Palladium Superoxido Complexes. In What Way (σ or π) is O_2^- co-ordinated? A Quantum Chemical Approach†

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The relative stability of palladium superoxido complexes, formed *via* σ- or π-type co-ordination of a superoxide ion in monomeric and trimeric palladium species, has been investigated by CNDO-S^2, a semi-empirical quantum chemical SCF-m.o. method. The CNDO-S^2 method has been adapted to calculate the energetic and geometric properties of transition-metal compounds. A π-type co-ordination for O_2^- is calculated to be most stable for monomeric palladium species, while σ-type co-ordination is favoured for trimeric species. Experimental data on the reactivity of palladium superoxido complexes towards the epoxidation of simple alkenes are in agreement with the results of CNDO-S^2 calculations.

Homogeneous oxidation in the presence of a transition-metal complex is one of the most widely used homogeneous catalytic reactions. Complexes with $M(O_2R)$,[1,2] $M(O_2^{2-})$,[3] or $M(O_2^-)$[4,5] fragments, the so-called alkylperoxo, peroxo, or superoxido complexes respectively, are assumed to be the key intermediates of many homogeneous catalytic oxidation reactions. In recent years, the number of investigations concerning the synthesis and reactivity of alkylperoxo and peroxo complexes of transition metals has increased.[2,6–8] However, very little reliable quantitative data are available on the reactivity of superoxido complexes, although superoxido complexes of Zn^{II}, Co^{III}, Ti^{IV}, Sn^{IV}, Hf^{IV}, Zr^{IV}, V^{V}, and Mo^{VI} are known.[9–12] We are aware of only two investigations which have established unambiguously that superoxido complexes are able to oxidize organic molecules, *viz.* the oxidation of hindered phenols to quinones by cobalt superoxido complexes[4,5,13] and the oxidation of some organic molecules with low ionization potentials (*p*-toluidine, aniline, phenol, or hydroquinone) by titanium superoxido complexes.[14]

It is noteworthy that data on the reactivities of superoxido complexes are also of interest for heterogeneous catalytic oxidation. For example, silver is known to be an extremely efficient catalyst for the oxidation of ethylene to ethylene oxide. However, the detailed mechanism of this reaction is still uncertain. According to one hypothesis, molecular oxygen acts as the epoxidative agent,[15–17] while according to another it is the oxygen atom adsorbed on the surface that serves as the oxidant.[18–20] In the former hypothesis, the unique epoxidative activity of silver is assumed to be due to superoxide ion formation, preceded by oxygen adsorption. However, no experimental information was available to show that the metal-co-ordinated superoxide ion was able to oxidize ethylene to ethylene oxide.

We have recently found that palladium superoxido complexes are formed in reactions of palladium(II) acetate, palladium(II) propionate, bis(acetylacetonato)palladium(II), or tetrakis(triphenylphosphine)palladium with hydrogen peroxide and potassium superoxide.[21,22] Some of these complexes are sufficiently stable to determine their reactivity towards the oxidation of simple alkenes to epoxides.

According to their e.s.r. parameters, the superoxido complexes observed fall into two main types. For type I complexes $g_1 = 2.08$—2.1, $g_2 = 2.01$, and $g_3 = 2.001$—2.002 and for type II complexes $g_1 = 2.075$—2.085, $g_2 = 2.028$—2.04, and $g_3 = 2.006$—2.01.[22] Type I superoxido complexes are characteristic of trimeric palladium species and type II complexes of monomeric species.[22]

The reactivity of trimeric and monomeric palladium superoxido complexes towards simple olefins was found to be different.[22] While the trimeric complexes oxidized simple olefins easily, the monomeric complexes were found to be inert with respect to these compounds. The trimeric superoxido complex of palladium(II) acetate oxidizes ethylene to ethylene oxide, 1 ± 0.1 mol of ethylene oxide being formed per 1 ± 0.3 mol of the superoxido complex decomposed. No other products were detected by n.m.r. spectroscopy. The same superoxido complex oxidizes propylene to propylene oxide and acetone in 1:2 ratio, again no other products being detected.[22]

In this connection, it is interesting to elucidate what electronic and geometric structural features lead to the observed differences in reactivity and e.s.r. spectra. In previous work[22] it was suggested that the differences are associated with differing modes of co-ordination of O_2^- to palladium in the trimeric and monomeric species. Thus, it was of interest to perform quantum chemical calculations in order to determine the preferred mode of co-ordination of a superoxide ion (σ or π) to a metal in the monomeric and trimeric palladium species.

Details of the Calculations

As discussed above, an attempt has been made to investigate the relative stabilities and electronic structures of complexes with σ- or π-type co-ordination of O_2^- to a metal atom in monomeric and trimeric palladium species. The palladium formate complexes $Pd(HCO_2)_2$ and $[Pd_3(HCO_2)_6]$ were chosen as the representative monomeric and trimeric palladium species, respectively. Substitution of one formate ligand by a superoxide ion to give the complex $[Pd(HCO_2)(O_2)]$ was studied. Quantum chemical calculations were carried out for the following conformations of $[Pd(HCO_2)(O_2)]$: the planar π conformation (**1a**), the perpendicular π conformation (**1b**), and the σ conformation (**1c**) (see Figure 1). In the calculations all bond lengths and valence angles were optimized except for the formate C–H bond distance, which was fixed at 1.1 Å. The spatial symmetry of each conformation was kept rigid during the geometric optimization so that individual conformations were not interconvertible.

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† *Non-S.I. units employed:* eV ≈ 1.60×10^{-19} J, a.u. ≈ 4.36×10^{-18} J, G = 10^{-4} T, and cal = 4.184 J.

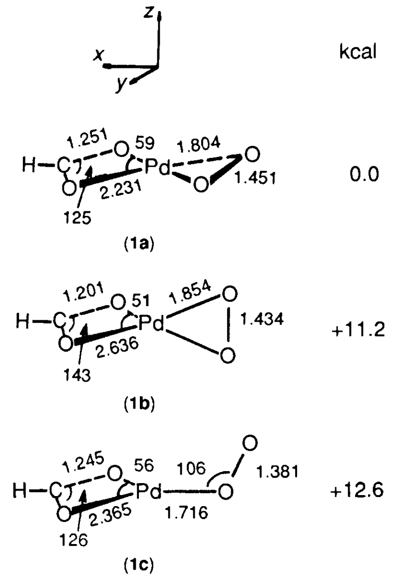

Figure 1. Calculated geometries and relative energies for planar π (**1a**), perpendicular π (**1b**), and σ (**1c**) conformations of the superoxido complex [Pd(HCO$_2$)(O$_2$)] (bond lengths in Å, angles in °)

Table 1. Geometric parameters [bond lengths (Å) and angles (°)] for the Pd$_3$(HCO$_2$)$_5$ fragment

Pd–O	1.992	Pd–O–C	130.3
Pd–Pd	3.203	O–C–O	126.4
C–O	1.238	O–Pd–O (*trans*)	166.4
C–H	1.100		

Co-ordination of superoxide ion to [Pd$_2$(HCO$_2$)$_6$] was assumed to lead to the trimeric superoxido complex [Pd$_3$(HCO$_2$)$_5$(O$_2$)]. Three possible conformations of [Pd$_3$(HCO$_2$)$_5$(O$_2$)] were used in the calculation: the π conformation with O_2^- lying in the Pd(O)$_3$ plane (**2a**), the π conformation with O_2^- perpendicular to the Pd(O)$_3$ plane (**2b**), and the σ conformation (**2c**) (see Figure 2). Table 1 lists the geometric parameters for the Pd$_3$(HCO$_2$)$_5$ fragment based on *X*-ray data for the parent acetate complex [Pd$_3$(O$_2$CMe)$_6$].[23] The geometry of the Pd(1)–O_2^- fragment was optimized for all three conformations of [Pd$_3$(HCO$_2$)$_5$(O$_2$)]. The Pd$_3$(HCO$_2$)$_5$ fragment was held rigid.

In both the monomeric and trimeric systems the geometric optimization was performed according to the procedure proposed by Fletcher and Powell.[24] As both the monomeric and trimeric superoxido complexes have an unpaired electron, a restricted Hartree–Fock method in the 'half-electron' approximation[25] was used for quantum chemical calculations.

Results and Discussion

The optimized structures and relative energies for conformations (**1a**)—(**1c**) of [Pd(HCO$_2$)(O$_2$)] are presented in Figure 1. The planar π conformation (**1a**) is of lowest energy, being 12.6 kcal more stable than conformation (**1c**). This difference in stability is determined by the differing degrees of interaction between the singly occupied π* molecular orbital (m.o.) of the superoxide ligand and the vacant b_1 orbital of the Pd(HCO$_2$)$^+$ fragment in these conformations and is illustrated by the interaction diagram in Figure 3. As can be seen for (**1a**) the interaction between the vacant b_1 fragment orbital (primarily of metal d_{xy} character) and the singly occupied π* m.o. of O_2^- is greater than for (**1c**). Apparently, this is connected with the symmetry of the co-ordination sphere of the palladium atom. The spatial symmetry of the palladium co-ordination sphere in (**1a**) corresponds much better to the symmetry of palladium d orbitals than that in the σ conformation (**1c**) (see Figure 3).

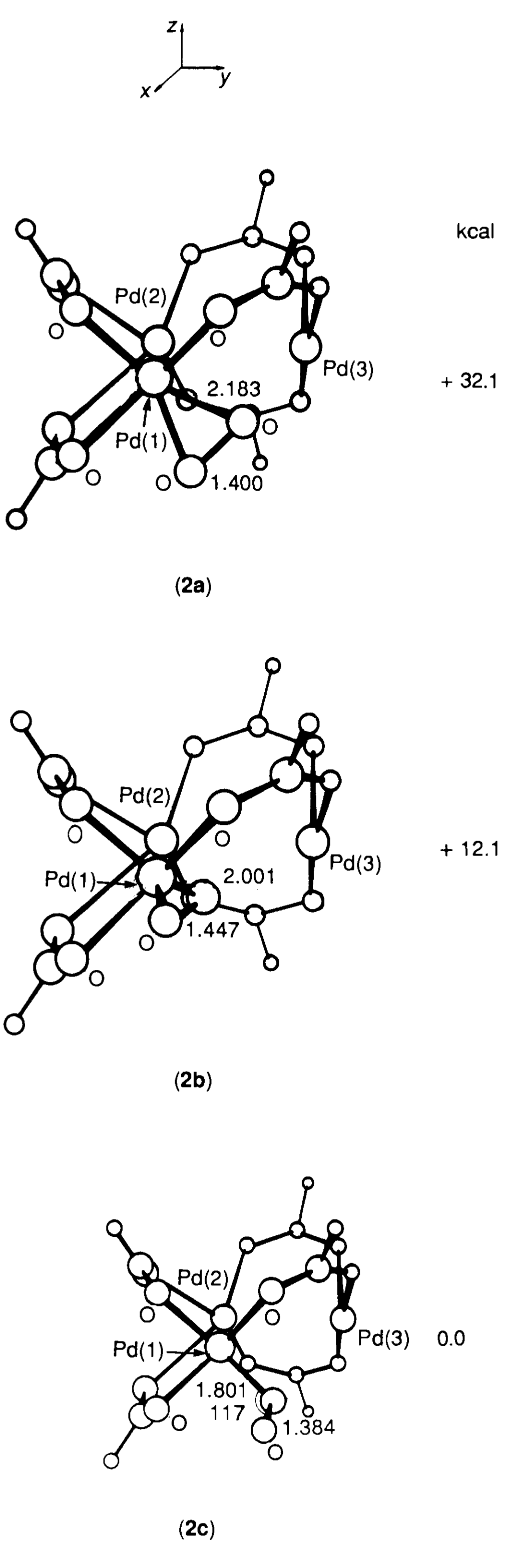

Figure 2. Calculated geometries and relative energies for planar π (**2a**), perpendicular π (**2b**), and σ (**2c**) conformations of the superoxido complex [Pd$_3$(HCO$_2$)$_5$(O$_2$)] (bond lengths in Å, angles in °)

The above ordering in the relative stability of the σ and π

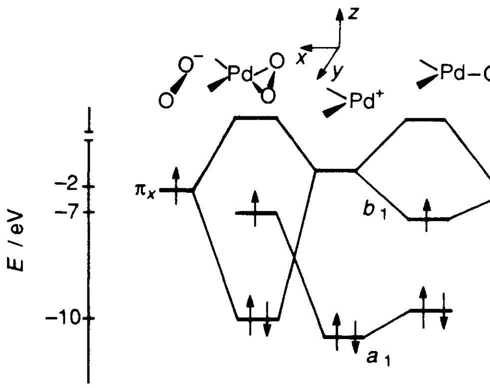

Figure 3. Interaction diagram for conformations (**1a**) and (**1c**) of the $[Pd(HCO_2)(O_2)]$ superoxido complex. Molecular orbitals are considered in the C_{2v} point group, whose principal axis is directed along the x axis of the co-ordinate system

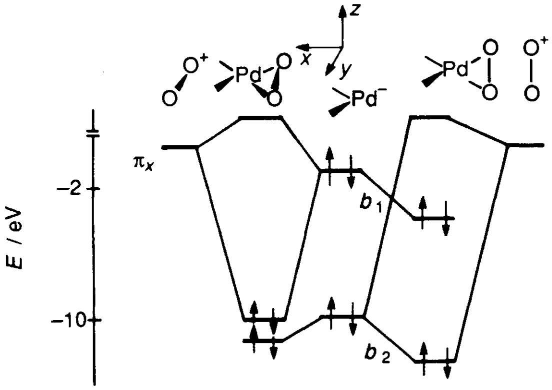

Figure 4. Interaction diagram conformations (**1a**) and (**1b**) of $[Pd(HCO_2)(O_2)]$. Molecular orbitals are considered in the C_{2v} point group, whose principal axis is directed along the x axis of the co-ordinate system

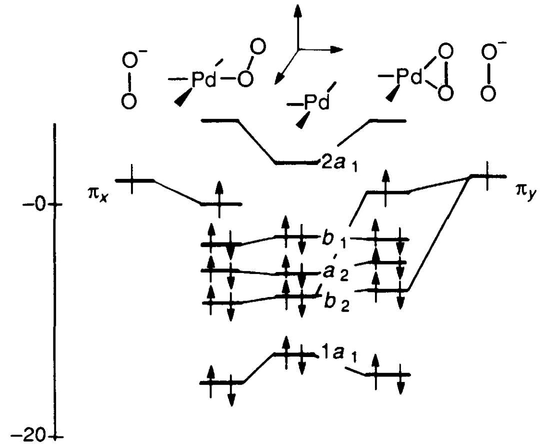

Figure 5. Partial interaction diagram for conformations (**2b**) and (**2c**) of $[Pd_3(HCO_2)_5(O_2)]$. Molecular orbitals are considered in the C_{2v} point group, whose principal axis is directed along the y axis of the co-ordinate system

Table 2. Atomic integrals and empirical parameters for palladium

U_{ss} = −88.25 eV	γ_{ss} = 7.46 eV	γ_{sd} = 9.02 eV
U_{pp} = −72.60 eV	γ_{sp} = 6.42 eV	γ_{pd} = 7.72 eV
U_{dd} = −110.21 eV	γ_{pp} = 6.22 eV	γ_{dd} = 11.32 eV
ζ_s = 1.77 a.u.	ζ_p = 1.80 a.u.	ζ_d = 2.87 a.u.
α = 1.566 619 Å^{-1}	β^{sp} = 0.686 893	δ^{sp} = 0.028 284
	β^{d} = 2.048 567	δ^{d} = 0.578 139

complexes $ML_2(O_2^-)$ is quite general and essential for the geometric structure of some transition metal complexes (*e.g.* Ni^{II}, Cu^{II}). Indeed, if the spatial symmetry of the immediate co-ordination sphere of the transition metal atom corresponds to the symmetry of the central atom d orbitals, as in a planar π-bonding arrangement, then the resulting complex will be more stable. This suggests, in the general case, that complexes formed *via* a π-type co-ordination of O_2^- to the planar ML_2 organometallic d^8 fragment appear to be more stable than those with a σ-type co-ordination.

As can be seen in Figure 1, the rotational barrier in the monomeric π superoxido complex $[Pd(HCO_2)(O_2)]$ is 11.2 kcal with the planar conformation being of lowest energy. The interaction diagram presented in Figure 4 shows that the difference in $Pd \longrightarrow O_2$ π donation for the planar (**1a**) and perpendicular (**1b**) conformations is responsible for the barrier to rotation. {Since the b_1 orbital of the $Pd(HCO_2)^+$ fragment is empty, the $[Pd(HCO_2)(O_2)]$ complex is derived from $Pd(HCO_2)^-$ and O_2^+ fragments.} In the case of the planar π-bonding complex (**1a**) the antibonding b_1 orbital of the $Pd(HCO_2)^-$ fragment interacting with an empty π* orbital of O_2^+ serves as a better π donor than the non-bonding b_2 fragment orbital in the 'perpendicular' complex (**1b**).[26]

The optimized structures and relative energies for conformations (**2a**)—(**2c**) of the trimeric superoxido complex $[Pd_3(HCO_2)_5(O_2)]$ are shown in Figure 2. The σ conformation (**2c**) is 12.1 kcal more stable than the perpendicular conformation (**2b**). The factor responsible for the relative stability of these structures is an exchange repulsion between the filled d orbitals of the $Pd(O)_3$ fragment and the singly occupied π* orbital of the O_2^- ligand. Figure 5 shows schematically the interactions between the frontier orbitals of the T-shaped $Pd(O)_3$ fragment and the singly occupied superoxide π* orbital. When O_2^- is bound in a σ fashion, this interaction is negligible. However in conformation (**2b**) the π* orbital has the proper symmetry to interact with the filled b_2 fragment orbital. This interaction raises the energy level of the highest-occupied molecular orbital (h.o.m.o.) of (**2b**) relative to (**2c**) and so destabilizes this conformation.

The planar π conformation (**2a**) shown in Figure 2 is 20 kcal higher in energy than the perpendicular π conformation (**2b**). This barrier to rotation is a consequence of the greater exchange repulsion between the filled antibonding b_1 fragment orbital (see Figure 5) and the π* orbital for the planar conformation (**2a**) than that between the non-bonding b_2 orbital and π* for (**2b**) [the h.o.m.o. energy levels for conformations (**2a**) and (**2b**) being −4.19 and −4.67 eV, respectively].

Thus, the results of our calculations on trimeric and monomeric palladium superoxido complexes enable a conclusion to be made concerning the most preferable co-ordination mode, which depends on the electronic structure of these complexes, with the four-co-ordinate planar configurations (**1a**) and (**2c**) being favoured for monomeric and trimeric respectively.

Studies of cobalt(II) dioxygen adducts[27] offer considerable support for the observations made above on the relative stability of trimeric palladium superoxido complexes with σ- and π-type co-ordination of O_2^-. As for the trimeric palladium(II) compounds, the five-co-ordinate cobalt(II) complexes were established to form dioxygen adducts with O_2 bound in a σ fashion. Significantly there is a marked resemblance between the valence orbitals of the square-pyramidal CoL_4B and T-shaped PdL_3 fragments.[26,28] In both cases there are unshared electron pairs that destabilize dioxygen

Table 3. Molecules used for parametrization

Molecule	$2S + 1$	Bond	Binding energy/kcal mol^{-1}			Geometry (bond lengths in Å, angles in °)
			CNDO-S^2	*ab initio*	exptl.	
PdCO	1	Pd–CO	28.2	—	34.0[a]	PdC, 1.784 (1.820)[b]
PdH	2	Pd–H	70.1	—	76.1[c]	PdH, 1.440 (1.534)[c]
PdO	1	Pd–O	59.0	—	66.2[d]	PdO, 1.794
Pd(C_3H_6)	1	Pd–C_3H_6	3.5	-4.3[34] (+5.0)[e]		PdC, 2.010 (2.140)[34] CPdC, 69.0 (70.0)[34]

[a] H. Conrad, G. Ertle, J. Koch, and E. E. Latta, *Surf. Sci.*, 1974, **43**, 462. [b] P. E. M. Siegbahn, *Chem. Phys. Lett.*, 1987, **133**, 317. [c] P. S. Bagus and C. Bjorkman, *Phys. Rev. A*, 1981, **23**, 461. [d] K. R. Huber and G. Herzberg, 'Molecular Spectra and Molecular Structure, IV. Constants of Diatomic Molecules,' Van Nostrand Reinhold, New York, 1979. [e] From experience in calculations for other molecules with similar basis sets, which have always led to too small binding energies, a positive binding energy from 5 to 10 kcal mol^{-1} has been predicted[34] for palladocyclobutane.

adducts with π type co-ordination of O_2^- owing to repulsion with a singly occupied dioxygen π* orbital.

There is a close similarity between the anisotropy of the e.s.r. spectra for the trimeric palladium superoxido complexes and that for the cobalt(II) dioxygen complexes[22] {*e.g.*, for [Co(acacen)(py)(O_2)] $g_1 = 2.082$, $g_2 = 2.000$, and $g_3 = 2.000$[27] [Hacacen = 4,4′-(1,2-ethanediyldinitrilo)bis(2-pentanone), py = pyridine]}. According to our calculations, the delocalization of the unpaired spin density over O_2 in the trimeric σ complex (0.64 and 0.31 e on the terminal and middle oxygen π* orbitals respectively) is in good agreement with the ^{17}O hyperfine results for the cobalt dioxygen complexes[27] (0.60 and 0.40 spin densities on the terminal and middle oxygens, respectively). The small calculated spin densities associated with the Pd 4*d* orbitals [d_{z^2} (0.0230), d_{xz} (0.0), d_{yz} (0.0115), $d_{x^2-y^2}$ (0.0043), and d_{xy} (0.0), *s* (0.0004)] correlate with the small hyperfine constants observed for the trimeric palladium superoxido complexes [A_1^{Pd} (6.7 G), A_2^{Pd} (3.0 G), and A_3^{Pd} (4.5 G)]. Finally, the net charge on the dioxygen ligand in σ complex (**2c**) is calculated to be −0.46 compared to the experimental estimate of −0.40 in [Co(acacen)(py)(O_2)].[27]

The results of our calculations are in conformity with the explanation of the different reactivities of trimeric and monomeric palladium superoxido complexes towards the oxidation of simple olefins to epoxides.[22] During epoxidation addition of one oxygen atom to the olefin double bond occurs; thus σ complexes appear to be more reactive as there is a terminal oxygen atom present as distinguished by the spin density and geometric structure.

As mentioned previously, the difference in the e.s.r. spectra and reactivities of the two types of palladium superoxido complexes seems to be attributed to different types of O_2^- co-ordination to the metal atom. The results of CNDO-S^2 calculations verify this assumption. According to the calculations, a π-type superoxide co-ordination is preferred for monomeric palladium complexes, while σ-type co-ordination is favoured for trimeric palladium superoxido complexes.

Experimental

Method of Calculation.—The semi-empirical SCF-m.o. method CNDO-S^2,[29,30] suitable for the calculation of the energy and geometry of transition-metal complexes was used in this work. Contrary to the conventional ZDO techniques, applied to transition-metal complexes[31,32] CNDO-S^2 takes into account the non-orthogonality of the basis set in the calculation of the core-Hamiltonian diagonal elements (up to the terms $\sim S^2$). A new formula for the resonance integral is used in CNDO-S^2. The latter is an orthogonal basis analogue of the so-called 'weighted' formula for the off-diagonal matrix elements[33] used in the extended Hückel calculations. Only one-centre empirical parameters are adopted in CNDO-S^2. Atomic integrals and empirical parameters for palladium (see Table 2) have been found in a similar manner as for iron and nickel atoms.[30] For the determination of empirical parameters both experimental data on the energy and geometry of simple palladium containing molecules, and results of *ab initio* (CASSCF + CCI) calculations for palladocyclobutane[34] have been used (see Table 3).

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Received 4*th May* 1990; *Paper* 0/01981J