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Electronic Structures and Stereochemistry of Some Side-on Dioxygen Complexes

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A number of side-on dioxygen complexes, such as $M(PH_3)_2(O_2)$ (M = Ni(0), Pd(0), or Pt(0)) and $M'X(CO)(PH_3)_2(O_2)$ (M′ = Rh(I) or Ir(I), $X^- = Cl^-$ or I^-), were investigated with a CNDO-type MO method. MO calculations showed that the metal ion has a formal charge of 2+ in the former complexes and 3+ in the latter. The dioxygen ligand donates about 0.1 electron from its $1\sigma_g$ orbital to the metal and about 0.2 electron from its π_u orbital and accepts 1.0–1.4 electrons from the metal d_π orbital into its π_g orbital. There are three important interactions between the metal ion and the dioxygen ligand: the metal d_π–dioxygen π_g, the metal sp_σ–dioxygen π_u, and the metal sp_σ–dioxygen $1\sigma_g$ interactions. The dioxygen coordination bond can be considered to have isosceles or triangular character, which agrees with the results of previous IR studies. The O—O bond is much weakened by the π back-donation and, to some extent, by the σ donation. The stereochemistry of the dioxygen coordination is also discussed; the orientation of the dioxygen ligand is such that the d_π–π_g interaction makes the Ir–O bond most stable in $IrI(CO)(PH_3)_2(O_2)$ and the Pt–P bond most stable in $Pt(PH_3)_2(O_2)$.

Introduction

Dioxygen adducts of transition-metal ions have received much attention in the last decade, for they catalyze oxidation reactions of organic compounds under mild conditions and they are considered as potential models of oxygen carriers.[2] Various types of dioxygen adducts are known. Dioxygen complexes with end-on coordination are formed from cobalt(II)–ammine complexes of Shiff base chelates, which are of interest as models of oxygen carriers, since hemoglobin has an end-on coordinated oxygen molecule. Dioxygen complexes with side-on coordination are derived from some d^{10} and d^8 metal ions such as Pt(0), Pd(0), Ni(0), Ir(I), and Rh(I), which often catalyze oxidation reactions of organic substrates. Much work has been carried out, e.g., syntheses of new types of dioxygen adducts, kinetic studies of oxidation reactions, and spectroscopic studies. Some MO studies also have been performed, which have clarified the driving force for end-on vs. side-on dioxygen coordination in Co(II) complexes.[3-5] For side-on complexes, only one MO study[6] has been performed to aid in assessing quantitatively the importance of π back-donation from the filled metal d_π orbital to the half-filled dioxygen π_g orbital. The conclusion needs, however, to be reinvestigated in more detail, because the proposed bonding nature is in conflict with the usual concept that the d_π–π_g interaction is important in dioxygen coordination.[2] It seems worthwhile to perform MO studies of various side-on dioxygen complexes in order to investigate electronic structure, coordination bonding nature, and stereochemistry.

In this work, CNDO-type MO studies were carried out on some dioxygen complexes with side-on coordination such as $M(PH_3)_2(O_2)$ (M = Ni(0), Pd(0), or Pt(0)) and $M'X(CO)(PH_3)_2(O_2)$ (M′ = Rh(I) or Ir(I), $X^- = Cl^-$ or I^-). The purposes of this work are threefold: first, to present a detailed discussion regarding electron distribution; second, to elucidate the dioxygen coordination bonding nature and to reassess the importance of π back-donation; third, to clarify the reason the dioxygen ligand is coplanar with two phosphine ligands in $M(PR_3)_2(O_2)$ but with the carbonyl and halide ligands in $M'X(CO)(PR_3)_2(O_2)$. MO studies have never been carried out on $IrX(CO)(PH_3)_2(O_2)$, although this complex is of interest in transition-metal chemistry. It should be also emphasized that the first MO study on this complex is presented here.

Computational Details

MO method. The MO method employed was a CNDO-type approximated semiempirical SCF–MO method.[7] This method, described elsewhere, has yielded successful results regarding electronic spectra and electronic structures of the third-transition-series metal complexes.[7,8] The bond index, E_{AB} value,[9,10] used in the previous works[7,8] is defined as the energy contribution of the AB bond to the total energy.

$$E_{AB} = E_{AB}^{(1)} + E_{AB}^{(2)} + E_{AB}^{(3)} = 2\sum_r^A\sum_s^B P_{rs}H_{rs} - 0.5\sum_r^A\sum_s^B P_{rs}^2\gamma_{rs} + \sum_r^A\sum_s^B (P_{rr} - N_r)(P_{ss} - N_s)\gamma_{rs} \quad (1)$$

A large negative value of E_{AB} represents a large bonding interaction between A and B atoms. The quantities of $E_{AB}^{(1)+(2)}$ $(=E_{AB}^{(1)} + E_{AB}^{(2)})$ and $E_{AB}^{(3)}$ indicate approximately the covalent and electrostatic interactions, respectively. $E_{AB}^{(1)+(2)}$ was divided into each type of interaction, such as $E_{d_\pi-\pi_g}^{(1)+(2)}$, $E_{sp_\sigma-\pi_u}^{(1)+(2)}$, and $E_{sp_\sigma-1\sigma_g}^{(1)+(2)}$; the first quantity represents approximately a covalent interaction between the metal d_π and the dioxygen π_g orbitals, the second between the metal sp_σ and the dioxygen π_u orbitals, and the third between the metal sp_σ and the dioxygen $1\sigma_g$ orbitals.

Configuration Analysis. Configuration analysis[11-15] is expected to give important and useful information regarding the electron distribution and the bonding nature of the metal complexes. The method proposed by Fujimoto et al.[15] was employed in this work. Here, it is briefly described for the discussion. The wave function, Ψ, of a complex AB as given in eq 2 is represented by the configuration interaction (CI) wave functions, Φ_0, $\Phi_{i\to j}$, etc., where the meanings of the wave functions, Φ_0, $\Phi_{i\to l}$, ..., are given in ref 14. The CI wave function is constructed by means of a Slater determinant which is composed of MO's ϕ_{Ap} and ϕ_{Bq} of isolated molecules A and B, respectively.

$$\Psi = C_0\Phi_0 + \sum_i^{occ}\sum_l^{unocc} C_{i\to l}\Phi_{i\to l} + \sum_k^{occ}\sum_j^{unocc} C_{k\to j}\Phi_{k\to j} + \sum_i^{occ}\sum_j^{unocc} C_{i\to j}\Phi_{i\to j} + \sum_k^{occ}\sum_l^{unocc} C_{k\to l}\Phi_{k\to l} + \ldots \quad (2)$$

The dioxygen complex was divided into two submolecules, i.e., the dioxygen part and such metal parts of $M(PH_3)_2$ or $M'X(CO)(PH_3)_2$. MO's of each part were obtained with the same MO method. Although the oxygen molecule has a triplet ground state, it was assumed that, prior to coordination, the oxygen molecule formed its singlet valence state $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 \pi_u^4 \pi_{g'}^2 \pi_g^0$. This assumption is essentially the same as the consideration of Griffith[16] and Ibers[17] regarding the bonding nature of dioxygen complexes. Thus, MO's of the singlet oxygen molecule were used in configuration analysis. MO's, ψ_m, of the dioxygen complex are represented by the linear combination of MO's of these two submolecules, ϕ_{Ap} and ϕ_{Bq}, as in eq 3. Then, the coefficients C_0, $C_{i\to j}$, ... were obtained from these

$$\psi_m = \sum_p a_{mp}\phi_{Ap} + \sum_q b_{mq}\phi_{Bq} \quad (3)$$

a_{mp} and b_{mq}, according to each electron configuration.

Geometries. Although these dioxygen complexes have tertiary phosphines as ligands, we employed the PH_3 group for simplicity; its structure was taken as that of the free molecule.[18] Bond lengths and bond angles of $Pt(PH_3)_2(O_2)$ and $IrX(CO)(PH_3)_2(O_2)$ ($X^- = Cl^-$ or

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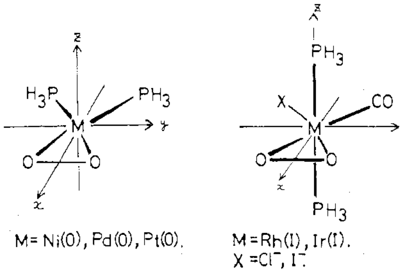

Figure 1. Geometries of calculated complexes.

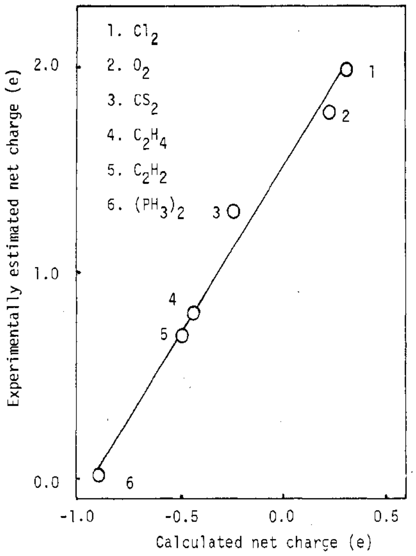

Figure 2. Comparison of calculated net charges of the Pt atom with experimentally estimated charges[21] in $Pt(PH_3)_2L$, $Pt(PH_3)_4$, and *cis*-$PtCl_2(PH_3)_2$.

Table I. Net Charge (e) of the Central Metal Ion and the Dioxygen Ligand

	metal	O_2
$Pt(PH_3)_2(O_2)$	0.21	−0.82
$Pd(PH_3)_2(O_2)$	0.23	−0.80
$Ni(PH_3)_2(O_2)$	0.38	−1.02
$IrI(CO)(PH_3)_2(O_2)$	0.32	−0.77
$IrCl(CO)(PH_3)_2(O_2)$	0.39	−0.77
$RhCl(CO)(PH_3)_2(O_2)$	0.26	−0.62

I^-) were taken from X-ray studies.[17,19,20] Since no X-ray study has been reported for $M(PR_3)_2(O_2)$ (M = Pd or Ni) and $RhCl(CO)(PR_3)_2(O_2)$, those structures were assumed to be the same as those of $Pt(PR_3)_2(O_2)$ and $IrCl(CO)(PR_3)_2(O_2)$, respectively. Geometries of these complexes are shown in Figure 1.

Results and Discussion

Net Charge, Oxidation State of the Central Metal Ion, and Electron Distribution. MO calculations were performed for $Pt(PH_3)_2L$ (L = O_2, CS_2, C_2H_4, or C_2H_2), $Pt(PH_3)_4$, and *cis*-$PtCl_2(PH_3)_2$. Calculated net charges on the Pt atom were compared with the experimental ones obtained from Pt $4f_{7/2}$ ESCA chemical shift,[21] as is shown in Figure 2. A linear relation was obtained between these two values, with the calculated ones somewhat less than the experimental ones. It can be concluded that the electron distribution obtained here is reasonable.[22]

The net charges are given in Table I. That of the central metal ion was 0.2–0.4 e in $M(PH_3)_2(O_2)$ and was 0.3–0.4 e in $M'X(CO)(PH_3)_2(O_2)$. MO calculations for *cis*-$PtCl_2(PH_3)_2$, $Pt(PH_3)_4$, $IrCl_3(CO)(PH_3)_2$, and $IrCl(CO)(PH_3)_2$ gave +0.24, −0.87, +0.36, and −0.13 e net charges on the central metal ions. The central metal ion has 2+ formal charge in the first, 0 in the second, 3+ in the third, and 1+ in the fourth. The net charges of the central metal ions in $Pt(PH_3)_2(O_2)$ and $IrCl(CO)(PH_3)_2(O_2)$ agree fairly well with those of metal ions in *cis*-$PtCl_2(PH_3)_2$ and $IrCl_3(CO)(PH_3)_2$, respectively. Thus, it can be concluded that the metal ions have 2+ and 3+ formal charges in $M(PH_3)_2(O_2)$ and $M'X(CO)(PH_3)_2(O_2)$, respectively. This result agrees with the general concept that the oxygen molecule coordinates to the metal ion through oxidative addition.

Table II. Coefficients[a,b] of One- and Two-Electron CI Wave Functions[c]

	$Pt(PH_3)_2(O_2)$	$Pd(PH_3)_2(O_2)$
	π Back-Donation	
$2b_2 \rightarrow \pi_g$	0.462 (0.428)	0.527 (0.452)
	σ Donation	
$2\pi_u \rightarrow 7a_1$	0.137	0.105
$1\sigma_g \rightarrow 7a_1$	0.087	0.073

	$IrI(CO)(PH_3)_2(O_2)$	$IrCl(CO)(PH_3)_2(O_2)$	$RhCl(CO)(PH_3)_2(O_2)$
		π Back-Donation	
$10a' \rightarrow \pi_g$	0.245 (0.109)	0.154 (0.044)	0.295 (0.115)
$13a' \rightarrow \pi_g$	0.407 (0.302)	0.499 (0.372)	0.426 (0.242)
		σ Donation	
$\pi_u \rightarrow 14a'$	0.078	0.080	0.063
$\pi_u \rightarrow 15a'$	0.138	0.133	0.169
$1\sigma_g \rightarrow 15a'$	0.052	0.052	0.042
$1\sigma_g \rightarrow 15a'$	0.090	0.084	0.112

[a] Negligibly small coefficients are found for the CI wave functions representing polarization. These are omitted in this table. [b] Configuration analysis could not be performed on $Ni(PH_3)_2(O_2)$, because the MO's of $Ni(PH_3)_2$ are so different from the $Ni(PH_3)_2$ part in $Ni(PH_3)_2(O_2)$ that the ground state of $Ni(PH_3)_2$ cannot be considered as a submolecule of $Ni(PH_3)_2(O_2)$. [c] Unparenthesized values are one-electron-transfer wave functions; parenthesized values are two-electron-transfer wave functions.

The net charge of the dioxygen ligand was calculated to be −0.8 to −1.0 e in $M(PH_3)_2(O_2)$ and to be −0.6 to −0.8 e in $M'X(CO)(PH_3)_2(O_2)$. The dioxygen ligand resembles a superoxide from the viewpoint of electron distribution, but the former does not have an odd electron.

The electron distribution was investigated in more detail with a configuration analysis method. The following electron transfers are expected to occur due to the dioxygen coordination: (1) electrons are donated from the dioxygen-occupied orbital to the unoccupied ones of the metal (σ donation), (2) electrons are donated from the occupied orbital of the metal to an unoccupied dioxygen orbital (π back-donation),[23] and (3) intra-submolecular electron excitation occurs from an occupied orbital to an unoccupied one (polarization). Table II gives coefficients of CI wave functions corresponding to these electron transfers, where the coefficients of polarization wave functions are negligibly small and are omitted. Table III gives the changes in electron numbers of the dioxygen orbitals, and Figure 3 shows metal orbitals concerned with these electron transfers. Remarkably large coefficients were found for the wave functions of π-back-donation electron transfers. This large contribution of π back-donation results in a great accumulation of electrons (0.9–1.4 e) on the dioxygen π_g orbital, as is shown in Table III. Because the metal orbitals contributing to the π back-donation are primarily composed of the metal d_π orbital (see the $2b_2$, $10a'$, and $13a'$ MO's in Figure 3), this type of electron transfer can be related to the d_π–π_g interaction. Thus, it can be presumed that a d_π–π_g interaction greatly contributes to the coordinate bond, while the previous Xα–SW calculation gave no significant mixing between the Pt $5d_\pi$ and the dioxygen π_g orbitals.[6] Rather large coefficients were also found for the CI wave function corresponding to σ-donor electron transfers, in which electrons

Table III. Changes[a] in Electron Numbers of the Dioxygen MO's

	$1\sigma_g$			π_u			π_g		
	CT[b]	P[c]	total	CT[b]	P[c]	total	CT[b]	P[c]	total
$Pt(PH_3)_2(O_2)$	−0.120	0.0	−0.120	−0.257	0.0	−0.257	1.266	0.0	1.266
$Pd(PH_3)_2(O_2)$	−0.144	0.0	−0.144	−0.213	0.0	−0.213	1.182	0.005	1.187
$Ni(PH_3)_2(O_2)$[d]			−0.195			−0.159			1.473
$IrI(CO)(PH_3)_2(O_2)$	−0.120	0.0	−0.120	−0.269	0.0	−0.269	1.203	0.006	1.209
$IrCl(CO)(PH_3)_2(O_2)$	−0.112	0.0	−0.112	−0.256	−0.003	−0.259	1.178	0.009	1.187
$RhCl(CO)(PH_3)_2(O_2)$	−0.100	0.0	−0.100	−0.199	0.0	−0.199	0.937	0.009	0.946

[a] A negative sign indicates a decrease in the electron numbers in the MO. [b] Charge transfer. [c] Polarization. [d] Because configuration analysis could not be performed for the Ni complex, these values were estimated from MO's of $Ni(PH_3)_2(O_2)$; for example, an electron decrease in the $1\sigma_g$ MO was estimated under the assumption that this quantity is almost the same as twice the electron decrease in the oxygen 2s and $2p_\sigma$ orbitals. This assumption is reasonable, for the electron donation from the other MO's containing the oxygen 2s and $2p_\sigma$ orbitals is negligibly small in the Pt and Pd analogues.

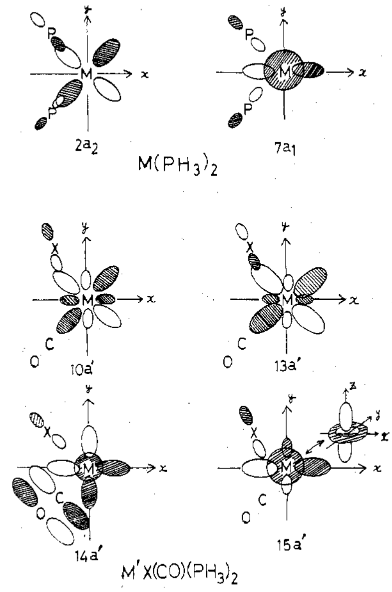

Figure 3. Molecular orbitals concerned with Lewis basicity and acidity of the metal atom.

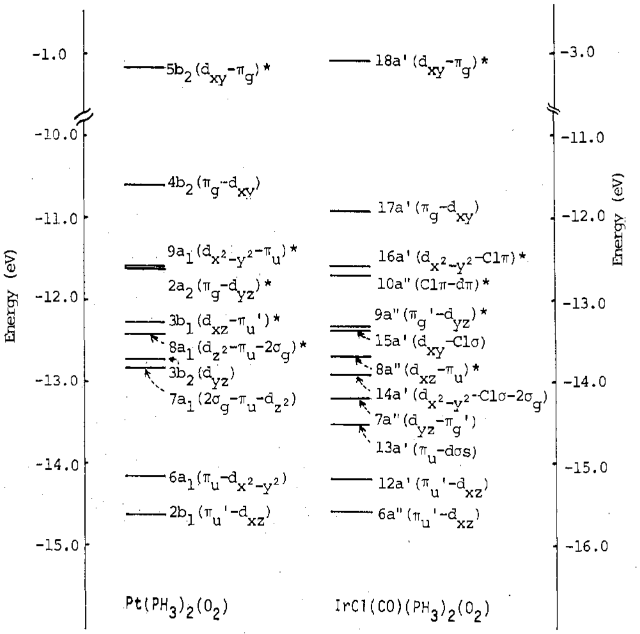

Figure 4. Upper portions of the MO energy diagrams of $Pt(PH_3)_2(O_2)$ and $IrCl(CO)(PH_3)_2(O_2)$. [The lower portions include the Pt–PH_3, Ir–PH_3, and Ir–CO interactions and the intraligand (PH_3, CO) MO's. The * symbol implies an antibonding interaction. (π_g–d_{xy}) etc. represent mixing between the dioxygen π_g and the metal d_{xy} orbitals, where the AO on the left-hand side of the hyphen has a greater LCAO coefficient than that on its right-hand side.]

are donated from the dioxygen π_u and $1\sigma_g$ orbitals to unoccupied ones mainly composed of the metal s and p orbitals (see the $7a_1$, 14a′, and 15a′ MO's in Figure 3). These electron transfers are related to the sp_σ–π_u and the sp_σ–$1\sigma_g$ interactions.[24] The π_u orbital loses about 0.2–0.25 electron through the sp_σ–π_u interactions as is given in Table III. This electron transfer gives a moderately large contribution to the electron distribution. The $1\sigma_g$ orbital loses about 0.1 electron through the sp_σ–$1\sigma_g$ interaction, as is shown in Table III. Although both the coefficient of the CI wave function corresponding to this electron transfer and the quantity of transferred electrons are rather small, the electron transfer of this type should be emphasized since this electron transfer has never been noticed because of the stability of the $1\sigma_g$ orbital.

In conclusion, the electron transfer in the dioxygen complexes is mainly contributed from the π back-donation, through which about 0.9–1.4 electrons are transferred to the dioxygen ligand. Simultaneously, about 0.3 electron is donated from the dioxygen π_u and $1\sigma_g$ orbitals to the metal atom through the sp_σ–π_u and sp_σ–$1\sigma_g$ interactions; these electron transfers play a moderately important role in the electron distribution. As a result, the dioxygen ligand includes about −0.6 to −1.0 e of negative net charge.

The Dioxygen Coordinate Bond and the O–O Bond. Figure 4 gives the upper portions of MO energy diagrams of $Pt(PH_3)_2(O_2)$[25] and $IrCl(CO)(PH_3)_2(O_2)$. These MO's have the following characters: (1) significant mixing between the metal d_π and the dioxygen π_g orbitals was found in all the complexes, whereas such mixing was not found in the Xα–SW calculation of $Pt(PH_3)_2(O_2)$.[6] In the present calculation of $Pt(PH_3)_2(O_2)$ the $5b_2$ MO (the highest occupied MO) is about 30% Pt $5d_\pi$, 60% π_g, and 1.5% P 3p, and the $6b_2$ MO (the lowest unoccupied MO) is about 60% Pt $5d_\pi$ and 17% π_g. On the other hand, the previous Xα–SW calculation gave quite different results: the $18b_2$ (the occupied level) is about 50% π_g, 30% P 3p, and 15% Pt $6p_\pi$, and the $19b_2$ (the lowest unoccupied MO) is about 50% Pt $6p_\pi$ and 50% π_g. Although there is no direct evidence showing that the results of the Xα–SW calculation are in error, those results seem unreasonable from the following reason: it is unnatural that the π_g orbital interacts with the Pt $6p_\pi$ orbital more greatly than the Pt $5d_\pi$, for the $6p_\pi$ lies at higher energy level than the $5d_\pi$, and the resonance integral between the Pt $6p_\pi$ and the O p_π orbitals is less than that between the Pt $5d_\pi$ and the O p_π ones. It seems reasonable that the d_π–π_g mixing plays an important role in the dioxygen coordination of all the complexes. (2) The dioxygen π_u orbital moderately mixes with the Pt 6s and $6p_\sigma$ orbitals in the $6a_1$, $7a_1$, $8a_1$, and $9a_1$ MO's and the $1\sigma_g$ does with the Pt 6s and $6p_\sigma$ in the $1a_1$ and $6a_1$ MO's in $Pt(PH_3)_2(O_2)$. The same types of mixing were found in all the complexes. Such mixing was less than the d_π–π_g mixing; for example, the 6s–π_u bond order is 0.664, the 6s–$1\sigma_g$ bond order is 0.645, and the $5d_\pi$–π_g bond

Table IV. Decomposition of the $E_{\mathrm{M-O_2}}$ (eV)

(1) $\mathrm{M(PH_3)_2(O_2)}$

	M		
	Ni	Pd	Pt
$E_{\mathrm{M-O_2}}$	−25.26	−22.06	−23.70
$E_{\mathrm{d}_\pi-\pi_\mathrm{g}}{}^{(1)+(2)}$	−3.55	−4.88	−4.99
$E_{\mathrm{sp}_\sigma-\pi_\mathrm{u}}{}^{(1)+(2)}$	−2.84	−4.76	−5.47
$E_{\mathrm{sp}_\sigma-1\sigma_\mathrm{g}}{}^{(1)+(2)}$	−12.06	−7.32	−7.40
$E_{\mathrm{M-O_2}}{}^{(3)}$	−3.98	−1.88	−1.82

(2) $\mathrm{M'X(CO)(PH_3)_2(O_2)}$[a]

	M′X		
	RhCl	IrCl	IrI
$E_{\mathrm{M-O_2}}$	−20.32	−23.83	−23.86
$E_{\mathrm{d}_\pi-\pi_\mathrm{g}}{}^{(1)+(2)}$	−4.42	−4.53	−4.19
$E_{\mathrm{sp}_\sigma-\pi_\mathrm{u}}{}^{(1)+(2)}$	−3.73	−4.56	−4.86
$E_{\mathrm{sp}_\sigma-1\sigma_\mathrm{g}}{}^{(1)+(2)}$	−6.48	−6.78	−6.94
$E_{\mathrm{M-O_2}}{}^{(3)}$	−1.64	−2.72	−2.41

[a] See footnote 31.

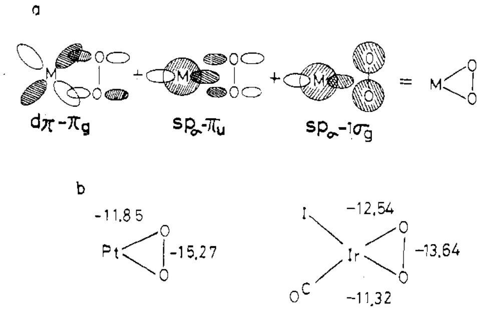

Figure 5. Bonding scheme of dioxygen coordination: (a) interaction scheme of dioxygen coordination; (b) E_{AB} values (eV).

order is 1.266 (note that these values are not usual bond orders between two AO's but those between the Pt AO and the dioxygen MO). In spite of the rather small mixing, these interactions contribute remarkably to the $\mathrm{M-O_2}$ bond strength, as will be discussed below, for the dioxygen π_u–metal sp_σ and the dioxygen $1\sigma_\mathrm{g}$–metal sp_σ resonance integrals are considerably larger than the dioxygen π_g–metal d_π one. (3) The Xα–SW calculation gave extensive mixing of the Pt $5\mathrm{d}_\pi$ (d_{xy}) and $5\mathrm{d}_\pi'$ (d_{xz}) with the dioxygen π_u and $3\sigma_\mathrm{g}$. Although such mixing was also found in this work, their antibonding levels were occupied and contributed little to the $\mathrm{M-O_2}$ bond.

Next, it was attempted to investigate the nature of the dioxygen coordination in more detail. An $E_{\mathrm{M-O_2}}{}^{(1)+(2)}$, which represents the strength of the $\mathrm{M-O_2}$ covalent interaction, was divided into various types of interactions, as is shown in Table IV. The absolute value of $E_{\mathrm{M-O_2}}{}^{(3)}$, which approximately represents the strength of an electrostatic interaction, is rather large, as is also shown in Table IV. This interaction may be attributed to the π-back-donating interaction, for no π back-donation gives no negative net charge on the dioxygen ligand. The absolute value of $E_{\mathrm{d}_\pi-\pi_\mathrm{g}}{}^{(1)+(2)} + E_{\mathrm{M-O_2}}{}^{(3)}$ is large in all the complexes, which suggests the importance of the π back-donation or the $\mathrm{d}_\pi-\pi_\mathrm{g}$ interaction in the $\mathrm{M-O_2}$ bond.[26] The absolute values of $E_{\mathrm{sp}_\sigma-\pi_\mathrm{u}}{}^{(1)+(2)}$ and $E_{\mathrm{sp}_\sigma-1\sigma_\mathrm{g}}{}^{(1)+(2)}$ are also remarkably large, which suggests that although the electron transfers due to the $\mathrm{sp}_\sigma-\pi_\mathrm{u}$ and $\mathrm{sp}_\sigma-1\sigma_\mathrm{g}$ interactions are rather small (see the discussion of the previous section) these two interactions greatly contribute to the coordinate bond strength. Thus, the metal–dioxygen bond is mainly stabilized by the above three interactions: the $\mathrm{d}_\pi-\pi_\mathrm{g}$ interaction, the $\mathrm{sp}_\sigma-\pi_\mathrm{u}$, and the $\mathrm{sp}_\sigma-1\sigma_\mathrm{g}$. These interactions are pictured in Figure 5a. This bonding scheme is essentially the same as the isosceles- or the triangular-bonding model. The isosceles bond is also supported by the result that the $E_{\mathrm{M-O}}$ value is almost the same as the $E_{\mathrm{O-O}}$ one, as is shown in Figure 5b. This conclusion agrees with that of previous IR studies of these complexes.[27]

It is well-known that the O–O bond is remarkably lengthened by the dioxygen coordination to the metal ion. In this work, the absolute value of $E_{\mathrm{O-O}}$ was remarkably decreased by the coordination, which accords with the O–O bond lengthening. The $\Delta E_{\mathrm{O-O}}{}^{(1)+(2)}$ defined in footnote *a* of Table V was divided into various types of interactions such as 2s–2s, $2\mathrm{p}_\pi-2\mathrm{p}_\pi$, ... Table V gives those values contributing to the O–O bond weakening; the positive value represents a weakening of the interactions. The greatest value of $\Delta E_{\mathrm{p}_\pi-\mathrm{p}_\pi}{}^{(1)+(2)}$ ($=\Delta E_{\mathrm{p}_\pi-\mathrm{p}_\pi(\pi_\mathrm{u})}{}^{(1)+(2)} + \Delta E_{\mathrm{p}_\pi-\mathrm{p}_\pi(\pi_\mathrm{g})}{}^{(1)+(2)}$, vide infra) means that the $2\mathrm{p}_\pi-2\mathrm{p}_\pi$ interaction is most weakened by the coordination, while rather small values of $\Delta E_{\mathrm{O-O}}{}^{(3)}$, $\Delta E_{\mathrm{s-s}}{}^{((1)+(2)}$, and $\Delta E_{\mathrm{p}_\sigma-\mathrm{p}_\sigma}{}^{(1)+(2)}$ mean that the electrostatic, the 2s–2s, and the $2\mathrm{p}_\sigma-2\mathrm{p}_\sigma$ interactions are moderately weakened. The weakening of the $2\mathrm{p}_\sigma-2\mathrm{p}_\sigma$ interaction is not directly induced by the coordination, because the $2\mathrm{p}_\sigma-2\mathrm{p}_\sigma$ bond order is slightly increased by the coordination. This weakening would be attributed to the decrease in the $2\mathrm{p}_\sigma-2\mathrm{p}_\sigma$ overlap integral resulting from the O–O bond lengthening. The $\Delta E_{\mathrm{p}_\pi-\mathrm{p}_\pi}{}^{(1)+(2)}$ is brought about by both the electron release from the π_u orbital and the electron accumulation on its π_g one. It seems reasonable to assume that the contribution of these two types of electron transfer is proportional to transferred electron number

$$\Delta E_{\mathrm{p}_\pi-\mathrm{p}_\pi(\pi_\mathrm{u})}{}^{(1)+(2)} = [\Delta Q_{\pi_\mathrm{u}}/(\Delta Q_{\pi_\mathrm{u}} + \Delta Q_{\pi_\mathrm{g}})]\Delta E_{\mathrm{p}_\pi-\mathrm{p}_\pi}{}^{(1)+(2)}$$

$$\Delta E_{\mathrm{p}_\pi-\mathrm{p}_\pi(\pi_\mathrm{g})}{}^{(1)+(2)} = [\Delta Q_{\pi_\mathrm{g}}/(\Delta Q_{\pi_\mathrm{u}} + \Delta Q_{\pi_\mathrm{g}})]\Delta E_{\mathrm{p}_\pi-\mathrm{p}_\pi}{}^{(1)+(2)}$$

where $\Delta E_{\mathrm{p}_\pi-\mathrm{p}_\pi(\pi_\mathrm{u})}{}^{(1)+(2)}$ and $\Delta E_{\mathrm{p}_\pi-\mathrm{p}_\pi(\pi_\mathrm{g})}{}^{(1)+(2)}$ mean the $\Delta E_{\mathrm{p}_\pi-\mathrm{p}_\pi}{}^{(1)+(2)}$ value due to the electron release from the π_u orbital and that due to the electron accumulation on its π_g one, respectively, and $\Delta Q_{\pi_\mathrm{u}}$ and $\Delta Q_{\pi_\mathrm{g}}$ represent the numbers of the electrons released from the π_u orbital and those of the electrons accumulated on the π_g one, respectively. As is shown in Table V, $\Delta E_{\mathrm{p}_\pi-\mathrm{p}_\pi(\pi_\mathrm{g})}{}^{(1)+(2)}$ is much larger than $\Delta E_{\mathrm{p}_\pi-\mathrm{p}_\pi(\pi_\mathrm{u})}{}^{(1)+(2)}$, which shows that the O–O bond is weakened mainly by the electron accumulation on the π_g orbital. Further, this electron accumulation also brings about the increase in O–O electrostatic

Table V. The $E_{\mathrm{O-O}}{}^{(1)+(2)}$ and $E_{\mathrm{O-O}}{}^{(3)}$ Values[a] of Dioxygen Complexes (eV)

	$\Delta E_{\mathrm{s-s}}^{(1)+(2)}$	$\Delta E_{\mathrm{p}_\sigma-\mathrm{p}_\sigma}^{(1)+(2)}$	$\Delta E_{\mathrm{p}_\pi-\mathrm{p}_\pi(\pi_\mathrm{u})}^{(1)+(2)}$[b]	$\Delta E_{\mathrm{p}_\pi-\mathrm{p}_\pi(\pi_\mathrm{g})}^{(1)+(2)}$[c]	$\Delta E_{\mathrm{O-O}}^{(3)}$
$\mathrm{Pt(PH_3)_2(O_2)}$	2.30	1.12	3.05	15.01	1.36
$\mathrm{Pd(PH_3)_2(O_2)}$	2.29	1.11	2.67	14.85	1.31
$\mathrm{Ni(PH_3)_2(O_2)}$	2.64	1.09	1.71	15.81	2.07
$\mathrm{IrI(CO)(PH_3)_2(O_2)}$	2.45	1.64	3.25	14.60	1.16
$\mathrm{IrCl(CO)(PH_3)_2(O_2)}$	2.30	1.24	3.17	14.52	1.19
$\mathrm{RhCl(CO)(PH_3)_2(O_2)}$	2.30	1.21	2.94	13.96	0.75

[a] $\Delta E_{\mathrm{O-O}}{}^{(1)+(2)} = [E_{\mathrm{O-O}}{}^{(1)+(2)}$ in the dioxygen complex$] - [E_{\mathrm{O-O}}{}^{(1)+(2)}$ in the free oxygen$]$. The $\Delta E_{\mathrm{O-O}}{}^{(3)}$ is similarly defined from the $E_{\mathrm{O-O}}{}^{(3)}$ value. [b] The change in the $\Delta E_{\mathrm{p}_\pi-\mathrm{p}_\pi}{}^{(1)+(2)}$ value brought about by the electron release from the dioxygen π_u orbital. [c] The change in the $\Delta E_{\mathrm{p}_\pi-\mathrm{p}_\pi}{}^{(1)+(2)}$ value brought about by the electron accumulation on the dioxygen π_g orbital.

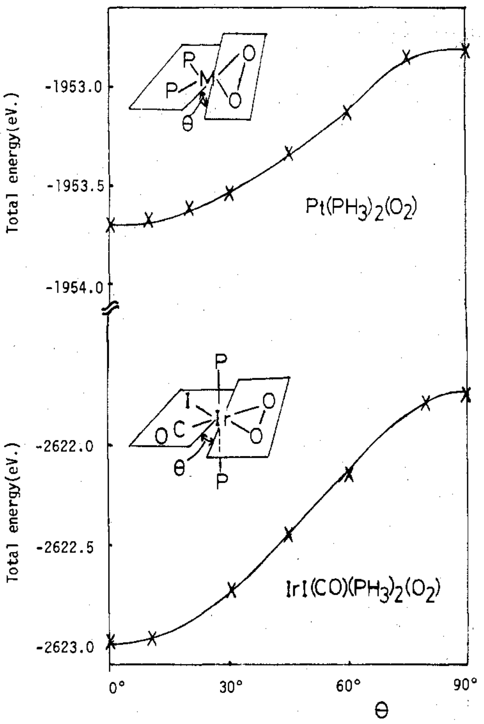

Figure 6. Total energy (eV) vs. dioxygen rotation.[28]

repulsion, that is, the positive value of $\Delta E_{\text{O-O}}^{(3)}$, which moderately weakens the O–O bond. The $\Delta E_{\text{s-s}}^{(1)+(2)}$ value is mainly attributed to the electron release from the $1\sigma_g$ orbital, since the electron number is little changed in the other orbitals including the oxygen 2s orbital. The contribution of this term is of almost the same magnitude as $\Delta E_{p_\pi\text{-}p_\pi(\pi_u)}^{(1)+(2)}$. Thus, the O–O bond is weakened mainly by the electron accumulation on the π_g orbital and moderately by the electron release from the π_u and $1\sigma_g$ orbitals.

In summary, the dioxygen π_g orbital mixes significantly with the metal d_π orbital. The π back-donation contributes to both the electron distribution, the metal–O_2 bond strength, and the O–O bond weakening. The sp_σ–π_u and the sp_σ–$1\sigma_g$ σ-donation interactions also contribute to the coordinate bond strength, while these interactions moderately influence the electron distribution and the O–O bond weakening.

Dioxygen Ligand Rotation about the Coordinate Bond. Two oxygen atoms and two phosphine ligands lie on the same plane in $M(PH_3)_2(O_2)$, while two oxygen atoms, the carbonyl, and the halide ligands are on the same plane in $M'X(CO)(PH_3)_2(O_2)$. It is interesting to discuss this structural feature in terms of the electronic structures of these dioxygen complexes.

The total energies of $Pt(PH_3)_2(O_2)$ and $IrI(CO)(PH_3)_2(O_2)$[28] are given as a function of the θ value in Figure 6, where θ indicates the angle between the O–Pt–O′ and P–Pt–P′ planes in the former complex and between O–Ir–O′ and I–Ir–CO planes in the latter. Here, A and B denote the structure with $\theta = 0°$ and that with $\theta = 90°$, respectively. The energy minima were obtained at $\theta = 0°$ for both complexes which agree with previous X-ray studies.[19,20] This dioxygen rotation results in some changes of the electronic structures given in Table VI. In $Pt(PH_3)_2(O_2)$, as the θ value increases from 0 to 90°, (1) the electron density of the Pt atom decreases, (2) the electron density of the dioxygen ligand decreases, which seems to be due to the decrease in the electron density of the dioxygen π_g orbital (see the electron number of the π_g orbital given in Table VI), this behavior suggesting that the A structure includes a stronger π back-donation than B, (3) the electron density of the PH_3 ligand increases, and (4) the Pt–P bond becomes remarkably weak, while the Pt–O bond also slightly weakens. The weakening of the Pt–P bond seems a main factor in destabilizing the B structure. Hence, it should be investigated as to why the Pt–P bond of B is remarkably weaker than that of A. Both the electron donation from the $1\sigma_g$ orbital and that from the π_u orbital hardly depend on rotation, which suggests that the strength of the σ donation is hardly influenced by the dioxygen rotation. The orbitals involved in the π-back-donating interaction are shown in Figure 7. The $2b_2$ orbital of $Pt(PH_3)_2$, mainly composed of the Pt $5d_{xy}$ orbital, is destabilized by an antibonding interaction between the Pt $5d_{xy}$ and the PH_3 lone-pair orbitals, whereas the $1b_1$ orbital, mainly composed of the Pt $5d_{xz}$, includes no antibonding interaction between the Pt and the PH_3 orbitals and is not destabilized. The dioxygen π_g orbital interacts with the d_{xy} orbital to form a π-back-donating interaction in A, while it interacts with the d_{xz} orbital in B. Since the high orbital energy of the doubly occupied d_π orbital is favorable for π back-donation, A includes a stronger π back-donation than B. As a result, the former has a greater electron density on the dioxygen ligand and a stronger Pt–O bond than the latter. In the A structure, electrons are donated from the $2b_2$ orbital to the dioxygen π_g orbital through the π back-donation. Because the $2b_2$ is composed of the antibonding interaction between the Pt $5d_{xy}$ and the PH_3 lone-pair orbitals, the π back-donation strengthens the Pt–P bond. On the other hand, the π back-donation little influences the Pt–P bond in the B structure, for the $1b_1$ includes no interaction between the Pt and PH_3 orbitals. Thus, the Pt–P bond is remarkably stronger in A than in B.

Table VI. Some Changes in the Electron Distribution and the Bond Strength Resulting from Dioxygen Rotation

	$Pt(PH_3)_2(O_2)$			$IrI(CO)(PH_3)_2(O_2)$		
	0°	90°	$\Delta_{0-90°}$	0°	90°	$\Delta_{0-90°}$
			Electron Density			
M	9.787	9.771	0.019	8.677	8.666	0.011
O_2	12.818	12.776	0.041	12.765	12.619	0.147
PH_3	7.697	7.726	−0.029	7.657	7.651	0.006
π_g	1.266	1.185	0.081	1.208	1.005	0.203
π_u	1.743	1.754	−0.011	1.731	1.778	−0.047
$1\sigma_g$	1.880	1.884	−0.004	1.880	1.887	−0.007
			E_{AB}, eV			
E_{M-O_2}	−23.70	−23.43	−0.27	−23.86	−22.55	−1.31
E_{M-P}	−21.34	−20.18	−1.16	−20.83	−19.98	−0.85
E_{M-I}				−8.27	−7.89	−0.38
E_{M-C}				−12.90	−12.63	−0.27
E_{O-O}	−15.27	−15.58	0.31	−13.62	−14.46	0.84

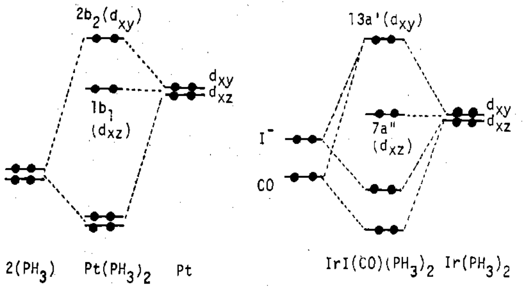

Figure 7. d-Orbital energy level concerned with π back-donation.

Similar features were found in the dioxygen rotation of $IrI(CO)(PH_3)_2(O_2)$, although some differences were observed: (1) the dioxygen ligand in A has a significantly larger electron density than that in B, whereas the former has a slightly larger one than the latter in $Pt(PH_3)_2(O_2)$, (2) the Ir–O bond strength strongly depends on the rotation, whereas the Pt–O bond strength is only slightly altered, and (3) the Ir–C, Ir–I, and Ir–P bonds are slightly stronger in A than in B, whereas the Pt–P bond is remarkably stronger in A than in B. Thus, in the Ir–dioxygen complex, the stabilization of the Ir–O bond is a main factor to stabilize A. The 13a′ (d_{xy}) orbital is destablized by interactions with the I^- and CO ligands. On the other hand, the 7a″ (d_{xz}) orbital is nonbonding and, therefore, cannot be destabilized by any ligand.[29] Thus, the dioxygen π_g orbital interacts with the unstable d_{xy} orbital to form a strong π-back-donating interaction in A, which makes the Ir–O bond strong and stabilizes the A structure. In B, however, the π_g orbital interacts with the stable d_{xz} orbital to form a relatively weak π-back-donating interaction, which results in a relatively weak Ir–O bond.

Different features described above are due to the difference in Lewis basicity between $Pt(PH_3)_2$ and $IrI(CO)(PH_3)_2$. The $2b_2$ (−7.35 eV) and $1b_1$ (−7.86 eV) levels of the former exist at higher energies than the 13a′ (−9.39 eV) and 7a″ (−11.06 eV) of the latter, which suggests that the former has stronger Lewis basicity than the latter. This result agrees with the experimental proposal regarding Lewis basicity of Pt(0) and Ir(I) ions.[30] Further, the energy difference between $2b_2$ and $1b_1$ is less than that between 13a′ and 7a″. As a result, the π back-donation does not depend so much on the dioxygen rotation in $Pt(PH_3)_2(O_2)$. Thus, the Pt–O and O–O bond strength and the electron density of the π_g orbital depend slightly on the rotation. In $IrI(CO)(PH_3)_2(O_2)$, electron donation from the stable 7a″ orbital is difficult relative to that from the unstable 13a′ one. Thus, the dioxygen rotation strongly influences the electron density of the π_g orbital and the strength of the Ir–O and O–O bonds. The Ir–I, the Ir–P, and the Ir–C bond strengths depend slightly on the rotation, due to the relatively strong Lewis acidity of $IrI(CO)(PH_3)_2$.[31]

In conclusion, the orientation of the dioxygen ligand is determined by the π-back-donating interaction between the metal d_π and the dioxygen π_g orbitals. The Pt–P bond of $Pt(PH_3)_2(O_2)$ is most stabilized by the π-back-donation in the A structure, which stabilizes A. On the other hand, the Ir–O bond is most stabilized in the A structure of $IrI(CO)(PH_3)_2(O_2)$; this is a main factor in the stabilization of A. It is of interest that although the σ-donating interaction greatly contributes to the $M–O_2$ bond strength, the π-back-donating interaction determines the orientation of the dioxygen ligand and influences both the electron distribution and the O–O bond weakening.

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Registry No. $Pt(PH_3)_2(O_2)$, 53195-21-4; $Pd(PH_3)_2(O_2)$, 67488-62-4; $Ni(PH_3)_2(O_2)$, 67488-61-3; $IrI(CO)(PH_3)_2(O_2)$, 67488-58-8; $IrCl(CO)(PH_3)_2(O_2)$, 67488-59-9; $RhCl(CO)(Ph_3)_2(O_2)$, 67488-60-2.

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(22) The experimental estimation was carried out under an assumption that the platinum atom has a zero net charge in $Pt(PPh_3)_4$ and 2+ in *cis*-$PtCl_2(PPh_3)_2$. Thus, it cannot be said that the estimated values are quantitatively true.
(23) Strictly speaking, a σ back-donation is also possible. MO calculations, however, showed that this interaction was not present in these complexes.
(24) Whereas the 14a′ and the 15a′ orbitals are also contributed from the metal $d_{x^2-y^2}$ and the d_{z^2} orbitals, respectively, the contribution of the d orbital is considerably less that that of the metal sp_σ orbitals. Further, the resonance integrals between the oxygen 2s, $2p_\pi$ and the metal d orbitals are considerably smaller than those between the oxygen 2s, $2p_\pi$ and the metal sp_σ ones. Thus, electron transfers from the dioxygen π_u and $1\sigma_g$ orbitals to the metal 14a′ and the 15a′ orbitals are related to the $sp_\sigma-\pi_u$ and the $sp_\sigma-1\sigma_g$ interactions, respectively.
(25) The MO's of $Pt(PH_3)_2(O_2)$ obtained here are more stable than those obtained by the Xα–SW calculation, and the order of the present MO energy levels is somewhat different. In general, Koopman's theorem cannot be successfully applied to transition-metal complexes [for example: M. B. Hall, I. H. Hillier, J. A. Connor, M. F. Guest, and D. R. Lloyed, *Mol. Phys.*, **30**, 839 (1975)]. Thus, no discussion is presented here about this issue.
(26) The σ donation from the π_u and the $1\sigma_g$ orbitals reduces the electrostatic interaction, for the σ donation gives positive net charge on the dioxygen ligand. Thus, this quantity underestimates the strength of the π-back-donating interaction.
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(28) In $IrI(CO)(PH_3)_2(O_2)$, it seems unreasonable to freeze the phosphine ligand for large θ values. Two possibilities can be considered regarding the position of the phosphines: the phosphines are pushed away from the dioxygen ligand (1) where the I^- and CO ligands are frozen at the same positions as those in the equilibrium structure or (2) where these two ligands exist on the *y* axis (see Figure 1). The first structure is analogous to the square-pyramidal one. The second is similar to the structures of $IrI(CO)(PPh_3)_2(C_2F_4)$ and $IrBr(CO)(PPh_3)_2[C_2(CN)_4]$ [J. A. Ibers, J. McGinnety, and N. Kime, *Proc. Int. Conf. Coord. Chem., 10th*, 93 (1967); J. A. McGinnety and J. A. Ibers, *Chem. Commun.*, 235 (1968)] and can be considered as a distorted trigonal bipyramid. The first structure becomes unstable as the phosphines move. The second becomes stable as the phosphines move and is the most stable at ∠PIrP′ = ca. 140°. However, the most stable one is more unstable than the equilibrium one by ca. 1 eV. Thus, the positions of phosphines are unchanged by the dioxygen rotation. The potential curve of Figure 6 was obtained, where the phosphines are frozen on the *z* axis.
(29) The 3d orbitals of the P atom are not included in AO basis. The $3d_{xz}$ orbital of the P atom interacts with the Ir $5d_{xz}$ orbital to form a π-back-donating interaction. This interaction stabilizes the Ir $5d_{xz}$ orbital. Thus, the present conclusion is not altered, even if the 3d orbitals of the P atom are considered.
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(31) The I^- and the PH_3 ligands donate their electrons to the metal to form coordinate bonds. Where the metal has relatively strong Lewis acidity, the strength of this bond is not influenced much by the dioxygen rotation. In fact, $IrI(CO)(PH_3)_2$ has relatively stable unoccupied 14a′ (−1.32 eV) and 15a′ (−0.32 eV) MO's concerned with Lewis acidity, while $Pt(PH_3)_2$ has a relatively unstable unoccupied $7a_1$ MO (LUMO) (1.10 eV) concerned with Lewis acidity. The CO ligand accepts electrons from the metal through the π-back-donating interaction and donates its lone-pair electrons to the metal through the σ-donating interaction. As θ increases, the former interaction becomes weak, while the latter grows strong. Thus, the Ir–CO bond strength scarcely depends on the rotation.