroxide is discussed in terms of absolute acidity and coordinating capability of the X^- groups. This allows interpretation of the more peculiar aspects of the chemical activation of dioxygen that leads to the coordinated hydroperoxide species or hydrogen peroxide.

1. Introduction

Dioxygen transition metal complexes and their derivatives have received considerable attention as they are considered potential models of key intermediates in catalytic reactions involving molecular oxygen, hydrogen peroxide, or alkyl hydroperoxide as the oxygen source.[1,2] The chemical behavior of the η^2-O_2 dioxygen ligand coordinated to transition metals has been investigated in detail,[3] with particular attention to reactions with organic carbonyl compounds,[4] carbon dioxide,[5] activated olefins,[6] and amines.[7]

The coordinated η^2-dioxygen is commonly classified as a peroxide ligand. Such an assumption is qualitatively justified by the observation that OO distances in metal complexes are longer (1.40–1.50 Å) and the $\tilde{\nu}$(O–O) vibrational energies lower (700–900 cm^{-1})[3,8] than in the free diatomic molecule (r_e = 1.21 Å, ω_e = 1580.2 cm^{-1}),[9] and close to the corresponding values of the peroxide ion.[10] However, theoretical studies of electron distribution on the η^2-O_2 ligand carried out with different methods[11] suggest that the excess of negative charge is much smaller than in the free peroxo anion O_2^{2-}. In particular, a recent ab initio study on the model complex $(PH_3)_2Pt(\eta^2\text{-}O_2)$,[12,13a] carried out with full geometry optimization has shown that the charge on the dioxygen group is about –0.8. The theoretical optimum OO distance of 1.44 Å is in a very good agreement with the experimental value for the related complex $(PPh_3)_2Pt(\eta^2\text{-}O_2)$ (1.45 Å).[14] Therefore, the important elongation of the OO distance in η^2-O_2 complexes with respect to the free oxygen molecule is not necessarily caused by a very large negative charge on the η^2-O_2 ligand. Its classification as a peroxide ligand may therefore be considered as only very qualitative. However, a general consensus exists about the strong nucleophilic character of such a ligand in d^6–d^8 complexes, which seems to be unambiguously proved by a wide series of experimental observations.[15–17]

In the present paper, the dioxygen complex considered is of type $L_2Pt(\eta^2\text{-}O_2)$, where L = PH_3 is assumed to be representative of alkyl- or arylphosphine ligands usually employed in synthetic work. With these latter complexes, experiments have shown that the reaction with molecules having positively polarized protons takes place easily.[1–7,15–17] The general proposed scheme of proton transfer from the reacting molecule HX ($H^{\delta+}$–$X^{\delta-}$) to the coordinated dioxygen is reported in Scheme 1. The mechanism is essentially a two-step process leading to the formation of an hydroperoxide intermediate $L_2Pt(OOH)X$ which may further reacts with HX, eventually giving hydrogen peroxide. This stepwise reaction scheme has experimental support in the case of the interaction of $(PPh_3)_2M(\eta^2O_2)$ (M = Pt, Pd) with acids conjugated to anions of low nucleophilicity such as carboxylic acids[17] or with formanilides and imides.[7] In fact, infrared measurements[17] support a stepwise mechanism of the formation

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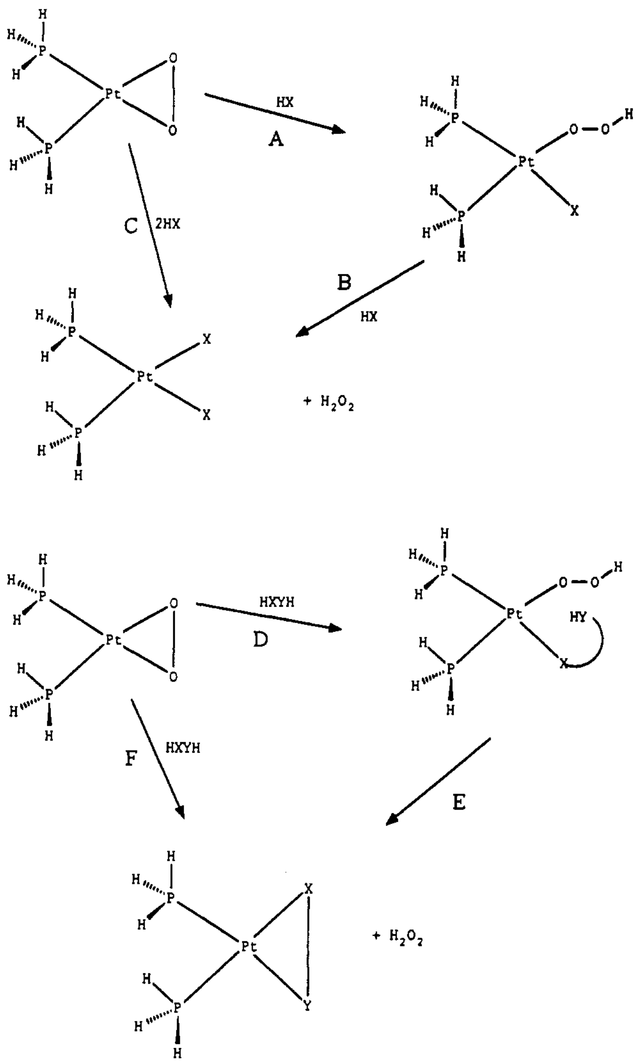
Scheme 1



of the hydroperoxide intermediate when the protonation reaction is carried out with stoichiometric amount of acid.

Hypotheses have already been put forward about electronic factors that control the chemical behavior of the coordinated dioxygen[3] but a more direct approach based on quantum chemical studies is still lacking. The aim of the present paper is to contribute to the understanding of the electronic and energetic factors which can favor the formation of the hydroperoxide intermediate or the formation of the final L_2PtX_2 species together with hydrogen peroxide. Extended ab initio calculations have been carried out on a wide series of $L_2Pt(OOH)X$ and L_2PtX_2 complexes, formed by reaction of $L_2Pt(\eta^2\text{-}O_2)$ with different HX molecules, which here are considered as representative of species containing protons directly bonded to oxygen, nitrogen, or chlorine atoms. The series of HX molecules considered includes water, hydrochloric, formic and, oxalic acid, *o*-catechol, ammonia, hydrazine, hydroxylamine, ethylenediamine, and *o*-phenylenediamine. The reacting protons of these chemical species are characterized by a quite different electrophilic character, since the corresponding H–X bonds have various degrees of polarization. In addition, the X groups can exhibit different coordinating capabilities with respect to the Pt(II) center. Thus, the series of the HX species considered in this study is broad enough to include the most peculiar chemical features which can affect the reactivity of the $L_2Pt(\eta^2\text{-}O_2)$ and $L_2Pt(OOH)X$ complexes.

This paper deals first with the description of the computational approach, which is an Hartree–Fock (HF) type method corrected by correlation effects. The results of the full geometry optimizations carried out on $L_2Pt(\eta^2\text{-}O_2)$, $L_2Pt(OOH)X$, and L_2PtX_2 complexes are reported later, together with the analysis of the electron distribution for each species considered. The discussion of the results, particularly those concerning the reaction energies, are given in the Conclusions.

2. Computational method

The theoretical study was carried out within the framework of the Hartree–Fock (HF) method, using an effective core potential (ECP) scheme to simulate the effect of the core electrons on the valence electrons. The atomic cores considered are the ($1s^2$) for C, N, and O atoms, ($1s^22s^22p^6$) for the P atoms and ($1s^2...4s^24p^64d^{10}$) for the Pt atom. The atomic basis sets and the corresponding expressions of the ECP operators were derived from the work of Stevens[18] and Hay.[19] The contraction schemes adopted are of type (311/41/21) for Pt (considered as a 18-valence electrons atom) and (31/31) for C, N, O, and P atoms.

To overcome the large deficiencies of the independent particle models (like the HF one) in correctly predicting the stability of the complexes and, as a consequence, the heat of reaction, the HF energies were corrected for the electron correlation by means of the density functional proposed by Lee, Yang, and Parr (LYP),[20] along the computational line outlined in ref 21. The total energies reported in the following section are computed according to $E_T = E_{HF} + E_{LYP}$. Correspondingly, the reaction energies $\Delta E = E_{T(products)} - E_{T(reagents)}$ are evaluated also using correlated energies for products and reagents, considered in their HF minimum geometry. The wave functions of open-shell species were always computed according to the restricted HF formalism.

Owing to the complexity of the systems investigated, the adopted theoretical scheme (an ab initio HF–ECP approach with correlation corrections) can be considered accurate enough for a semiquantitative prediction of the reaction energies and therefore for a meaningful discussion of the general features of the systems under investigation. The present study includes the global geometry optimization of all the species, a procedure which is an unavoidable task if one is to obtain a reliable answer to questions related to the dependency of the molecular geometry modifications on changes in electron distribution.

Due to obvious computational limitations, only model complexes were considered. The tertiary aryl- or alkylphosphine ligands (commonly present in real complexes)[1–7] were substituted for by the simpler PH_3 ligand (hereafter indicated also as L). Such an approximation, accepted in the theoretical works of other authors,[22,23] does not produce strong modifications in the metal–phosphorus bond properties and does not alter the general binding capabilities of the metal center toward the dioxygen moiety.

Some correlations between chemical behavior and electron distribution presented in the following sections are based on population analysis performed according to the Mulliken scheme.[24] In spite of some intrinsic limitations,[25] we believe that such a procedure can give useful chemical suggestions, especially when interest is focused on the trend of charge distribution (and not absolute values) in complexes of similar structure (e.g. similar metal–ligand distances and coordination geometry) described at the same level of theory (e.g. with the same double-ζ basis and contraction scheme).

All the calculations were made using the Gamess set of programs[26] on HP 9000/720 workstations.

3. Results and Discussion

The reactions considered are schematically presented on Scheme 1: HX is a molecule containing only one reacting proton,

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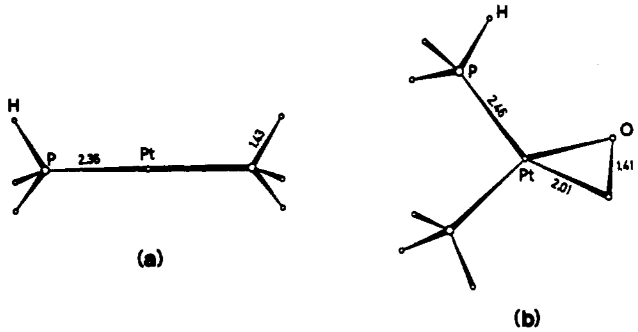

Figure 1. Theoretically optimized molecular structures of (a) $(PH_3)_2Pt$ and (b) $(PH_3)_2Pt(\eta^2\text{-}O_2)$. Bond distances are given in Å.

Table 1. Mulliken Atomic Net Charges (Q) in $(PH_3)_2Pt$ and $(PH_3)_2Pt(\eta^2\text{-}O_2)$ Complexes

	Q			
	Pt	P	H	O
$(PH_3)_2Pt$	−0.3404	0.2347	−0.0215	
$(PH_3)_2Pt(\eta^2\text{-}O_2)$	0.4328	0.2324	−0.0064	−0.4296

while HXYH is a molecule able to give a double protonation. As shown in Scheme 1, the first reaction produces hydroperoxide species of type $L_2Pt(OOH)X$ (reaction A) or $L_2Pt(OOH)(XYH)$ (reaction D), while the second step leads to the formation of L_2PtX_2 (reaction B) or $L_2Pt(XY)$ (reaction E) and hydrogen peroxide. Since the XY group always acts as a bidentate ligand, the energetics of formation of both $L_2Pt(XY)$ and H_2O_2 are expected to also be affected by the chelating ability of the ligand XY.

We have considered molecules which, in water solution, are conventionally classified as acids or bases. In particular, the molecules HX are water, hydrochloric acid, formic acid, and ammonia. The HXYH molecules are HOOCCOOH, oxalic acid (H_2ox); HOC_6H_4OH, catechol (H_2catech); H_2NNH_2, hydrazine; *HHNOH*, hydroxylamine; $H_2NC_2H_4NH_2$, ethylenediamine (H_2en); and $H_2NC_6H_4NH_2$, *o*-phenylenediamine (H_2phed). As indicated, abbreviations will be used throughout the paper (H_2ox, H_2catech, H_2en, H_2phed) and, when necessary, the reacting protons are labeled with asterisks. The main features concerning molecular structure and charge distribution of each type of complexes are discussed.

Structural, Electronic, and Energetic Features of the Complexes. $(PH_3)_2Pt$ and $(PH_3)_2Pt(\eta^2\text{-}O_2)$ Complexes. The zerovalent L_2-Pt species is taken as the reference to identify the effects on the Pt–P bond caused by the coordination of the dioxygen group to the platinum center. The coordination of $\eta^2\text{-}O_2$ produces an increase in the Pt–P bond distance (see Figure 1) as large as 0.1 Å. Although the present computational approach tends to overestimate the length of the metal–phosphorus bond (it has been found experimentally equal to 2.23 Å in the related complex $(PPh_3)_2Pt(\eta^2\text{-}O_2)$[14]) the computed elongation of the Pt–P bond is relevant and is an indication that the electron-withdrawing character of the $\eta^2\text{-}O_2$ group produces a weakening of the Pt–P bond. The reason for the relatively large overestimation of the Pt–P bond distance given by the present theoretical treatment is the lack of d polarization functions on P atoms and the non inclusion of correlation effects in the geometry optimization procedure.

Coordination of the $\eta^2\text{-}O_2$ ligand induces an important charge transfer (about 0.86 electron) from the metal to the coordinated dioxygen (see Table 1). Since the amount of charge donated from PH_3 to the metal essentially remains constant in both $(PH_3)_2$-Pt and $(PH_3)_2Pt(\eta^2\text{-}O_2)$, the charge transfer to $\eta^2\text{-}O_2$ corresponds to an oxidation of the Pt center. The σ–π mechanism of coordination of $\eta^2\text{-}O_2$ can be analyzed in terms of the occupation of the MOs centered on the dioxygen. First of all, it is apparent that the Pt–O_2 interaction produces a removal of the degeneracy of the bonding (π^b) and antibonding (π^*) MOs on O_2. The in-plane component of π^b ($\pi_{ip}{}^b$, the plane being identified by the metal and oxygen atoms) interacts as well with the dσ orbitals of Pt and, as a consequence, can act as the donor MO. The π orbitals of the metal center can interact with $\pi_{ip}{}^*$, $\pi_{op}{}^b$, and $\pi_{op}{}^*$ MOs (op stands for out-of-plane). Metal to oxygen back-bonding is mainly directed to the $\pi_{op}{}^*$, and it is much larger than the $\pi_{ip}{}^b$ → Pt donation. The situation is clearly depicted by writing the actual electronic configuration of the coordinated O_2 species as: $(\sigma)^{5.957}(\pi_{ip}{}^b)^{1.868}(\pi_{op}{}^b)^{1.976}(\pi_{ip}{}^*)^{1.065}(\pi_{op}{}^*)^{1.993}$, which should be compared with that of the free O_2 molecule: $(\sigma)^{6.000}(\pi_{ip}{}^b,\pi_{op}{}^b)^{4.000}(\pi_{ip}{}^*,\pi_{op}{}^*)^{2.000}$.

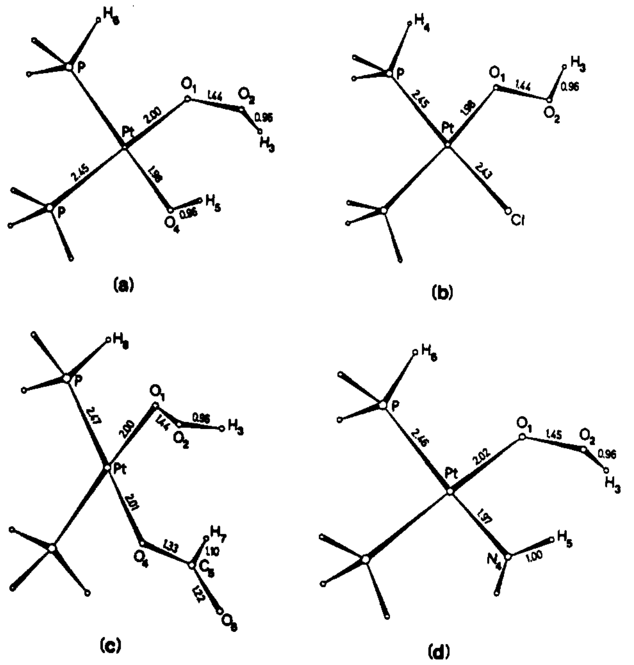

Figure 2. Theoretically optimized molecular structures of the $(PH_3)_2$-Pt(OOH)X complexes obtained by the reaction of $L_2Pt(\eta^2\text{-}O_2)$ + HX, where HX = H_2O (a), HCl (b), *HOOCH (c), and NH_3 (d). Bond distances are given in Å. Different values for the PPt distance are quoted only for the cases where they differ substantially. In all other cases only mean values for PPt are reported: the two symmetry independent distances differ by no more than ∓0.02 Å. The computed values of the angles (deg) PPtP, PPtO, OPtX are as follows: (a) 98.23, 82.36, 97.38; (b) 97.80, 78.47, 98.98; (c) 97.38, 85.01, 97.27; (d) 96.96, 84.87, 90.69.

Some computational details make the present study somewhat different from previous ones[12,13a] but do not change, in essence, the basic conclusions about the electron density on the coordinated dioxygen. In fact the coordination of $\eta^2\text{-}O_2$ as a real oxidative addition, mostly affecting the platinum center, seems to be well proved. The concentration of negative charge on the $\eta^2\text{-}O_2$ moiety (which is, however, definitively smaller than that assumed on the basis of a Pt(II) formal oxidation state), clearly suggests that such a ligand should act as a good nucleophile[17] and should react easily, for instance with molecules having positively polarized hydrogen atoms.

***cis*-$(PH_3)_2Pt(OOH)X$ Complexes.** Let us first examine the reaction $(PH_3)_2Pt(\eta^2\text{-}O_2)$ + HX → $(PH_3)_2Pt(OOH)X$, leading to the formation of a hydroperoxide intermediate. The reactants HX are considered to possess just one positively charged hydrogen. The structures of the hydroperoxide complexes with HX = H_2O, HCl, HOOCH and NH_3 obtained from calculations are shown in Figure 2; the corresponding data for the electron distribution are reported in Table 2. All the complexes are characterized by a coordination around the Pt atom very close to the planar one. The sum of the four angles PPtP, PPtO, PPtX, and OPtX is always equal to 360 ∓ 0.5°, and the maximum displacement of the ligand atoms P, X, or O from the mean-square coordination plane does not exceed 0.2 Å (see Figure 2). The computed

Table 2. Stabilities and Atomic Net Charges in the Complexes $(PH_3)_2Pt(OOH)OH$, $(PH_3)_2Pt(OOH)Cl$, $(PH_3)_2Pt(OOH)(OOCH)$, and $(PH_3)_2Pt(OOH)(NH_2)$

complex	stability (HF)[a]	stability (HF–LYP)[a]
$(PH_3)_2Pt(OOH)(OH)$	178.5	429.0
$(PH_3)_2Pt(OOH)Cl$	285.5	510.1
$(PH_3)_2Pt(OOH)(OOCH)$	232.7	461.1
$(PH_3)32Pt(OOH)(NH_2)$	146.7	378.8

Mulliken Atomic Net Charges[b]

$(PH_3)_2Pt(OOH)(OH)$	Pt	P	O_1	O_2	H_3	O_4
Q	0.5467	0.3593	–0.6118	–0.4187	0.3697	–0.9752
	H_5	H_6				
Q	0.3772	–0.0011				
$(PH_3)_2Pt(OOH)Cl$	Pt	P	O_1	O_2	H_3	H_4
Q	0.3350	0.3322	–0.6550	–0.3658	0.3701	0.0046
	Cl					
Q	–0.3763					
$(PH_3)_2Pt(OOH)(OOCH)$	Pt	P	O_1	O_2	H_3	O_4
Q	0.4984	0.4077	–0.6214	–0.3783	0.3696	–0.5952
	C_5	O_6	H_7	H_8		
Q	0.0734	–0.2598	0.0889	0.0015		
$(PH_3)_2Pt(OOH)NH_2$	Pt	P	O_1	O_2	H_3	N_4
Q	0.4498	0.3891	–0.5922	–0.4341	0.3685	-1.0737
	H_5	H_6				
Q	0.2847	–0.0110				

[a] The stabilities of the complexes ($kJ{\cdot}mol^{-1}$) are evaluated with respect to dissociation limit $2PH_3 + Pt + O_2 + HX$ (see text), using Hartree–Fock (HF) or energies corrected for electron correlation (HF–LYP, see text). [b] The atom numbering is reported in the figures. A(B) indicates the atom A directly bonded to B.

distances between the Pt atom and the oxygen atom of hydroperoxide group (PtO) are very close to 2.02 Å and very similar to the PtO distance computed for the related η^2-O_2 derivative (2.01 Å). Also the geometrical structure of the hydroperoxide group does not seem to be significantly influenced by the nature of X: the OO and OH distances are found to be equal to 1.44 and 0.96 Å, respectively, with variations smaller than 0.01 Å. As found experimentally the $L_2Pt(OOH)X$ complexes are usually characterized by a quite low stability (or a too high reactivity)[17] so that very few examples of structures having OOH groups coordinated to transition metal atoms are reported. All the X-ray experimentally investigated complexes have a OOH group bridging two metal centers. However in two Mo(VI)[27] and Co(III)[28] complexes, the experimental OO distances are 1.46 and 1.42 Å, respectively, which compare fairly well with our computed values.

The value 1.44 Å computed for OO in hydroperoxide complexes is intermediate between the values 1.37 and 1.53 Å computed for neutral and anionic hydroperoxide species OOH and $(OOH)^-$, respectively, using the same basis sets and theoretical procedure adopted for Pt complexes (more accurate ab initio calculations[29] give quite similar values of 1.33 and 1.52 Å, respectively). Qualitatively, one can expect that the global charge on the coordinated OOH group should be intermediate between 0 and 1. In fact, the protonation reaction of the coordinated dioxygen only partially quenches the negative charge of this group: the residual charge left on OOH is about –0.6 (Table 2). The charge distribution within the coordinated OOH group is strongly asymmetric, the most negatively charged atom being that directly bonded to the Pt center.

In order to evaluate the stabilities of the various intermediates an appropriate dissociation reference needs to be defined. Complexes $(PH_3)_2Pt(OOH)X$ can lead to five different low-energy dissociation channels. The first produces neutral fragments via the process $(PH_3)_2Pt(OOH)X \rightarrow 2PH_3 + Pt + O_2 + HX$. The second is a "vertical" dissociation leading to radical fragments X and OOH: $(PH_3)_2Pt(OOH)X \rightarrow 2PH_3 + Pt + X + OOH$. All the other dissociations produce mainly ions, according to the following processes: $(PH_3)_2Pt(OOH)X \rightarrow 2PH_3 + Pt^+ + X^- + OOH$; $(PH_3)_2Pt(OOH)X \rightarrow 2PH_3 + Pt^+ + X + (OOH)^-$ and $(PH_3)_2Pt(OOH)X \rightarrow 2PH_3 + Pt^{2+} + X^- + (OOH)^-$. Taking into account the relative magnitude of the computed first and second ionization potentials of Pt (8.07 and 18.04 eV, respectively), and the electron affinities of OH, Cl, OOH, and NH_2 (0.31, 3.21, 0.81 and 0.42 eV, respectively),[30] one can conclude that the gas-phase dissociation into ions, in the absence of stabilizing solvation effects) is always energetically unfavored with respect to the dissociation into neutral fragments. However all of the dissociation channels leading to neutral radical species are, in principle, forbidden by the spin-conservation rule since open-shell species such as Pt (^3D), O_2 ($^3\Sigma_g^-$) and various doublet radicals are produced. The dissociation channel $(PH_3)_2Pt(OOH)Cl \rightarrow 2PH_3 + Pt + O_2 + HX$, giving the lowest total energy of products, will be used as the reference process in order to evaluate the stabilities of the different hydroperoxide complexes, both at HF and HF–LYP levels (see Table 2). The most stable complex is the chloride derivative (510.1 $kJ{\cdot}mol^{-1}$), followed by the complexes in which the reactive proton is initially bonded to oxygen (X = OH, OOCH). The complex $L_2Pt(OOH)NH_2$ is characterized by the lowest stability (378.8 $kJ{\cdot}mol^{-1}$). It follows that the stability of the hydroperoxidic platinum species is related to the electron affinity[30] (or electron withdrawing ability) of the X ligand, an observation in agreement also with the experimental evidence of the relatively high stability of complexes carrying CF_3 groups.[17a]

***cis*-$(PH_3)_2Pt(OOH)(XYH)$ Complexes.** The HXYH molecules studied, possessing two positively polarized hydrogens that can protonate the η^2-O_2 group, are the following: H_2ox, H_2catech, H_2NNH_2, *$HONH_2$, H_2en, and H_2phed. In the case of $HONH_2$ it is considered that the more positively charged hydrogen bonded

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(30) The experimental values of the ionization potential (IP) for Pt are 9.1 and 19.2 eV, respectively.[31] Our theoretical values are in error by about 1 eV. The electron affinity values recommended by Pearson[31] for OH, Cl, OOH, and NH_2 are 1.83, 3.61, 0.74, and 1.19 eV, respectively, in disagreement with the theoretical values reported in text only for OH and NH_2. The disagreement is due to intrinsic limitations of the Hartree–Fock approach which can be only partially removed by the LYP treatment. The conclusions about the preferred dissociation channels for $L_2Pt(OOH)X$ complexes remain unaltered even considering the experimental values for IP and EA.

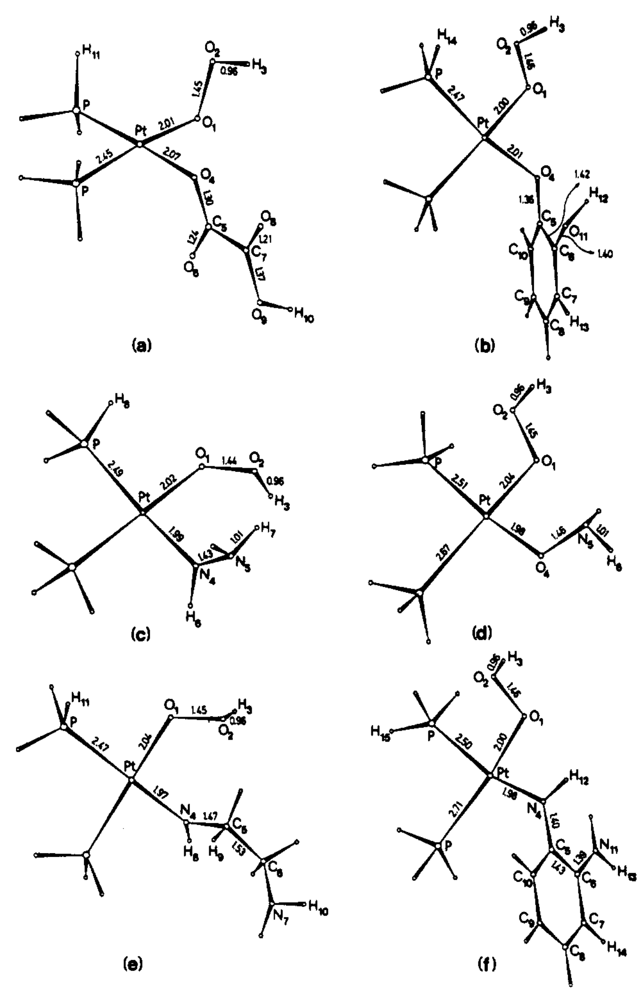

Figure 3. Theoretically optimized molecular structures of the $(PH_3)_2Pt(OOH)(XYH)$ complexes obtained by internal protonation reaction. XYH are chelating groups derived from oxalic acid (a), *o*-catechol (b), H_2NNH_2 (c), $^*HONH_2$ (d), ethylenediamine (e), and *o*-phenylenediamine (f). Bond distances are given in Å. Different values for the PPt distance are quoted only for the cases where they differ substantially. In all other cases only mean values for PPt are reported: the two symmetry independent distances differ by no more than ∓0.02 Å. The computed values of the angles (deg) PPtP, PPtO, OPtX are as follows: (a) 98.21, 86.27, 93.97; (b) 91.58, 88.02, 83.31; (c) 96.91, 81.86, 93.39; (d) 93.67, 83.47, 89.38; (e) 97.47, 82.60, 97.14; (f) 85.18, 84.64, 80.73.

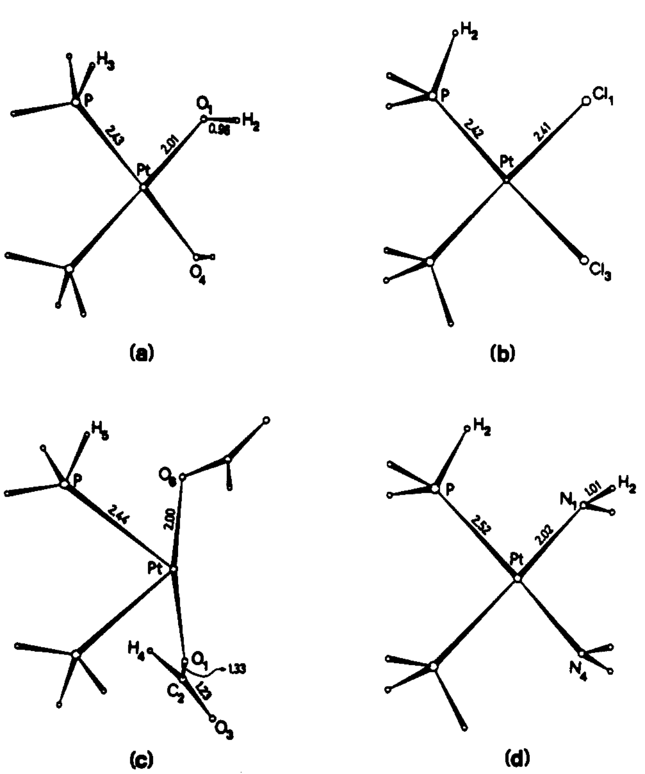

Figure 4. Theoretically optimized molecular structures of the $(PH_3)_2PtX_2$ complexes obtained by the reaction $L_2Pt(OOH)X + HX$. HX = H_2O (a), HCl (b), *HOOCH (c), and NH_3 (d). Bond distances are given in Å. Different values for PPt distance are quoted only for the cases where they differ substantially. In all other cases only mean values for PPt are reported: the two symmetry independent distances differ by no more than ∓0.02 Å. The computed values of the angles PPtP, PPtX, XPtX are as follows: (a) 97.58, 81.41, 99.69; (b) 96.30, 85.87, 91.96; (c) 102.65, 79.64, 98.07; (d) 94.48, 83.34, 98.83.

to the oxygen atom reacts first. The hydroperoxide intermediates are produced by the reaction $L_2Pt(\eta^2O_2) + HXYH \rightarrow L_2Pt(OOH)(XYH)$: their best HF molecular structures are shown schematically in Figure 3 (where only the most significant geometrical parameters are quoted). The $L_2Pt(OOH)(XYH)$ complexes can be considered as square planar species to a good degree of approximation (see Figure 3), in analogy with the $L_2Pt(OOH)X$ complexes: the PtO computed bond distance of the coordinating hydroperoxide ligand is fairly constant, close to 2.01 Å with variations as small as 0.01–0.03 Å. Also the global negative charge on OOH is close to that found for $L_2Pt(OOH)X$ species (−0.65 ± 0.03). The corresponding charges on the metal atom fall within the narrow range (0.55 ± 0.05). Only the complex with X = ONH_2 deviates from such a general trend as it promotes a slightly higher ionicity of the Pt–OOH bond. It follows that the hydroperoxide complexes obtained by interaction with HXYH are characterized by geometrical and electronic features very similar to those of the complexes obtained by the reaction of $L_2Pt(\eta^2\text{-}O_2)$ with HX species.

In analogy to the $L_2Pt(OOH)X$ complexes, the best dissociation channel to be taken as the stability reference of the various intermediates is $(PH_3)_2Pt(OOH)(XYH) \rightarrow 2PH_3 + Pt + O_2 + HXYH$. The HF–LYP stabilities of the hydroperoxide complexes of the series considered (XYH = Hox, Hcatech, $HNNH_2$, ONH_2, Hen, Hphed) vary from 554.4 to 374.0 kJ·mol^{-1} (see Table 3). It is evident that all the molecules having the reacting proton attached to a nitrogen atom give complexes less stable than those originated by proton bonded to an oxygen atom; the complex obtained from $^*HONH_2$ has, as expected, an intermediate stability.

In order to show to what extent the electronic structure of the OOH group is affected by the coordination bond to a Pt(II) center, we carried out HF–ECP geometry optimization of the free *tert*-butyl hydroperoxide (*t*-BuOOH) and phenyl hydroperoxide (PhOOH), using the same basis sets of the complexes. The OO, OH, and CO distances have been found to be equal to 1.44, 0.97, and 1.48 Å in *t*-BuOOH and 1.45, 0.97, and 1.42 Å in PhOOH. The OO equilibrium distances fall within the range 1.44–1.46 Å, which is characteristic of the coordinated hydroperoxide group. The global charge on the OOH group is equal to −0.33 and −0.20 in *t*-BuOOH and PhOOH, respectively, and this difference reflects the stronger electron donor ability of *t*-Bu than Ph. In both free hydroperoxide derivatives, the O(C) atoms carry a negative charge (−0.30 and −0.22 in *t*-BuOOH and PhOOH, respectively) smaller than the O(H) atoms (−0.41 and −0.40). When such results are compared with the data of Tables 2 and 3, it becomes apparent that the polarity of the OOH group in free organic hydroperoxide compounds is exactly opposite to that found in Pt(II) complexes. In fact the charge on O(Pt) is always more negative (with the exception of the $L_2Pt(OOH)(Hcatech)$ than that localized on O(H), and in several cases the differences between the two charges is as large as −0.2.

***cis*-$(PH_3)_2PtX_2$ Complexes.** The $L_2Pt(OOH)X$ intermediates are assumed to react further with HX to give hydrogen peroxide and L_2PtX_2 complexes (see Scheme 1). The complexes with HX = H_2O, HCl, *HOOCH and NH_3, after HF-ECP geometry

Table 3. Stabilities and Atomic Net Charges in the Complexes $(PH_3)_2Pt(OOH)(Hox)$, $(PH_3)_2Pt(OOH)(Hcatech)$, $(PH_3)_2Pt(OOH)(HNNH_2)$, $(PH_3)_2Pt(OOH)(ONH_2)$, $(PH_3)_2Pt(OOH)(Hen)$, and $(PH_3)_2Pt(OOH)(Hphed)$

complex	stability (HF)[a]	stability (LYP)[a]
$(PH_3)_2Pt(OOH)(Hox)$	239.7	460.9
$(PH_3)_2Pt(OOH)(Hcatech)$	220.1	451.7
$(PH_3)_2Pt(OOH)(HNNH_2)$	126.0	370.2
$(PH_3)_2Pt(OOH)(ONH_2)$	163.4	379.7
$(PH_3)_2Pt(OOH)(Hen)$	102.4	347.9
$(PH_3)_2Pt(OOH)(Hphed)$	141.3	374.0

Mulliken Atomic Net Charges[b]

$(PH_3)_2Pt(OOH)(Hox)$	Pt	P	O_1	O_2	H_3	O_4
Q	0.5566	0.4080	−0.5594	−0.4468	0.3853	−0.5558
	C_5	O_6	C_7	O_8	O_9	H_{10}
Q	0.0869	−0.2492	0.1159	−0.1224	−0.5069	0.4519
$(PH_3)_2Pt(OOH)(Hcatech)$	Pt	P	O_1	O_2	H_3	O_4
Q	0.4853	0.4384	−0.5064	−0.5337	0.4008	−0.6173
	C_5	C_6	C_7	C_8	C_9	C_{10}
Q	0.0390	−0.2287	−0.1974	−0.2987	−0.1851	0.0073
	O_{11}	H_{12}	H_{13}	H_{14}		
Q	−0.5234	0.4309	0.2179	−0.0035		
$(PH_3)_2Pt(OOH)(HNNH_2)$	Pt	P	O_1	O_2	H_3	N_4
Q	0.4638	0.3783	−0.6018	−0.4256	0.3720	−0.8072
	N_5	H_6	H_7	H_8		
Q	−0.5075	0.2780	0.2642	−0.0095		
$(PH_3)_2Pt(OOH)(ONH_2)$	Pt	P	O_1	O_2	H_3	O_4
Q	0.6411	0.3217	−0.5501	−0.5169	0.4022	−0.7377
	N_5	H_6	H_7			
Q	−0.3960	0.2694	−0.0041			
$(PH_3)_2Pt(OOH)(Hen)$	Pt	P	O_1	O_2	H_3	N_4
Q	0.4520	0.4108	−0.5978	−0.4300	0.3601	−1.0120
	C_5	C_6	N_7	H_8	H_9	H_{10}
Q	0.0655	−0.1053	−0.6801	0.2792	0.1016	0.2711
	H_{11}					
Q	−0.0172					
$(PH_3)_2Pt(OOH)(Hphed)$	Pt	P	O_1	O_2	H_3	N_4
Q	0.5333	0.3662	−0.5385	−0.5174	0.3983	−0.7139
	C_5	C_6	C_7	C_8	C_9	C_{10}
Q	−0.2472	0.2165	−0.3532	−0.2798	−0.2758	−0.1979
	N_{11}	H_{12}	H_{13}	H_{14}	H_{15}	
Q	−0.6534	0.3746	0.3661	0.2127	−0.0101	

[a] The stabilities of the complexes ($kJ\cdot mol^{-1}$) are evaluated with respect to dissociation limit $2PH_3 + Pt + O_2 + HX$ (see text), using Hartree–Fock (HF) or energies corrected for electron correlation (HF–LYP, see text). [b] The atom numbering is reported in the figures. A(B) indicates the atom A directly bonded to B.

optimization result to be planar species (see Figure 4). All the complexes in which X is an oxygen donor group are characterized by a PtO bond distance which falls in the range 2.00–2.01 Å, a specific value almost unaffected by the particular nature of X. The PtCl distance in the dichloro complex L_2PtCl_2 is equal to 2.41 Å, only slightly shorter than in the corresponding hydroperoxide derivative (2.43 Å). Finally, PtN distances for $L_2Pt(NH_2)_2$ have been computed and are virtually identical to that of $L_2Pt(OOH)(NH_2)$. The net charge on the Pt atom (see Table 4) is equal to 0.55, 0.04, 0.46, and 0.40 for X = OH, Cl, OOCH, and NH_2, respectively, which clearly differentiate the O- and N-donor ligands from the chloride one. The above values are, in general, equal to or smaller than the corresponding charges computed for the related hydroperoxide derivatives (0.55, 0.34, 0.50, and 0.45, respectively).

The computed charge on Pt in L_2PtCl_2 (0.04) is definitely smaller than that expected on the basis of a formal Pt(II) oxidation state. The charge donated by the PH_3 ligands is quite similar in the three complexes $L_2Pt(OH)_2$ (0.68), $L_2Pt(NH_2)_2$ (0.65), and L_2PtCl_2 (0.59). However, the total charge transfer $Pt \rightarrow Cl$ (0.69) almost exactly compensates the donation $(PH_3) \rightarrow Pt$, causing a nearly zero charge on Pt. Obviously a higher electron withdrawing ability of the OH and NH_2 ligands produces higher positive charge on the metal center.

By means of the quantities χ and η (the absolute electronegativity and hardness) of atoms A and B ($\chi_A > \chi_B$), the amount of charge transferred $Q_{B \rightarrow A}$ is given by

$$Q_{B \rightarrow A} = \frac{\chi_A - \chi_B}{2(\eta_A + \eta_B)}$$

in agreement with the principle of chemical potential equalization.[32]

Using the data given by Hinze and Jaffè[33] for O(sp_3), N(sp^3), and Cl(s^2p^5) and by Pearson[31] for the neutral Pt atom, one can compute that the excesses of charge on O, N, and Cl in the diatomic systems PtO, PtN, and PtCl are equal to −0.38, −0.27 and −0.19, respectively. The trend of these values (largely approximated because the infuence of all the other ligand atoms is completely neglected) parallels the trend of values reported in Table 4: −0.61, −0.59, and −0.35 for O, N, and Cl, respectively.

Some problems arise in the evaluation of the relative stability of the L_2PtX_2 complexes since it is difficult to find a common dissociation channel for all the species considered. A possible choice is the reaction $L_2PtX_2 \rightarrow 2L + Pt + X_2$, which was found to be the favored dissociation when X_2 = H_2NNH_2, H_2O_2, and Cl_2, i.e. when the radical X (NH_2, OH, Cl) can dimerize, leading to stable species. In the case of the complex $L_2Pt(OOCH)_2$ the

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Table 4. Stabilities and Atomic Net Charges in the Complexes $(PH_3)_2Pt(OH)_2$, $(PH_3)_2Pt(Cl)_2$, $(PH_3)_2Pt(OOCH)_2$, and $(PH_3)_2Pt(NH_2)_2$

complex	stability (*HF*)[a]	stability (LYP)[a]
$(PH_3)_2Pt(OH)_2$	359.5	524.6
$(PH_3)_2Pt(Cl)_2$	460.4	621.6
$(PH_3)32Pt(OOCH)_2$	465.6	739.1
$(PH_3)_2Pt(NH_2)_2$	158.8	310.8

Mulliken Atomic Net Charges[b]

$(PH_3)_2Pt(OH)_2$	Pt	P	O_1	H_2	H_3	
Q	0.5478	0.3714	−0.9729	0.3623	−0.0116	
$(PH_3)_2Pt(Cl)_2$	Pt	P	Cl_1	H_2		
Q	0.0430	0.2790	−0.3460	0.0150		
$(PH_3)_2Pt(OOCH)_2$	Pt	P	O_1	C_2	O_3	H_4
Q	0.4638	0.4849	−0.6785	0.0993	−0.2755	0.1239
	H_5					
Q	0.0047					
$(PH_3)_2Pt(NH_2)_2$	Pt	P	N_1	H_2	H_3	
Q	0.4006	0.3771	−1.0582	0.2663	−0.0172	

[a] The stabilities of the complexes ($kJ \cdot mol^{-1}$) are evaluated with respect to dissociation limit $2PH_3 + Pt + X_2$, for X_2 = HOOH, Cl_2, and H_2NNH_2 and with respect to the limit $2PH_3 + Pt + 2X$ for OOCH using Hartree–Fock (HF) or energies corrected for electron correlation (HF–LYP, see text). [b] The atom numbering is reported in the figures. A(B) indicates the atom A directly bonded to B.

dissociation channel giving two OOCH radicals is the preferred one, being more stable, for instance, than that producing ionic species. The sequence of the HF–LYP stabilities results is as follows: 524.6, 621.6, 739.1, and 310.8 $kJ \cdot mol^{-1}$, for X = OH, Cl, OOCH, and NH_2, respectively. However, the high stability of the complex with X = OOCH is probably due to the relatively low stability of the radical species.

***cis*-$(PH_3)_2Pt(XY)$ Complexes.** The complexes $L_2Pt(OOH)(XYH)$ can undergo a second intramolecular protonation reaction, leading to the formation of hydrogen peroxide together with a chelated species $L_2Pt(XY)$ (see Scheme 1). The molecular structures corresponding to the optimum HF-ECP geometry are reported in Figure 5, for all the compounds of the series XY = ox, catech, HNNH, ONH, en, and phed, which, in analogy with all the previous cases, can be considered as planar complexes (see Figure 5). Mulliken gross atomic charges are reported in Table 5. The dissociation limit used in the evaluation of the stability of complexes L_2PtXY always corresponds to the formation of a biradical species XY.

The two complexes $L_2Pt(ox)$ and $L_2Pt(catech)$ show a five-member chelating ring, with two O-donor atoms. The computed PtO bond distances 2.01 and 1.99 Å, respectively, are very similar to those found for the related non-chelated complexes, a fact indicating that the occurrence of a chelating ring does not essentially influence the PtO bond distance (see Table 5). The two complexes are characterized by HF-LYP stabilities equal to 1433.1 and 1339.1 $kJ \cdot mol^{-1}$, much higher than those of the L_2PtX_2 complexes with similar coordinating groups (X = OOCH, OH), a fact proving the stabilizing effect of the chelation.

The derivatives $L_2Pt(XY)$, with XY = HNNH and ONH, contain three-member chelating rings. The optimized geometry of the $L_2Pt(HNNH)$ complex is characterized by PtN and NN distances equal to 1.97 and 1.44 Å, quite comparable with the corresponding values computed for $L_2Pt(OOH)(HNNH_2)$ (1.99 and 1.43 Å) and the theoretical estimate of the NN distance in the free ligand, 1.42 Å (the experimental value is 1.45 Å[34]). In the $L_2Pt(ONH)$ species the computed PtO and PtN bond distances are very similar (2.06 Å), while the Pt–O bond is slightly longer than in the related hydroperoxide derivatives $L_2Pt(OOH)(ONH_2)$ (1.98 Å). On the contrary, the ON distance within the chelating ring is considerably shorter (1.38 Å) than that computed for the nonchelated species $L_2Pt(OOH)(ONH_2)$ (1.44 Å). Considering $L_2Pt(ONH)$ as a complex containing the simplest nitroso ligand ONH, the computed variations of the ON distances can be easily rationalized as follows: the O–N bond in $L_2Pt(OOH)(ONH_2)$ can be essentially considered a single bond (or weaker) since its length (1.44 Å) is even longer than that computed for the free $HONH_2$ molecule (1.42 Å). On the contrary, the ON distance in $L_2Pt(ONH)$ is shorter, indicating that the O–N bond in such a complex is stronger than a single bond, as in free nitroso compounds[36] or in the free ONH radical which is characterized by a ON distance equal to 1.21 Å.[34] However the strength of the O–N bond in $L_2Pt(ONH)$ is markedly reduced with respect to a true double bond, because about 0.63 electron is back-donated from the metal center to the π^*-type MO located essentially on the ON group. The hydrogen atom of the ONH group does not belong to the PtON plane (the HNOPt dihedral angle is equal to 104.1°): the geometry around the nitrogen atom is pyramidal, suggesting an hybridization intermediate between sp^2 and sp^3. The present results concerning the geometric distortion and the electronic activation of the ONH group basically agree with those

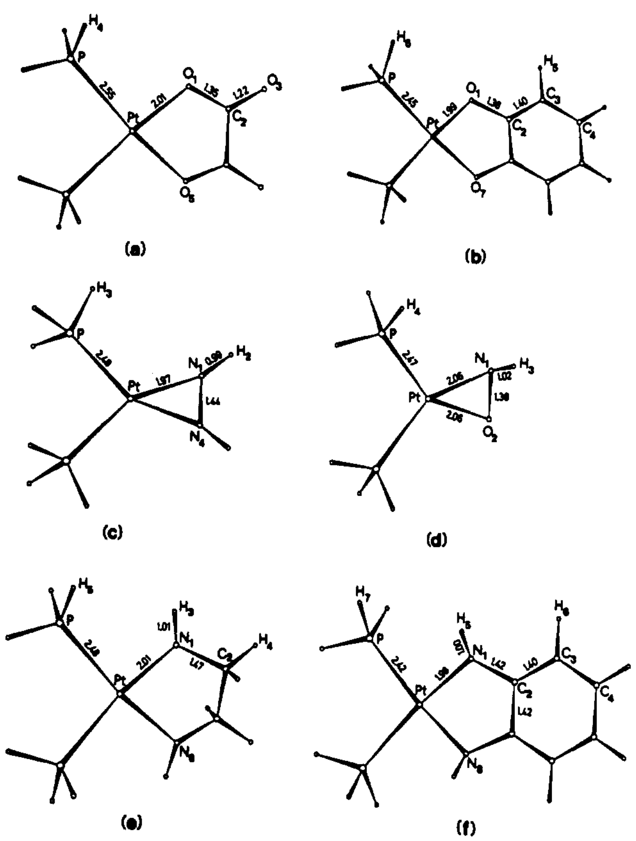

Figure 5. Theoretically optimized molecular structures of the $(PH_3)_2Pt(OOH)(XY)$ complexes obtained by an internal protonation reaction of $L_2Pt(OOH)(XYH)$. HXYH = oxalic acid (a), *o*-catechol (b), H_2NNH_2 (c), $^*HONH_2$ (d), ethylenediamine (e), *o*-phenylenediamine (f). Bond distances are given in Å. Different values for the PPt distance are quoted only in the cases that they differ substantially. In all other cases only mean values for PPt are reported: the two symmetry independent distances differ by no more than ∓0.02 Å. The computed values of the angles PPtP, PPtX, XPtY are as follows: (a) 91.77, 94.10, 79.70; (b) 94.03, 91.71, 82.55; (c) 97.72, 109.74, 42.80; (d) 102.08, 109.43, 38.91; (e) 97.87, 91.22, 79.70; (f) 94.87, 91.52, 82.08.

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Table 5. Stabilities and Atomic Net Charges in the Complexes $(PH_3)_2Pt(ox)$, $(PH_3)_2Pt(catech)$, $(PH_3)_2Pt(HNNH)$, $(PH_3)_2Pt(ONH)$, $(PH_3)_2Pt(en)$, and $(PH_3)_2Pt(phed)$

complexes	stability (HF)[a]	stability (LYP)[a]
$(PH_3)_2Pt(ox)$	1211.0	1433.1
$(PH_3)_2Pt(catech)$	1065.2	1339.1
$(PH_3)_2Pt(HNNH)$	324.6	553.6
$(PH_3)_2Pt(ONH)$	172.0	319.7
$(PH_3)_2Pt(en)$	213.5	450.0
$(PH_3)_2Pt(phed)$	1282.2	1498.2

Mulliken Atomic Net Charges[b]

$(PH_3)_2Pt(ox)$	Pt	P	O_1	C_2	O_3	H_4
Q	1.0357	0.2081	−0.6445	0.1025	−0.2017	0.0059
$(PH_3)_2Pt(catech)$	Pt	P	O_1	C_2	C_3	C_4
Q	0.4364	0.4384	−0.7334	0.1799	−0.2641	−0.2442
	H_5	H_6				
Q	0.2073	−0.0032				
$(PH_3)_2Pt(HNNH)$	Pt	P	N_1	H_2	H_3	
Q	0.4341	0.3367	−0.8166	0.3194	−0.0004	
$(PH_3)_2Pt(ONH)$	Pt	P	N_1	O_2	H_3	H_4
Q	0.2634	0.2256	−0.3888	−0.4870	0.2520	−0.0151
$(PH_3)_2Pt(en)$	Pt	P	N_1	C_2	H_3	H_4
Q	0.2411	0.4067	−0.8434	−0.0007	0.2259	0.0778
	H_5					
Q	−0.0194					
$(PH_3)_2Pt(phed)$	Pt	P	N_1	C_2	C_3	C_4
Q	0.2611	0.4753	−0.8180	0.1337	−0.2927	−0.2738
	H_5	H_6	H_7			
Q	0.2819	0.2061	−0.0164			

[a] The stabilities of the complexes (kJ·mol^{-1}) are evaluated with respect to dissociation limit $2PH_3 + Pt + HYXH$ (see text), using Hartree–Fock (HF) or energies corrected for electron correlation (HF–LYP, see text). [b] The atom numbering is reported in the figures. A(B) indicates the atom A directly bonded to B.

reached in a previous study on nitroso model complexes $(PH_3)_2Pt(ONR)$ ($R = CH_3, CF_3$).[12]

The low HF-LYP stabilities of the two complexes $L_2Pt(HNNH)$ and $L_2Pt(ONH)$ (553.6 and 319.7 kJ·mol^{-1}), can be explained by the presence of a three-member chelating ring that may be stable only in the presence of an important π back-bonding contribution that can compensate steric strains. The π mechanism is completely absent for the HNNH fragment and is also rather weak with the ONH ligand, due to the presence of a hydrogen atom, a poor electron-withdrawing N-substituent. It is known that the π-accepting ability of the ONR nitroso ligands is enhanced by strong electron withdrawing groups R.[12] The poor chelating ability of HNNH and ONH groups is clearly proved by the relative low stability of the two $L_2Pt(XY)$ complexes. This is in agreement with experimental results showing that three-member rings chelating the Pt atom occur only in complexes with strong π-acceptor ligands in the side-on coordination (e.g. η^2-O_2,[14] some nitroso ligands[12,37] and activated alkenes[35]). The last two complexes of the series $L_2Pt(XY)$ have a five-member chelating ring with two N-donor atoms, originally belonging to aliphatic (H_2en) and aromatic (H_2phed) amines. The optimized structures reported in Figure 4 are characterized by PtN bond distances equal to 2.01 and 1.98 Å for XY = en and phed, respectively. The latter value is virtually identical to that computed for $L_2Pt(OOH)(Hphed)$, while the former is higher than that observed in the corresponding hydroperoxo derivative (1.97 Å). The total charge transferred to the coordinated ligand is equal to 0.95 and 1.11 while the net charge on the Pt atom is equal to 0.24 and 0.26, for XY = en and phed, respectively. The negative charge is strongly localized on the NH group in the en ligand while it is also distributed on the phenyl ring in the case of the phed ligand. The large delocalization of the negative charge on phed accounts for the difference in stability of the two complexes, computed as equal to 450.0 and 1498.2 kJ·mol^{-1} for $L_2Pt(en)$ and $L_2Pt(phed)$, respectively.

Reactivity of the $L_2Pt(\eta^2\text{-}O_2)$ Complex and Its Hydroperoxide Derivatives $L_2Pt(OOH)X$ and $L_2Pt(OOH)(XYH)$. As shown in Scheme 1, the ultimate formation of hydrogen peroxide occurs via reactions B or E, involving hydroperoxide intermediates of types $L_2Pt(OOH)X$ and $L_2Pt(OOH)(XYH)$, respectively. Of course, the reaction energies (hereafter indicated as ΔE) of steps B and E are expected to be strongly dependent on the stability of the corresponding hydroperoxide intermediates, produced in steps A and D. Reaction C, corresponding to the direct formation of H_2O_2 according to $L_2Pt(\eta^2\text{-}O_2) + 2HX \rightarrow L_2PtX_2 + H_2O_2$, is actually the sum of the reactions A and B. Analogously, for the reactants HXYH, the global reaction F is the sum of reactions D and E. Correspondingly, the energies ΔE_C and ΔE_F are defined as $\Delta E_C = \Delta E_A + \Delta E_B$ and $\Delta E_F = \Delta E_D + \Delta E_E$.

The reaction energies of the A and D processes leading to $L_2Pt(OOH)X$ and $L_2Pt(OOH)(XYH)$ hydroperoxide species (see Scheme 1), computed at the HF–LYP level (see Table 6, negative values stand for exoergic processes) are all negative and vary from −254 to −91 kJ·mol^{-1}. The sequence of HX and HXYH reagents ordered according to the decreasing exoergic character is HCl, H_2ox, HOOCH, $H_2catech$, H_2O, $HONH_2$, HN_3, H_2phed, H_2NNH_2, and H_2en. The first terms of this sequence are all characterized by protons bonded to Cl or O atoms. The last terms are characterized by less "acid" protons of H–N groups, while $^{*}HONH_2$ shows an intermediate behavior.

The further protonation reaction of the coordinated hydroperoxide group may produce hydrogen peroxide (steps B and E of Scheme 1). This represents the final and most specific aspect of the activation of the molecular oxygen.[3] The energy data reported in Table 6 show that some reactions are even endoergic (i.e. characterized by positive ΔE_B or ΔE_E values) also with HX or HXYH species which exhibit, on the contrary, high reactivity in steps A and D (e.g. H_2O, H_2ox, $H_2catech$, H_2en, and H_2phed). In general, reactions B and E with the highest endoergic character are those in which the reacting proton is bonded to a nitrogen atom, confirming again the relatively low reactivity of N-bonded hydrogen atoms.

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Table 6. Reaction Energies for Formation of Hydroperoxide Derivatives and Hydrogen Peroxide[a]

Reaction[b]
$L_2Pt(\eta^2O_2) + HX \rightarrow L_2Pt(OOH)X$ (A)
$L_2Pt(OOH)X + HX \rightarrow L_2PtX_2 + H_2O_2$ (B)
$L_2Pt(\eta^2O_2) + 2HX \rightarrow L_2PtX_2 + H_2O_2$ (C)

HX	A	B	C
H_2O	−154.2	33.1	−121.2
HCl	−253.7	−116.6	−370.3
HOOCH	−204.6	−128.9	−333.5
NH_3	−122.4	64.3	−58.1

Reaction[b]
$L_2Pt(\eta^2O_2) + HXYH \rightarrow L_2Pt(OOH)(XYH)$ (D)
$L_2Pt(OOH)(XYH) \rightarrow L_2Pt(OOH)(XY) + H_2O_2$ (E)
$L_2Pt(\eta^2O_2) + HXYH \rightarrow L_2Pt(OOH)(XY) + H_2O_2$ (F)

HXYH	D	E	F
H_2ox	−204.5	10.0	−194.5
H_2catech	−195.3	17.6	−177.7
HHNNHH	−113.8	338.1	224.3
HONHH	−123.3	103.5	−19.8
H_2en	−91.6	51.6	−40.0
H_2phed	−117.6	5.0	−112.6

Reaction[c]
$L_2Pt(\eta^2O_2) + HX \rightarrow L_2Pt(\eta^2O_2) + H^+ + X^-$ (A_1)
$L_2Pt(\eta^2O_2) + H^+ + X^- \rightarrow [L_2Pt(OOH)]^+ + X^-$ (A_2)
$[L_2Pt(OOH)]^+ + X^- \rightarrow L_2Pt(OOH)X$ (A_3)

HX	A_1	A_3	$A = A_1 + A_2 + A_3$
H_2O	1704.7 (1663.6)	−828.8	−154.2
HCl	1336.7 (1408.7)	−560.1	−253.6
*HOOCH	1413.4 (1442.1)	−587.8	−204.6
NH_3	1824.3 (1709.6)	−916.5	−122.4

Reaction[c]
$L_2Pt(\eta^2O_2) + HXYH \rightarrow L_2Pt(\eta^2O_2) + H^+ + (XYH)^-$ (D_1)
$L_2Pt(\eta^2O_2) + H^+ + (XYH)^- \rightarrow [L_2Pt(OOH)]^+ + (XYH)^-$ (D_2)
$[L_2Pt(OOH)]^+ + (XYH)^- \rightarrow L_2Pt(OOH)(XYH)$ (D_3)

HXYH	D_1	D_3	$D = D_1 + D_2 + D_3$
H_2ox	1343.9	−518.2	−204.5
H_2catech	1459.4	−624.5	−195.3
HHNNHH	1785.9	−869.5	−113.8
HONHH	1676.0	−769.0	−123.2
H_2en	1781.2	−824.5	−91.5
H_2phed	1630.6	−717.9	−117.5

[a] The HF–LYP reaction energies are expressed in $kJ \cdot mol^{-1}$. Exothermic reactions have negative energies. [b] The reactions A, B, C, D, E, and F refer to Scheme 1. [c] The reactions A_1, A_2, A_3, D_1, D_2, and D_3 refer to Scheme 2. Note that $A = A_1 + A_2 + A_3$ and $D = D_1 + D_2 + D_3$. Steps A_2 and D_2 are identical and are characterized by a reaction energy equal to -1030.2 $kJ \cdot mol^{-1}$. The experimental values reported in parentheses are taken from ref 38 (see also ref 34), and are corrected for the zero-point energy at 0 K. Our theoretical results for A_1 reactions concerning H_2O, HCL, and NH_3, compare fairly well with tose of Shi and Boyd[39] obtained with very extended basis sets.

It is worth pointing out that all the global reactions C and F of Scheme 1 (with the exception of hydrazine) are characterized by negative energies. This behavior is due to two different energetic features: in some cases (HCl, HOOCH) both protonation reactions are exoergic, in other cases the exoergic character of step A (or D), giving $L_2Pt(OOH)X$ (or $L_2Pt(OOH)(XYH)$), overcompensates for the second energy-demanding step, which gives H_2O_2 and L_2PtX_2 (or $L_2Pt(XY)$). Taking into account the relative magnitude of the reaction energies of C and F processes, it is possible to predict that the exoergic character of the reactions involving NH_3, $HONH_2$, and H_2en is probably too low to give rise to an important production of H_2O_2. Finally, the hydrazine molecule seems to be characterized by the least favorable energetic conditions for the production of hydrogen peroxide.

A rationalization of the energetic trend for processes A and D of Scheme 1 can be attempted along different lines. The simplest approach would be based on the acidity of the proton of HX or *HXYH, which is responsible for the electrophilic attack. In turn, the most naive definition of acidity would be based on the net (positive) charge on the reacting proton, Q_H. The higher Q_H in HX and *HXYH is, the stronger the electrophilic character and the easier the protonation reaction (reactions A and D of Scheme 1).

However, it is easy to show that the use of the Q_H parameter is actually an oversimplified attempt at measuring such an effect. In fact, for HCl, H_2ox, HOOCH, H_2catech, H_2O, $HONH_2$, NH_3, H_2phed, H_2NNH_2, and H_2en the computed Q_H values are equal to 0.16, 0.45, 0.42, 0.44, 0.38, 0.37, 0.29, 0.35, 0.29, 0.26, which can hardly correlate with the reaction energies reported in Table 6. In particular, HCl has the lowest Q_H value, but the highest reaction energy. The only qualitative observation which can be derived from the computed Q_H values is that both the HX and HXYH species, in which X = O, have, in general, Q_H values and reaction energies higher than the species with X = N.

One must conclude that the acidity of the reactants cannot be predicted only on the basis of the net atomic charge Q_H of the proton, which in turn does not give an acceptable explanation of the reactivity of the HX or HXYH species toward the coordinated η^2-O_2 group. This is not unexpected since Q_H is a molecular characteristic concerning only the unperturbed reagents (in the initial state of the reaction) while the reactivity is fully controlled by stability of the final products).

A more satisfactory explanation of the reactivity of HX and HXYH species can be found considering contributions of both the (gas phase) absolute acidity and the coordinating capability of the related anionic groups. In order to carry out such an analysis we suppose that the reactions A and D of Scheme 1 can be decomposed in partial steps involving ionic species (see Scheme 1). In particular, we assume that $A = A_1 + A_2 + A_3$, where each step obeys the definition

$$L_2Pt(\eta^2\text{-}O_2) + HX + \xrightarrow{A_1} L_2Pt(\eta^2\text{-}O_2) + H^+ + H^- \xrightarrow{A_2}$$
$$[L_2Pt(OOH)]^+ + X^- \xrightarrow{A_3} L_2Pt(OOH)X$$

In the case of reaction D the corresponding steps are D_1, D_2 and D_3. Note that A_2 and D_2 are identical steps, and correspond to the gas phase protonation of $L_2Pt(\eta^2\text{-}O_2)$: its HF–LYP ΔE is equal to -1030.2 $kJ \cdot mol^{-1}$, a value much larger than all the reaction energies for the A and D steps reported in Table 6. This is a clear proof of the high nucleophilic character of the coordinated dioxygen.

The A_1 and D_1 reactions are the gas-phase dissociations of HX or HXYH, i.e. $HX \rightarrow H^+ + X^-$, $HXYH \rightarrow H^+ + (XYH)^-$ and they are characterized by positive energy values ranging from about 1300 to 1800 $kJ \cdot mol^{-1}$ (see Table 6). The energies of the A_1 and D_1 steps are a measure of the absolute acidity of HX and *HXYH: the lower the energies ΔE_{A_1} and ΔE_{D_1}, the higher the acidity of the species. The trend of the gas phase acidity is different from that expected on the basis of pK_a values in water solution, since solvation energies may play an important role, especially with small anions such as Cl^-, OH^-, or NH_2^-. Instead, the computed energies for the A_1 and D_1 processes can be compared with experimental data of gas phase processes[38] (see Table 6): the correlation between theory and experiment is quite satisfactory as our predicted values are in error by less than 10%.

The A_3 and D_3 reactions correspond to the coordination of X^- or $(XYH)^-$ ions to the hydroperoxide cationic intermediate $[L_2Pt(OOH)]^+$; their energies are obviously related to the coordinating ability of the X^- and $(XYH)^-$ anions. The computed ΔE_{A_3} and ΔE_{D_3} quantities are, as expected, all negative.

The energy behavior of the reactions A_1 and A_3 (D_1, D_3) which control the formation of the hydroperoxide derivatives, is

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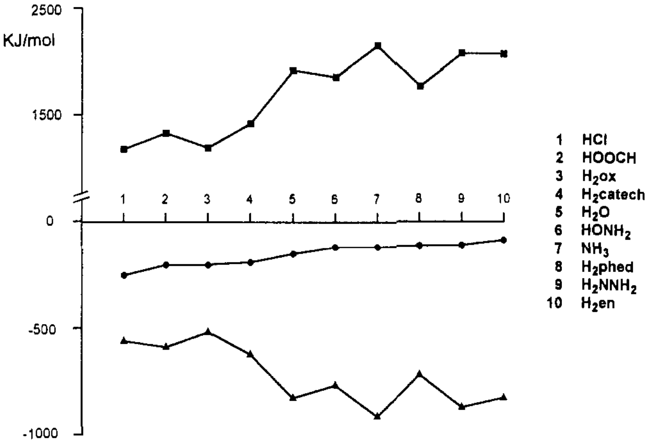
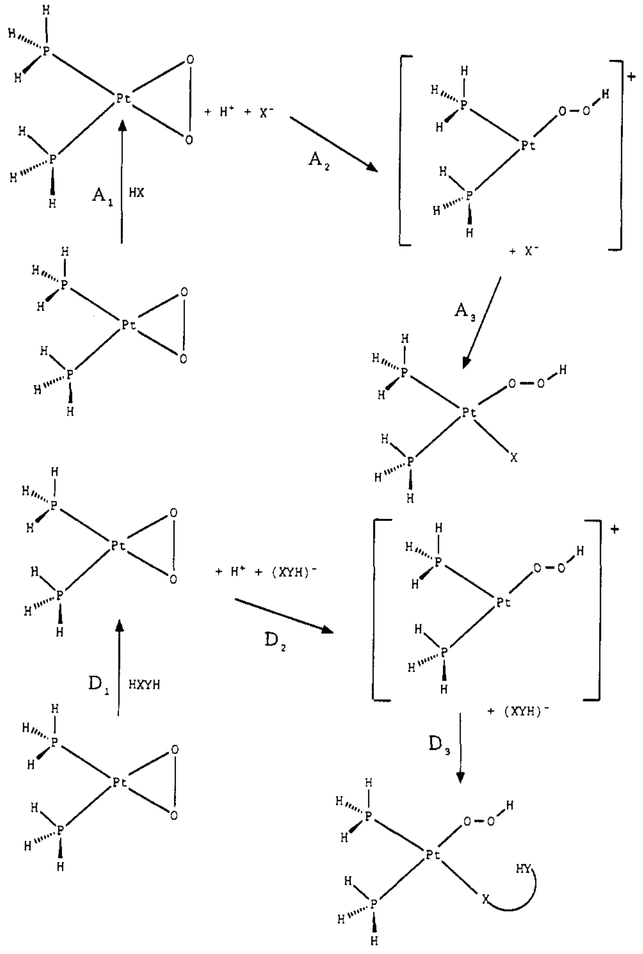


Figure 6. Analysis of reaction energy of formation of the hydroperoxide complexes $L_2Pt(OOH)X$ and $L_2Pt(OOH)(XYH)$: (■) energies for dissociation $HX \rightarrow H^+ + X^-$ and $HXYH \rightarrow H^+ + (XYH)^-$, ΔE_{A_1} and ΔE_{D_1} of Scheme 2, respectively; (▲) energies for the reactions $[L_2Pt(OOH)]^+ + X^- \rightarrow L_2Pt(OOH)X$ and $[L_2Pt(OOH)]^+ + (XYH)^- \rightarrow L_2Pt(OOH)(XYH)$, ΔE_{A_3} and ΔE_{D_3} of Scheme 2, respectively; (●) total reaction energies for the formation of hydroperoxide species, $\Delta E(A)$ and $\Delta E(D)$ of Scheme 1. [$\Delta E_A = \Delta E_{A_1} + \Delta E_{A_2} + \Delta E_{A_3}$, $\Delta E_D = \Delta E_{D_1} + \Delta E_{D_2} + \Delta E_{D_3}$; $\Delta E_{A_2} = \Delta E_{D_2}$ is the energy for the protonation of $L_2Pt(\eta^2\text{-}O_2)$, see Scheme 2].

Scheme 2



summarized in Figure 6 (see also Scheme 2). The reaction energies are plotted for the HX (HXYH) reactants ordered in the series HCl, HOOCH, H_2ox, $H_2catech$, H_2O, $HONH_2$, NH_3, H_2phed, H_2NNH_2, and H_2en: the formation of the hydroperoxide complex (reactions A and D) is less and less favored in the series. In the same series, despite some small oscillations, a trend is also evident for the increasing energy of the dissociation $HX \rightarrow H^+ + X^-$ or $HXYH \rightarrow H^+ + (XYH)^-$ (A_1, D_1) and for the decreasing (more exoergic) ΔE values for coordination of X^- and $(XYH)^-$ to $[L_2Pt(OOH)]^+$ (A_3, D_3). However the increasingly negative ΔE_{A_3} and ΔE_{D_3} values (which indicate that anions derived from H–N groups are strong coordinating agents) do not compensate the increasingly endoergic character of A_1 and D_1, which is due to the decreasing acidity of HX or HXYH. The net balance of A_1, A_2, and A_3 (D_1, D_2, and D_3) produces a trend toward less a less favored formation of hydroperoxides.

It is obvious to conclude that the formation of $L_2Pt(OOH)X$ and $L_2Pt(OOH)(XYH)$ is mainly controlled by the absolute acidity of HX and HXYH, while the coordinating ability of X^- and $(XYH)^-$ plays a minor role.

In order to show that the same effects control also the reactivity of the hydroperoxides to give H_2O_2, two reactions of type $L_2Pt(OOH)X + HX \rightarrow L_2PtX_2 + H_2O_2$ will be examined in detail. The first involves HCl and is largely exoergic; the second involves H_2O and is characterized by a positive ΔE_B value. For both reactions, steps analogous to the A_1, A_2, and A_3 ones can be defined: $B = B_1 + B_2 + B_3$.

$$L_2Pt(OOH)X + HX \xrightarrow{B_1} L_2Pt(OOH)X + H^+ + X^- \xrightarrow{B_2} [L_2PtX]^+ + H_2O_2 + X^- \xrightarrow{B_3} L_2PtX_2 + H_2O_2$$

The ΔE values for B_1, B_2, and B_3 are equal to 1336.7, –756.7, and –696.6 kJ·mol⁻¹ for HCl and 1704.7, –832.5, and –839.1 kJ·mol⁻¹ for H_2O. Again, the endoergic character of the reaction $L_2Pt(OOH)OH + H_2O \rightarrow L_2Pt(OH)_2 + H_2O_2$ is entirely due to the low absolute acidity of the water molecule. Instead, the protonation of the coordinated OOH group and the detachment of the neutral H_2O_2 molecule (step B_2) and the coordination of OH^- to the cation $[L_2Pt(OOH)]^+$ (step B_3) are even more favored than the corresponding steps for HCl. It is easy to extend such considerations to other species HX (and probably also XYH) that are characterized by highly positive energy for the process $HX \rightarrow H^+ + X^-$. This interpretation for instance is essentially confirmed by the case HX = *HOOCH, where a relatively easy dissociation of type B_1 ($\Delta E_{B_1} = -1442.1$ kJ·mol⁻¹) results in the formation of $L_2Pt(OOCH)_2$ and H_2O_2 with an important energy release ($\Delta E_B = -128.9$ kJ·mol⁻¹).

The discussion and interpretation of the energetics of the type E reactions giving chelated species $L_2Pt(XY)$ and hydrogen peroxide are more difficult since a quantitative estimate of the stabilizing contribution, due to ring-closing, cannot be done in a direct way. Also, the absolute acidity for the partially coordinated XYH group cannot be easily defined.

All the reactions of type E (see Scheme 1) giving rise to the formation of a chelate ring with XY = ox, catech, HNNH, ONH, en, and phed are endoergic. Such behavior could be explained (at least qualitatively) by assuming that the absolute acidity of the coordinated XYH fragment in the complex $L_2Pt(OOH)(XYH)$, related to the energy required for the process $L_2Pt(OOH)(XYH) \rightarrow [L_2Pt(OOH)(XY)]^- + H^+$, is roughly comparable to the absolute acidity of the free reactant: $(XYH)^- \rightarrow (XY)^{2-} + H^+$. The energy of this latter reaction in the case, for instance, of $Hox^- \rightarrow H^+ + ox^{2-}$, is 1888.1 kJ·mol⁻¹, a value higher than that corresponding to the first deprotonation process (see reaction A_1 in Table 6) and comparable in magnitude with those computed for very weak acids (H_2O, NH_3, H_2NNH_2, etc.). Similar qualitative considerations can be formulated also for other $(XYH)^-$ anions. In general the energy required for a second deprotonation reaction is not compensated in the successive exoergic steps, like the chelating ring formation and the hydrogen peroxide production.

4. Conclusions

The theoretical investigation of the electronic structure of the complex $(PH_3)_2Pt(\eta^2\text{-}O_2)$ has proved that the coordinated dioxygen, characterized by a strong nucleophilic character, and can easily react with hydrogen atoms positively polarized (H–Cl, H–O, or H–N) to give hydroperoxide complexes. The geometric and electronic structure of the coordinated OOH group is very similar in all the examined cases and seems to be quite unaffected by the specific nature of the HX or HXYH reactants. On the contrary, the energy release that accompanies the formation of the hydroperoxide intermediate is strongly influenced by the absolute acidity of the HX or HXYH species. The molecules with X = N are characterized by an absolute acidity much lower than those with X = O or Cl, and this is the main reason for a reduced reactivity toward the coordinated dioxygen. Note however that the anions X^- or $(XYH)^-$ with X = N show a strong tendency toward the coordination, which however do not completely compensate the low absolute acidity.

We have shown that in the $L_2Pt(OOH)X$ complexes the OOH group is characterized by a polarity opposite to that of the organic ROOH derivatives. This can, clearly, have an important influence on the stability of the O–OH bond and, as a consequence, on its reactivity.

The energetics of the further protonation of the coordinated OOH group leading to the formation of H_2O_2 are controlled by the same basic features, i.e. the absolute acidity of HX (or of the coordinated XYH group) and the coordinating power of the X^- and $(XY)^{2-}$ groups.

The second protonation reaction is, generally speaking, more difficult than the first one for the following reasons. (i) The nucleophilic character of the coordinated OOH group is less pronounced than that of η^2O_2; (ii) in the case of coordinated XYH groups the second deprotonation reaction is generally more difficult than the first one. The coordinating power of $(XY)^{2-}$ and the energy gain due to the chelating ring closure may not fully compensate the low acidity. This is particularly evident when the chelating ring is a three-member ring (XY = HNNH, ONH), not stabilized by π-back bonding effects.

Of all the considered reactants HX and HXYH, those having the reacting proton bonded to nitrogen atoms are characterized in general by a quite weak reactivity toward the coordinated η^2-O_2 or –OOH groups. As a consequence such species are expected to hardly react, in agreement with experimental observations.

Note that all the above considerations strictly apply to reactions considered in the gas phase. Nevertheless, our conclusions are in good agreement with the experimental observations.[7,15,17] This means that for the particular reactions considered in the present study, the solvation effects are not of dominant importance. On the other hand, it is worth mentioning that the reactions reported in Scheme 1 are usually experimentally carried out in nonpolar solvents.

Nonpolar weakly coordinating solvents used in the experiments create a chemical environment similar to the gas-phase conditions, implicitly assumed in our investigation. In particular, in the absence of water the pK_a values of the reactants lose significance. This can explain why our definition of the absolute (gas-phase) acidity is appropriate for the interpretation of the trend in reactivity and why the experimentally observed reactivity cannot be easily correlated with the pK_a of the reactants.[17b] We have shown that the absence of water is necessary because it can react with $L_2Pt(\eta^2\text{-}O_2)$ or produce exchange reactions with the $L_2Pt(OOH)X$ derivatives less stable than the $L_2Pt(OOH)(OH)$ one.

The case of the $L_2Pt(OOH)(OH)$ and $L_2Pt(OH)_2$ complexes needs a special comment. As shown in Table 6, the reaction $L_2Pt(OOH)(OH) + H_2O \rightarrow L_2Pt(OH)_2 + H_2O_2$ is energetically unfavored. Equivalently, our results show that the $L_2Pt(OH)_2$ complex can be converted into the hydroperoxide derivative by treatment with H_2O_2.

This type of behavior seems to be specific for all the cases in which the X groups of $L_2Pt(OOH)X$ has strong electronegativity. Our theoretical finding can explain the reactivity of the (diphos)-$Pt(CF_3)(OH)$ complex which gives the hydroperoxide derivative after treatment with H_2O_2,[17a] a behavior which is due to the presence of the CF_3 electron-withdrawing group.

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Supplementary Material Available: Complete tables of atom coordinates of all the complexes discussed in the text (9 pages). Ordering information is given on any current masthead page.