

# Electron Spin Resonance of $\text{Re}_2(\mu\text{-H})_2(\text{CO})_8^-$ and $\text{Re}_2(\mu\text{-H})_2(\text{CO})_6(\mu\text{-dppm})^-$ (dppm = $(\text{Ph}_2\text{P})_2\text{CH}_2$ ). An Indication of Large 5d-6p Mixing in the Odd-Electron Orbital

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**Abstract:**  $\text{Re}_2(\mu\text{-H})_2(\text{CO})_8^-$ ,  $\text{Re}_2(\mu\text{-D})_2(\text{CO})_8^-$ , and  $\text{Re}_2(\mu\text{-H})_2(\text{CO})_6(\mu\text{-dppm})^-$  have been examined with electron spin resonance spectroscopy. They have planar  $\text{Re}_2\text{H}_2$  rhomboids and their odd-electron orbitals are the  $\pi^*_{\text{ReRe}}$  orbital lying in the rhomboid. Rhenium hyperfine splitting tensors are interpreted most reasonably with the  $\pi^*_{\text{ReRe}}$  orbital consisting of rhenium 5d and 6p AO's. The odd-electron density on the 5d AO is estimated to be around 0.26 for  $\text{Re}_2(\mu\text{-H})_2(\text{CO})_8^-$ . The anisotropy of the rhenium hyperfine interaction due to the odd-electron density on the 6p AO is estimated as  $42 \times 10^{-4} \text{ cm}^{-1}$ , a magnitude similar to that due to the 5d odd-electron density,  $57 \times 10^{-4} \text{ cm}^{-1}$ . This large 5d-6p mixing is likely to arise from contraction and stabilization of 6p AO's and expansion and destabilization of 5d AO's due to relativistic effects.

Interpretation of roles of  $nd$ ,  $(n+1)s$ , and  $(n+1)p$  atomic orbitals (AO's) on transition-metal atoms in bonding in coordinatively saturated cluster complexes spans a wide range of aspects. By examining molecular orbitals (MO's) of rhodium clusters, Lauher<sup>2</sup> has shown that an overlap between metal AO's is large when the pair involves an s or p AO, that stoichiometry of a cluster complex is closely related to the number of high-lying antibonding MO's with dominant p character in the corresponding naked metal skeleton,<sup>3</sup> and that the MO approach cannot locate specific metal-metal bonds. This implies that net metal-metal bonding arises from metal-metal p-p overlaps. Rives, You, and Fenske<sup>4</sup> have analyzed Fenske-Hall<sup>5</sup>-type MO's of  $\text{Co}_3\text{Cp}_3(\mu^3\text{-S})_2$  (Cp =  $\eta^5$ -cyclopentadienyl) and related complexes with the natural hybrid orbital method<sup>6</sup> and have assigned the role played by the 3d AO's in metal-metal bonding to be secondary to that of the 4s and 4p AO's. It should be pointed out that all valence electrons have some importance for net bonding and for the relation between metal-atom arrangement and stoichiometry of cluster complexes.

Bonding models, quite different from the above-mentioned aspect, are also common.<sup>7-9</sup> The metal s and p AO's are diffuse and considered to be tied up in bonding to the ligands. Metal-metal bonds are presumed to be formed primarily by interactions between d AO's which are not used in the metal-ligand bonding. Metal-ligand interactions are thought to be greater than metal-metal d-d interactions, and energy levels and shapes of MO's with predominant metal d character are influenced strongly by nodal properties and characters of ligand orbitals.<sup>4,10,11</sup> This bonding model has been used to interpret geometrical changes of cluster complexes accompanying addition or removal of valence electrons.<sup>12,13</sup> photoelectron spectra,<sup>14</sup> and electron spin resonance

(ESR) of cluster complexes.<sup>15</sup> These phenomena are closely related to high-lying occupied and/or low-lying vacant MO's, i.e., frontier orbitals. These orbitals have been analyzed theoretically in terms of MO schemes from the frontier orbitals of their fragments.<sup>16</sup>

With respect to involvement of 4p AO's in frontier MO's of coordinatively saturated cluster complexes of the first transition series elements, special emphasis should be placed on ESR studies of  $\text{V}_2(\mu\text{-PPh}_2)_2(\text{CO})_8^-$  and  $\text{Mn}_2(\mu\text{-AsPh}_2)_2(\text{CO})_8^+$ <sup>10</sup> which have shown an absence of meaningful 3d-4p mixing in their odd-electron orbitals. Namely, the hyperfine splitting tensors of the metal nuclei in these ion radicals have axial symmetry within experimental error, although the symmetry-allowed d-p mixing in their odd-electron orbitals should have induced deviations of the tensors from the axial symmetry.

Relativistic effects, which become important in elements of the third transition series, expand and destabilize their 5d AO's and contract and stabilize their 6s and 6p AO's.<sup>17</sup> These effects would result in increased mixing of s and/or p AO's with d AO's in MO's of complexes of the third transition elements, but its extent and chemical significance have been scarcely explored<sup>18</sup> except for some platinum cluster complexes.<sup>16f</sup>

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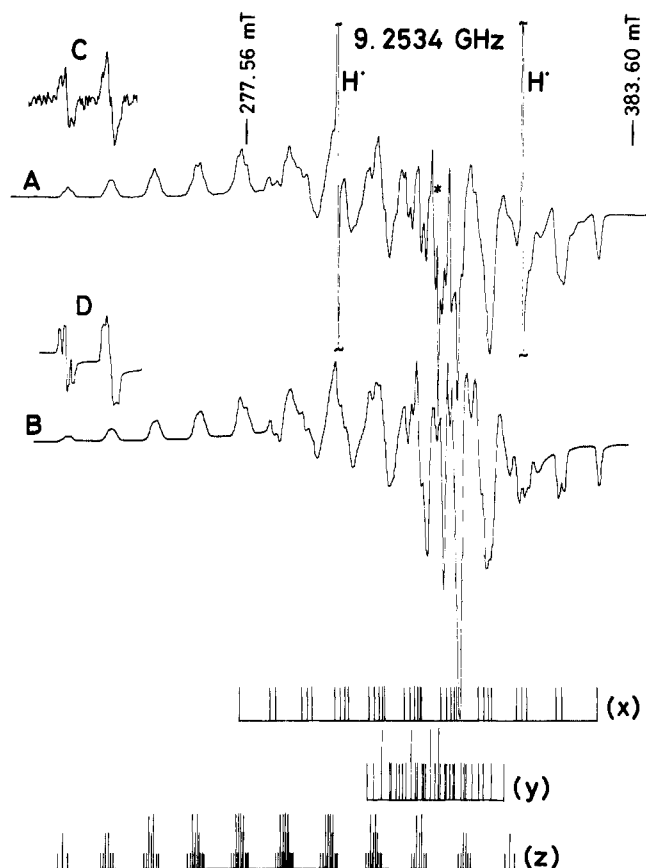
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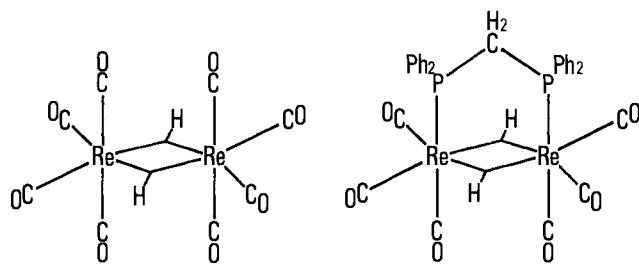
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**Figure 1.** First-derivative (A) and second-derivative (C) X-band ESR spectra of  $\text{Re}_2(\mu\text{-H})_2(\text{CO})_8^-$  in a frozen MTHF solution at 77 K. B and D are their simulations, respectively. The absorption with \* in A is due to unidentified species.

In this connection we have extended our ESR studies on paramagnetic cluster complexes<sup>10,15k-n</sup> to dirhenium complexes,  $\text{Re}_2(\mu\text{-H})_2(\text{CO})_8^-$  and  $\text{Re}_2(\mu\text{-H})_2(\text{CO})_6(\mu\text{-dppm})^-$  (dppm = bis(diphenylphosphinomethane)). Herein we report an indication

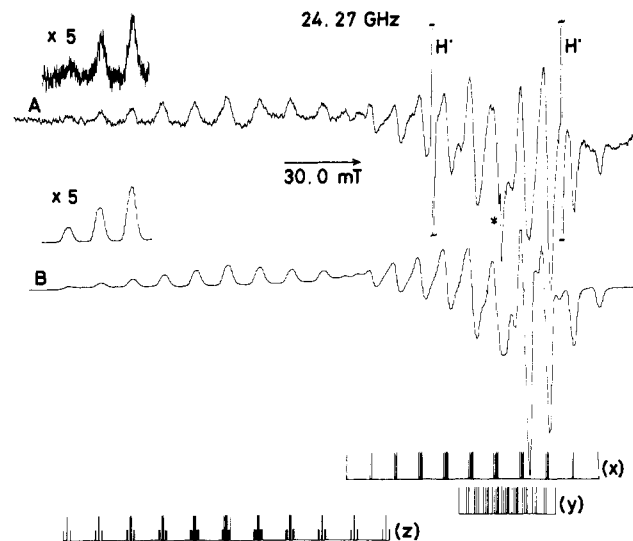


of appreciable 5d-6p mixing in their odd-electron orbitals, which is very different from that of a closely related manganese complex,  $\text{Mn}_3(\mu\text{-H})_3(\text{CO})_{12}^-$ , where 3d-4p mixing has not been detected beyond experimental errors.<sup>15n</sup>

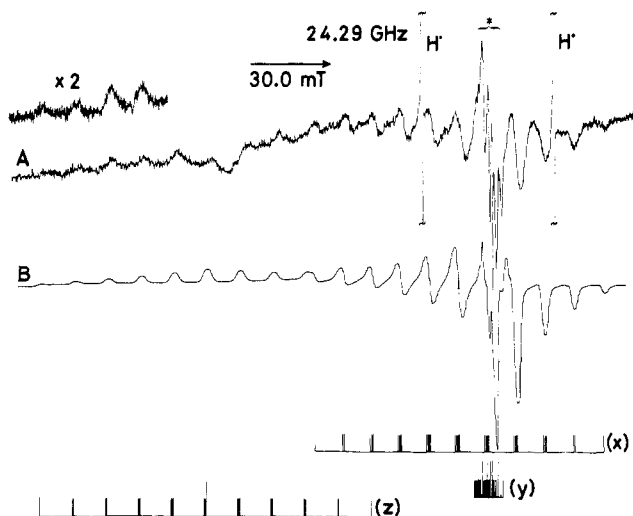
### Experimental Section

Hydrido-bridged complexes  $\text{Re}_2(\mu\text{-H})_2(\text{CO})_8$ <sup>19</sup> and  $\text{Re}_2(\mu\text{-H})_2(\text{CO})_6(\mu\text{-dppm})$ <sup>20</sup> were synthesized by literature methods. A deuterido-bridged complex,  $\text{Re}_2(\mu\text{-D})_2(\text{CO})_8$ , was obtained by the same method as that of the corresponding hydrido complex except for using  $\text{D}_2$  gas instead of  $\text{H}_2$  gas during the photolysis of  $\text{Re}_2(\text{CO})_{10}$ . Deuterium gas was evolved from reaction of  $\text{D}_2\text{O}$  and Ca metal.

A thoroughly degassed 2-methyltetrahydrofuran (MTHF) solution of a complex in an ESR sample tube was exposed to  $^{60}\text{Co}$   $\gamma$  rays at 77 K at a dose rate of  $3.3 \times 10^5 \text{ rad h}^{-1}$  for 3-5 h. X- and K-band ESR spectra were observed at 77 K. ESR instruments and equipment for sample



**Figure 2.** First-derivative K-band ESR spectrum of  $\text{Re}_2(\mu\text{-H})_2(\text{CO})_8^-$  in a frozen MTHF solution at 77 K (A) and its simulation (B). The signal with \* in A is due to unidentified paramagnetic centers.



**Figure 3.** First-derivative K-band ESR spectrum of  $\text{Re}_2(\mu\text{-H})_2(\text{CO})_6(\mu\text{-dppm})^-$  in a frozen MTHF solution at 77 K (A) and its simulation (B). Sharp absorptions with \* are due to unidentified species (see text).

annealing have been mentioned earlier.<sup>10,15k</sup> ESR spectra were simulated with use of a Fortran program<sup>10</sup> prepared according to a second-order perturbation solution for a coaxial spin Hamiltonian.<sup>21</sup>

### Results

Irradiation of  $\gamma$  rays to a frozen MTHF solution of  $\text{Re}_2(\mu\text{-H})_2(\text{CO})_8$  at 77 K produced paramagnetic species derived from both the solvent and the solute. After suitable annealing to decay the solvent radicals, the ESR spectrum shown in Figure 1A was obtained. Figure 1B shows its simulation on the basis of a coaxial spin Hamiltonian which includes a pair of magnetically equivalent rhenium nuclei ( $^{185}\text{Re}$  37%,  $^{187}\text{Re}$  63%, both with  $I = 5/2$ ; the difference between the magnetic moments of both nuclei is only 1% of their magnitudes, which is neglected in the present analyses) and a pair of magnetically equivalent protons. Proton splittings can be resolved only in the low-field part of the spectrum (shown as a second derivative spectrum in Figure 1C), which is confirmed by comparison with the spectrum of the radical derived from the corresponding deuteride complex. Spin-Hamiltonian parameters used for simulations are listed in Table I. In order to minimize uncertainties in the analyses of frozen-solution and powder spectra which are often pointed out by Morton, Preston, and their co-workers,<sup>15i,22</sup> we have examined the K-band ESR spectra of the

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**Table I.** Spin-Hamiltonian Parameters for  $\text{Re}_2(\mu\text{-H})_2(\text{CO})_8^-$ ,  $\text{Re}_2(\mu\text{-D})_2(\text{CO})_8^-$ , and  $\text{Re}_2(\mu\text{-H})_2(\text{CO})_6(\mu\text{-dppm})^-$ 

radical	g tensor			hyperfine splitting tensor <sup>a</sup>			
	x	y	z	nucleus	x	y	z
$\text{Re}_2(\mu\text{-H})_2(\text{CO})_8^-$	2.027 ± 0.001	1.995 ± 0.005	2.280 ± 0.001	Re H	(-93 ± 1) 0 ± 6 <sup>b</sup>	(-35 ± 5) 0 ± 8 <sup>b</sup>	(-131 ± 1) (-14 ± 1)
$\text{Re}_2(\mu\text{-D})_2(\text{CO})_8^-$	2.027 ± 0.001	1.995 ± 0.005	2.280 ± 0.001	Re	(-93 ± 1)	(-35 ± 5)	(-131 ± 1)
$\text{Re}_2(\mu\text{-H})_2(\text{CO})_6(\mu\text{-dppm})^-$	2.028 ± 0.001	2.001 ± 0.005	2.280 ± 0.001	Re	(-103 ± 1)	(-10 ± 5)	(-134 ± 1)

<sup>a</sup>In units of  $10^{-4} \text{ cm}^{-1}$ . Reasonable signs are given in parentheses (see text). <sup>b</sup>Allowable maximum error estimated from the line width in the X-band spectrum.

hydrido and deuterido complexes. These spectra can be reproduced well in simulations obtained with the same spin Hamiltonians as for the X-band spectra. Figure 2 shows the observed K-band spectrum of the hydrido complex together with its simulation.

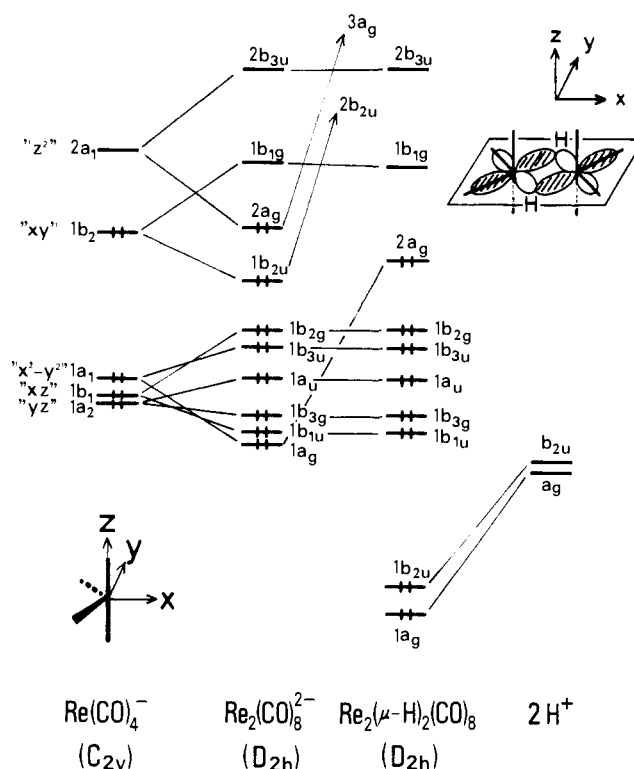
A frozen MTHF solution of  $\text{Re}_2(\mu\text{-H})_2(\text{CO})_6(\mu\text{-dppm})^-$ ,  $\gamma$ -irradiated at 77 K followed by appropriate annealing to decay solvent radicals, exhibited the ESR spectrum shown in Figure 3A (K band). The sharp absorptions in the  $g = 2.00$  region in Figure 3A are more persistent toward further annealing than the broad absorptions in the other part of the spectrum. The latter absorptions decayed simultaneously during further annealing and are simulated as shown in Figure 3B as arising from a radical with a pair of magnetically equivalent rhenium nuclei with the spin-Hamiltonian parameters listed in Table I. The same set of parameters has reproduced its experimental X-band spectrum. Because of the superimposition of sharp signals due to unidentified species in the  $g = 2.00$  region, we could not obtain the precise spin-Hamiltonian parameters for the  $y$  component of this radical.

### Discussion

Since  $\gamma$  irradiation of a frozen MTHF solution is well established to result in anionic species derived from the solute by electron capture,<sup>23</sup> the paramagnetic species exhibiting ESR spectra shown in Figures 1A and 3A are reasonably ascribed to anion radicals,  $\text{Re}_2(\mu\text{-H})_2(\text{CO})_8^-$  and  $\text{Re}_2(\mu\text{-H})_2(\text{CO})_6(\mu\text{-dppm})^-$ , respectively. Geometrical symmetries of both anions are suggested to be the same as those of their neutral parent molecules ( $\text{Re}_2(\mu\text{-H})_2(\text{CO})_8$ ,  $D_{2h}$ ;<sup>24</sup>  $\text{Re}_2(\mu\text{-H})_2(\text{CO})_6(\mu\text{-dppm})$ ,  $C_{2v}$ <sup>20</sup>) by the magnetic equivalence of the pair of rhenium nuclei in each of the anions and of the pair of protons in the former anion and by successful simulations of their spectra by coaxial spin Hamiltonians.

The small proton splittings show that the odd-electron densities on the hydrogen atoms are quite small. The large splittings due to the rhenium nuclei and the large anisotropy of the  $g$  tensors indicate that the odd electron is distributed mainly on the rhenium atoms. The dominant constituents of the odd-electron orbital are expected to be valence-shell d AO's on the rhenium atoms to a first approximation. Although we will propose later the involvement of rhenium 6p and 5d AO's in the odd-electron orbital to a similar extent to interpret the anisotropy of the rhenium hyperfine splitting tensor, we start analyses of the spin-Hamiltonian parameters by assuming that the valence-shell p AO's have negligible contribution to the odd-electron orbital as in the case of paramagnetic cluster complexes of the first-row transition elements.<sup>10,15</sup> This logic is forced by our poor knowledge of the radial function (especially that in proximity to the nucleus) and of the  $l$ - $s$  coupling constant of the rhenium 6p AO and by the complication of the problem.

**Qualitative MO Diagram and Assignment of Odd-Electron Orbital for  $\text{Re}_2(\mu\text{-H})_2(\text{CO})_8^-$ .** A qualitative MO diagram for  $\text{Re}_2(\mu\text{-H})_2(\text{CO})_8^-$  can be constructed as shown in Figure 4 by protonation to the Re-Re double bond of  $\text{Re}_2(\text{CO})_8^{2-}$ , whose MO



**Figure 4.** A qualitative MO diagram of  $\text{Re}_2(\mu\text{-H})_2(\text{CO})_8^-$ . The odd-electron orbital of the anion radical is  $1b_{1g}$ .

diagram can be constructed by interaction of a pair of  $\text{Re}(\text{CO})_4^-$  fragments.<sup>16d</sup> Two pairs of electrons in the  $1b_{2u}$   $\pi_{\text{ReRe}}$  and  $2a_g$   $\sigma_{\text{ReRe}}$  orbitals of  $\text{Re}_2(\text{CO})_8^{2-}$  are formally transferred into the  $1a_g$  and  $1b_{2u}$  MO's of  $\text{Re}_2(\mu\text{-H})_2(\text{CO})_8$  upon protonation corresponding to the model of protonated metal-metal bonds<sup>25</sup> for the hydrido bridges. The diagram is the same as that given by Dedieu, Albright, and Hoffmann<sup>16d</sup> on the basis of extended Hückel calculations except that the  $2a_g$  MO of  $\text{Re}_2(\mu\text{-H})_2(\text{CO})_8$  is located above the  $1b_{2g}$  MO in accord with observed  $g$  tensor of its anion radical (vide infra). The diagram predicts the odd-electron orbital of  $\text{Re}_2(\mu\text{-H})_2(\text{CO})_8^-$  to be the  $1b_{1g}$  MO, the  $\pi_{\text{ReRe}}^*$  orbital consisting mainly of the rhenium  $5d_{xy}$  AO's with nodes at the positions of the protons. This orbital is similar to the  $a_2'$  odd-electron orbital of  $\text{Mn}_3(\mu\text{-H})_3(\text{CO})_{12}^-$  reported previously.<sup>15n</sup>

**Assignment of Spin-Hamiltonian Axes for  $\text{Re}_2(\mu\text{-H})_2(\text{CO})_8^-$ .** Since the protons of  $\text{Re}_2(\mu\text{-H})_2(\text{CO})_8^-$  are located on the nodal plane of the odd-electron orbital in the present orbital assignment, the isotropic part of the proton hyperfine tensor arises from spin polarization of valence electrons and is expected to be small and negative. The anisotropy of the proton splitting tensor originates predominantly from the dipolar magnetic field exerted by the odd electron distributed on the metal atoms. The anisotropic part is calculated as 3.1, 0.9, and  $-4.0$  (in units of  $10^{-4} \text{ cm}^{-1}$ ) for the molecular  $x$ ,  $y$ , and  $z$  directions, respectively, by using point-dipole

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approximations.<sup>26</sup> The molecular  $z$  axis is thus assigned to the spin-Hamiltonian axis in which the observed proton hyperfine splitting tensor has the largest absolute principal value.

The shift of  $g_\alpha$  ( $\alpha = x, y,$  or  $z$ ) from the free spin value ( $g_e = 2.0023$ ) is expressed as follows:<sup>27</sup>

$$\Delta g_\alpha = g_\alpha - g_e \approx 2\zeta \sum_{\psi \neq 1b_{1g}} \sum_{i=1}^2 l_\alpha^i |\psi\rangle^2 / [\epsilon(1b_{1g}) - \epsilon(\psi)] \quad (1)$$

where  $\zeta$  is the one-electron spin-orbit coupling constant of the rhenium  $d$  AO,  $l_\alpha^i$  is the  $\alpha$  component of the orbital angular momentum of an electron around the  $i$ th rhenium nucleus,  $\psi$  represents an MO other than the odd-electron orbital, and  $\epsilon$  stands for an orbital energy. The integral in this equation can have a nonzero value only when  $\psi$  belongs to  $b_{2g}$ ,  $b_{3g}$ , or  $a_g$  symmetry for  $\Delta g_x$ ,  $\Delta g_y$ , or  $\Delta g_z$ , respectively.<sup>28</sup> Since the  $1b_{2g}$  (out-of-plane  $\pi_{\text{ReRe}}^*$ ) orbital is located above the  $1b_{3g}$  ( $\delta_{\text{ReRe}}$ ) orbital<sup>16d</sup> in the energy diagram in Figure 4,  $\Delta g_x$  is predicted to be larger than  $\Delta g_y$ . Thus the spin-Hamiltonian axis of the  $g$  principal value of 2.027 and that of 1.995 are assigned to the molecular  $x$  and  $y$  axes, respectively.<sup>29</sup>

**Re Hyperfine Splitting Tensor and Odd-Electron Orbital on Re Atom.** We have assigned spin-Hamiltonian axes and now can proceed to further analyses of the rhenium hyperfine splitting tensor. The observed hyperfine tensor,  $A(\text{Re})$ , can be divided into first-order terms due to Fermi contact and spin dipolar interactions,<sup>30</sup>  $A'(\text{Re})$ , and second-order terms due to unquenched orbital angular momenta of electrons as in the equations:<sup>15k</sup>

$$A_x(\text{Re}) = A'_x(\text{Re}) + (7/4)B_d\Delta g_x - (3/8)B_d\Delta g_y \quad (2)$$

$$A_y(\text{Re}) = A'_y(\text{Re}) + (7/4)B_d\Delta g_y - (3/8)B_d\Delta g_x \quad (3)$$

$$A_z(\text{Re}) = A'_z(\text{Re}) + (7/4)B_d\Delta g_z + (3/8)B_d(\Delta g_x + \Delta g_y) \quad (4)$$

where  $-2B_d$  ( $= -221 \times 10^{-4} \text{ cm}^{-1}$ )<sup>31</sup> is the splitting constant of a rhenium nucleus for the  $z$  direction with a unit spin density on its  $d_{xy}$  AO.

The  $1b_{1g}$  odd-electron orbital does not have rhenium  $6s$  components because of its symmetry. The Fermi contact term of the rhenium nucleus arises from spin polarization of inner-shell electrons and is negative.<sup>15b</sup> The  $z$  component of the dipolar interaction between the rhenium nucleus and the odd electron should be negative because the symmetry-allowed rhenium constituents of the odd-electron orbital are the  $5d_{xy}$  and  $6p_y$  AO's. Thus  $A_z(\text{Re})$  is expected to be negative. Among choices of signs for  $A_x(\text{Re})$  and  $A_y(\text{Re})$ , the assignment of negative signs to both of them gives physically meaningful results.<sup>32</sup> With this sign assignment, the first-order hyperfine tensor is obtained as  $A'_x(\text{Re}) = -98 \times 10^{-4}$ ,  $A'_y(\text{Re}) = -33 \times 10^{-4}$ , and  $A'_z(\text{Re}) = -185 \times 10^{-4} \text{ cm}^{-1}$  by using eq 2-4. This tensor is not axially symmetric, although it should be axially symmetric around the molecular  $z$  axis if the rhenium constituent of the  $1b_{1g}$  odd-electron orbital is only its  $5d_{xy}$  AO.<sup>33</sup>

(26) Two assumptions are used for the calculation. The  $\text{Re}_2\text{H}_2$  geometry is assumed to be planar with  $\text{ReRe}$  and  $\text{ReH}$  distances of 290 and 188 pm, respectively.<sup>24,25</sup> The odd-electron density on each of the  $\text{Re}$  atoms is assumed to be 0.5.

(27) Stone, A. J. *Proc. R. Soc. London, Ser. A* **1963**, 271.

(28) Because  $l_x$ ,  $l_y$ , and  $l_z$  belong to  $b_{3g}$ ,  $b_{2g}$ , and  $b_{1g}$  irreducible representations, respectively, in  $D_{2h}$  point group.

(29) (a) Because the  $z$  component of the  $g$  tensor shows the largest positive shift, the  $2a_g$  ( $\sigma_{\text{ReRe}}$ ) MO should have a higher orbital energy than the  $1b_{2g}$  and  $1b_{3g}$  orbitals. (b) In present assignments of the axes and of the odd-electron orbital, the  $z$  principal value of the rhenium hyperfine splitting tensor is predicted to have a larger absolute value than  $x$  and  $y$  principal values<sup>30</sup> in accord with the experimental observations.

(30) Atherton, N. M. "Electron Spin Resonance, Theory and Applications"; Ellis Horwood: Chichester, 1973.

(31) Morton, J. R.; Preston, K. F. *J. Magn. Reson.* **1978**, *30*, 577.

(32) In the sign assignment of  $A_x(\text{Re}) > 0$ , the odd-electron density on the  $5d_{xy}$  AO of each of the rhenium atoms exceeded 0.8, which is too large. If we assume  $A_x(\text{Re}) < 0$  and  $A_y(\text{Re}) > 0$ , the contribution of the  $6p$  odd-electron density to the rhenium hyperfine splitting tensor exceeded that of the  $5d$  odd-electron density which is not likely.

We can think of three possible origins for the deviation of the tensor from axial symmetry: (1) symmetry-allowed mixing of  $6p$  AO's into the odd-electron orbital, (2) spin polarizations of valence electrons inducing appreciable spin density on  $5d$  AO's other than the  $5d_{xy}$  AO, and (3) spin polarization of inner-shell electrons in  $p$ - and/or  $d$ -type orbitals.<sup>15d</sup> Origin 2 is less likely because the hyperfine splitting tensors of the metal nuclei of  $\text{V}_2(\mu\text{-PPH}_2)_2\text{(CO)}_8^-$  and  $\text{Mn}_2(\mu\text{-AsPh}_2)_2\text{(CO)}_8^+$  have axial symmetry<sup>10</sup> although spin polarization of their valence electrons would take place similarly as in the present dirhenium complex. Spin polarization of inner-shell electrons is a local phenomenon around the nucleus of the interest.<sup>34</sup> For inner-shell electrons in  $p$ - and  $d$ -type orbitals in the rhenium atom, the exchange field exerted by the odd electron in its  $5d_{xy}$  AO is axially symmetric around the local  $z$  axis. Thus the spin density distribution polarized by the field in the inner shell should have axial symmetry around the  $z$  axis and should not induce deviation of the tensor from the axial symmetry.

Thus we propose that the deviation originates from mixing of the  $b_{1g}$  combination of the  $6p_y$  AO's with the  $\pi_{\text{ReRe}}^*$  odd-electron orbital and assign an appreciable odd-electron density to the rhenium  $6p_y$  AO. The first-order tensor,  $A'(\text{Re})$ , can be divided into an isotropic part,  $a$ , arising from spin polarization of inner-shell  $s$  electrons, and a pair of anisotropic parts due to the odd-electron densities on the  $5d_{xy}$  and  $6p_y$  AO's ( $\rho_d$  and  $\rho_p$ , respectively):

$$A'_x(\text{Re}) = a + B_d\rho_d - B_p\rho_p \quad (5)$$

$$A'_y(\text{Re}) = a + B_d\rho_d + 2B_p\rho_p \quad (6)$$

$$A'_z(\text{Re}) = a - 2B_d\rho_d - B_p\rho_p \quad (7)$$

where  $2B_p$  is the splitting constant of a rhenium nucleus for the  $y$  direction with a unit spin density on its  $6p_y$  AO. The preceding principal values of  $A'(\text{Re})$  give  $a = -105 \times 10^{-4} \text{ cm}^{-1}$ ,  $\rho_d = 0.26$ ,<sup>35</sup> and  $2B_p\rho_p = 44 \times 10^{-4} \text{ cm}^{-1}$ . Unfortunately, we do not have a reliable value of  $B_p$  because of lack of a good radial function of the  $6p$  AO, and we cannot have an estimate of  $\rho_p$ . However, the value of  $2B_p\rho_p$  is of the same order of magnitude as that of the  $d$  contribution, i.e.,  $2B_d\rho_d = 58 \times 10^{-4} \text{ cm}^{-1}$ , suggesting that the  $6p$  AO has a size<sup>36</sup> similar to that of the  $5d$  AO and that  $\rho_p$  is of a similar order of magnitude to  $\rho_d$ ; since  $B_p/B_d = 7\langle r^{-3} \rangle_p / (5\langle r^{-3} \rangle_d)$ ,<sup>31</sup> the ratio between the values of  $2B\rho$  can be rewritten as  $\langle r^{-3} \rangle_p \rho_p / (\langle r^{-3} \rangle_d \rho_d) = 5 \times 44 \times 10^{-4} / (7 \times 58 \times 10^{-4}) = 0.54$ , where  $\langle r^{-3} \rangle_x$  designates the expectation value of  $r^{-3}$  for  $\chi$  AO and  $r$  is the distance between the electron and the nucleus.

**$\text{Re}_2(\mu\text{-H})_2(\text{CO})_6(\mu\text{-dppm})^-$ .** The spin-Hamiltonian parameters of this anion radical are quite similar to those of  $\text{Re}_2(\mu\text{-H})_2(\text{CO})_8^-$  (Table I). In analogy to  $\text{Re}_2(\mu\text{-H})_2(\text{CO})_8^-$ , the odd-electron orbital of the dppm complex is reasonably assigned to the out-of-phase combination of  $5d_{xy}$  AO's combined with that of  $6p_y$  AO's. By attributing negative signs for all the principal values of the rhenium hyperfine tensor as in the case of  $\text{Re}_2(\mu\text{-H})_2(\text{CO})_8^-$  and by using eq 2-7, we can estimate the odd-electron density on the rhenium  $5d_{xy}$  AO to be 0.24<sup>35</sup> and the principal value for the  $y$  direction of the anisotropic hyperfine tensor due to the odd-electron density on the rhenium  $6p_y$  AO to be  $66 \times 10^{-4} \text{ cm}^{-1}$ .

The absence of resolved splittings due to the  $^{31}\text{P}$  nuclei in the present anion needs some comments. A wide range of values of  $^{31}\text{P}$  splitting constants have been observed in the ESR of tran-

(33) The dipolar effect on the hyperfine splitting tensor of a rhenium nucleus from the odd-electron density on the neighboring rhenium atom is calculated to be less than  $1 \times 10^{-4} \text{ cm}^{-1}$  with point-dipole approximations and cannot explain the deviation of  $A'(\text{Re})$  from the axial symmetry.

(34) Goodman, B. A.; Raynor, J. B. *Adv. Inorg. Chem. Radiochem.* **1970**, *13*, 135.

(35) (a) The value of  $2B_0 = 221 \times 10^{-4} \text{ cm}^{-1}$ , on which the estimate of  $\rho_d$  is based, has been evaluated<sup>31</sup> by using nonrelativistic atomic orbital given by Herman and Skillman.<sup>35b</sup> Inclusion of relativistic effects into the calculation of atomic orbitals of a rhenium atom would induce an expansion of its  $5d$  orbital, which will decrease the value of  $2B_0$ . Thus the present estimate of  $\rho_d$  should be regarded as a possible minimum value. (b) Herman, F.; Skillman, S. "Atomic Structure Calculations"; Prentice-Hall: Englewood Cliffs, N. J., 1963.

(36) Note that the anisotropy parameter,  $B_d$  or  $B_p$ , is proportional to the expectation value of  $r^{-3}$  of the AO.

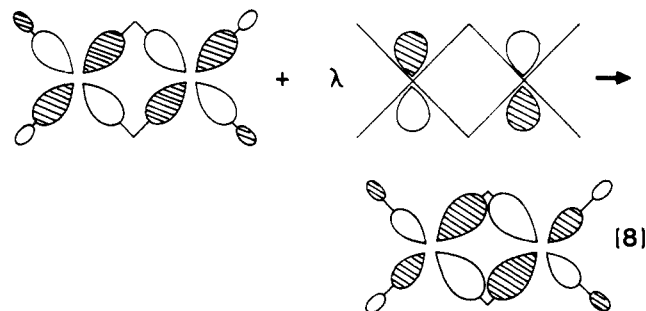
sition-metal complexes with phosphorus-centered ligands,<sup>15e,k,l,22,37</sup> when lone-pair orbitals on phosphorus atoms are symmetry-allowed to mix with odd-electron orbitals. However, the phosphorus splitting in  $\text{V}_2(\mu\text{-PPh}_2)_2(\text{CO})_8^-$  has been too small to be resolved in frozen-solution spectra, and in this anion the phosphorus lone-pair orbitals are symmetry-forbidden to mix with the odd-electron orbital.<sup>10</sup> The phosphorus lone-pair orbital of the present dirhenium anion lies approximately on the local  $z$  axis and is hard to mix with the odd-electron orbital consisting of  $5d_{xy}$  and  $6p_y$  AO's. Thus the absence of resolved  $^{31}\text{P}$  splittings would not be very abnormal.

**Mixing of 5d and 6p.** In both  $\text{Re}_2(\mu\text{-H})_2(\text{CO})_8^-$  and  $\text{Re}_2(\mu\text{-H})_2(\text{CO})_6(\mu\text{-dppm})^-$ , the  $b_{1g}$  odd-electron orbital contains rhenium  $5d_{xy}$  and  $6p_y$  AO's. This is very different from the cases of clusters of the first transition series elements such as  $\text{V}_2(\mu\text{-PPh}_2)_2(\text{CO})_8^-$ ,<sup>10</sup>  $\text{Mn}_2(\mu\text{-AsPh}_2)_2(\text{CO})_8^+$ ,<sup>10</sup> and  $\text{Co}_3(\mu^3\text{-CPh})_2\text{Cp}_3^-$ ,<sup>15m</sup> where anisotropies of metal hyperfine splitting tensors arising from odd-electron densities on 4p AO's have not been detected. Some comments are needed for  $\text{Co}_2(\mu\text{-CO})_2\text{Cp}_2^-$ ,<sup>15c,d</sup> for which spin-Hamiltonian axes have not been assigned yet. If we assign the spin-Hamiltonian axes of 1, 2, and 3 to the molecular axes of  $z$ ,  $x$ , and  $y$  in the notations of Symons and Bratt,<sup>15d</sup> respectively, an analysis of its spin Hamiltonian based on the MO diagram given by Pinhas and Hoffman<sup>16e</sup> shows that the first-order hyperfine tensor of the cobalt nucleus is axially symmetric, indicating minor or no contribution of the cobalt 4p AO's into the odd-electron orbital.<sup>38</sup> However, the assignment of the axes has not been straightforward and some confirmations are awaited.

Hydrido-bridging in the present dirhenium complexes is not likely an origin of the 5d-6p mixing because the manganese hyperfine splitting tensor of  $\text{Mn}_3(\mu\text{-H})_3(\text{CO})_{12}^-$ <sup>15n</sup> has not shown evidence of 3d-4p mixing in its odd-electron orbital beyond experimental error. Relativistic expansion and contraction of rhenium 5d and 6p AO's, respectively,<sup>17</sup> are most likely origins of the 5d-6p mixing.

Admixture of 6p AO's into MO's composed of 5d AO's should take place in a phase to convert bonding and antibonding MO's part way into still more bonding and nonbonding ones, respec-

tively.<sup>16f,g,39</sup> Since the present  $b_{1g}$  odd-electron orbital is  $\sigma$  antibonding between the rhenium atom and the equatorial carbonyl and nonbonding with respect to Re-H interactions, the 6p admixture is expected to take place so as to decrease the  $\sigma$ -antibonding character between the rhenium atom and the carbonyl at the sacrifice of some increase of Re-Re  $\pi$  antibonding character (see eq 8).



The present proposal that the  $b_{1g}$  odd-electron orbital is constructed primarily of rhenium  $5d_{xy}$  and  $6p_y$  AO's and that the 6p AO has a similar radius to that of the 5d AO suggests that the  $l$ - $s$  coupling in 6p AO's may have a similar significance to that in 5d AO's for the  $g$  tensor and for second-order hyperfine terms arising from  $l$ - $s$  coupling. The present analysis has taken only the 5d contributions into account. This approximation decreases the quantitative significance of the analysis, but this does not affect the main proposal mentioned above. It is difficult to analyze the parameters with better quantitative reliability only by using a qualitative MO scheme. A theoretical study on the electronic structure of the present anion including relativistic effects is awaited.

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**Registry No.**  $\text{Re}_2(\mu\text{-H})_2(\text{CO})_8^-$ , 98542-21-3;  $\text{Re}_2(\mu\text{-D})_2(\text{CO})_8^-$ , 98542-22-4;  $\text{Re}_2(\mu\text{-H})_2(\text{CO})_6(\mu\text{-dppm})^-$ , 98542-23-5.

(37) (a) Kidd, D. R.; Cheng, C. P.; Brown, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 4103. (b) Walker, H. W.; Rattinger, G. B.; Belford, R. C.; Brown, T. L. *Organometallics* **1984**, *2*, 775.

(38) Sowa, T.; Kawamura, T., unpublished results.

(39) Christoph, G. G.; Koh, Y.-B. *J. Am. Chem. Soc.* **1979**, *101*, 1422.