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# Electronic and ESR Spectral Studies of a Series of Phosphine and Phosphite Adducts with Cobaloxime Analog

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**Synopsis.** Electronic and ESR spectra were measured for solutions of $Co(dmgBF_2)_2$ in the presence of $PX_3$, where $Co(dmgBF_2)_2$ is a $BF_2$ capped species of bis(dimethylglyoximato)cobalt(II) ($Co(Hdmg)_2$) and $PX_3$ is $PBu_3$, $PPh_3$, $P(OEt)_3$, or $P(OPh_3)_3$. $^{31}P$ hyperfine splittings of their ESR spectra demonstrated that $Co(dmgBF_2)_2$ forms only 1 : 1 adducts with $PX_3$. The visible absorption spectrum of the dichloromethane solution of $Co(dmgBF_2)_2$ showed an absorption band at 444 nm at 20 °C. Upon $PX_3$ being added to the solution, the band shifted to a longer wavelength; the band shift increased with increasing the electron-donating ability of $PX_3$.

Bis(dimethylglyoximato)cobalt(II) complex ($Co(Hdmg)_2$) and its related compounds have been known as model compounds for vitamin $B_{12}$[1] or as hydrogenation catalysts.[2] Recently, during our investigation of the catalytic properties of those complexes, the methanol solution of $Co(dmgBF_2)_2$ (the $BF_2$ capped species of $Co(Hdmg)_2$, Fig. 1) was found to be thermochromic in the presence of tributylphosphine ($PBu_3$).[3] It was also found that the thermochromism is due to a shift of equilibrium between the $Co^{II}$ and $Co^{I}$ species.[3,4] On the other hand, no thermochromic behavior was observed for the methanol solution of $Co(dmgBF_2)_2$ in the presence of triphenylphosphine ($PPh_3$), triethylphosphite ($P(OEt)_3$), or triphenylphosphite ($P(OPh)_3$). In the present study, the electronic and ESR spectra of $Co(dmgBF_2)_2$ were measured in a methanol or dichloromethane solution in the presence of the above-mentioned four trivalent phosphorus ligands ($PX_3$); the influence of these phosphorus ligands is discussed in terms of the bonding properties between $Co(dmgBF_2)_2$ and $PX_3$.

## Experimental

The ESR spectra were observed at 77 K with a Bruker ESP-300 and a JES ME-1X type spectrometer in the X band with a field modulation of 100 kHz. $Co(dmgBF_2)_2(2H_2O)$ was prepared according to the method of Bakac and Espenson.[5] The preparation of ESR samples was carried out under a dry atmosphere of argon. $Co(dmgBF_2)_2(2H_2O)$ was dissolved in methanol, and an amount of phosphorus ligand was added. A 1 ml solution was transferred to a quartz ESR tube, and the tube was then sealed. The visible absorption spectra were measured at 20 °C by a method described in a previous paper.[4]

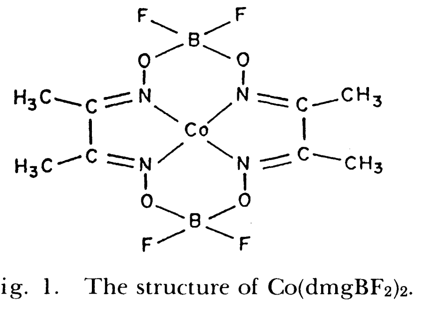

Fig. 1. The structure of $Co(dmgBF_2)_2$.

## Results and Discussion

Figure 2a shows the ESR spectrum of $Co(dmgBF_2)_2$ observed in a frozen methanol solution at 77 K. The spectrum is characterized by the lineshape for a random orientation of paramagnetic species with anisotropic $g$ values ($S=1/2$) and the hyperfine structure due to the magnetic interaction between an unpaired electron and a nucleus of $I=7/2$, where $S$ and $I$ denote an electron and a nuclear spin quantum number, respectively. No superhyperfine structure was resolved.

Figure 2b shows the ESR spectra of $Co(dmgBF_2)_2$ observed at 77 K in a frozen methanol solution in the presence of $P(OEt)_3$. The spectrum is distinctly different from that of the parent $Co(dmgBF_2)_2$ and is diagnostic for adduct formation. The additional doublet splitting of the hyperfine structure can be attributed to the superhyperfine structure due to the magnetic interaction of an unpaired electron with a $^{31}P$ nucleus ($I=1/2$). Assuming a tetragonal symmetry, $Co(Hdmg)_2$ is in the low-spin $^2A_1$ state and the unpaired electron is

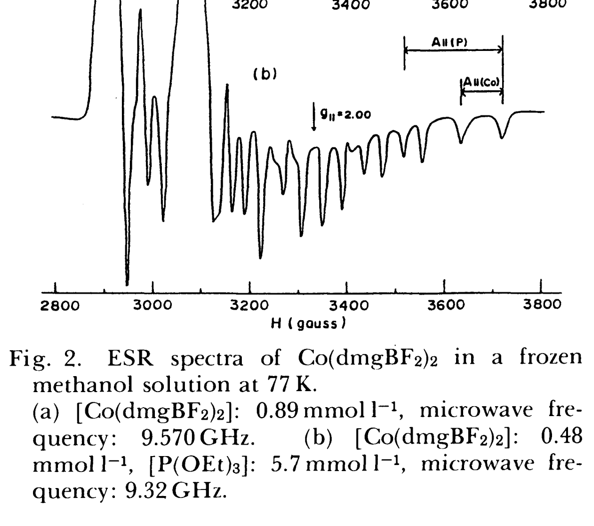

Fig. 2. ESR spectra of $Co(dmgBF_2)_2$ in a frozen methanol solution at 77 K.
(a) $[Co(dmgBF_2)_2]$: 0.89 mmol $l^{-1}$, microwave frequency: 9.570 GHz. (b) $[Co(dmgBF_2)_2]$: 0.48 mmol $l^{-1}$, $[P(OEt)_3]$: 5.7 mmol $l^{-1}$, microwave frequency: 9.32 GHz.

Table 1. ESR Parameters for Co(dmgBF$_2$)(PX$_3$) Complexes

| PX$_3$ | $g_{\parallel}$ | $A_{\parallel}$(Co) | $A_{\parallel}$(P) |
|---|---|---|---|
| | | G$^{a)}$ | |
| None | 2.01 | 120 | — |
| PBu$_3$ | 2.00 | 82 | 125 |
| PPh$_3$ | 2.00 | 92 | 127 |
| P(OEt)$_3$ | 2.00 | 83 | 208 |
| P(OPh)$_3$ | 2.00 | 89 | 230 |

a) 1 G=$10^{-4}$ T.

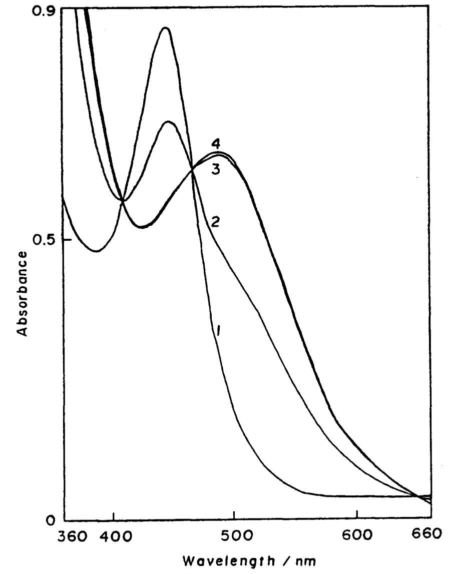

Fig. 3. Visible absorption spectra, 1, 2, 3, and 4 of 0.33 mM Co(dmgBF$_2$)$_2$ (1M=1 mol dm$^{-3}$) in the dichloromethane solution containing P(OEt)$_3$ with the concentration of 0, 0.22, 0.49, and 3.2 mM, respectively.

localized mainly in the d$_{z^2}$ orbital.[6,7] Thus, the superhyperfine structure arises from the axial coordination of the phosphorus ligand, P(OEt)$_3$. The superhyperfine structure was not affected by the addition of excess of P(OEt)$_3$ to the solution, suggesting that Co(dmgBF$_2$)$_2$ forms only 1 : 1 adducts with P(OEt)$_3$ in the methanol solution. This finding parallels observations with Co(Hdmg)$_2$(PX$_3$),[6,8] Co(tpp)(PX$_3$),[9] and Co(salen)(PX$_3$),[10–13] where Co(tpp) and Co(salen) are tetraphenylporphinatocobalt(II) and (*N,N′*-disalicylideneethylenediaminato)cobalt(II), respectively. A similar superhyperfine structure due to a $^{31}$P nucleus was observed at 77 K for Co(dmgBF$_2$)$_2$ in a frozen methanol solution in the presence of the other phosphorus ligands, viz., PBu$_3$, PPh$_3$, or P(OPh)$_3$, conforming the 1 : 1 adducts formation of Co(dmgBF$_2$)$_2$ with these phosphorus ligands. (In the presence of excess PBu$_3$, however, the ESR signal could not be observed, because under that condition Co$^{II}$(dmgBF$_2$)$_2$(PBu$_3$) is reduced to Co$^{I}$ species.) The ESR parameters are shown in Table 1. A similar superhyperfine structure was observed for the 1 : 1 adducts in dichloromethane solution. The ESR parameters are quite the same as those listed in Table 1.

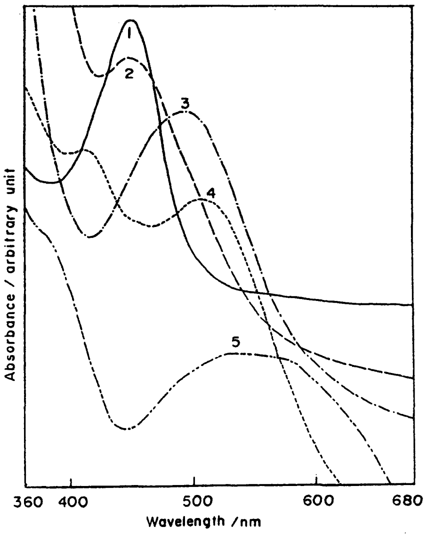

Fig. 4. Visible absorption spectra, 1, 2, 3, 4, and 5 of 0.30 mM Co(dmgBF$_2$)$_2$ in the dichloromethane solution containing none, 6.0 mM of P(OPh)$_3$, 6.0 mM of P(OEt)$_3$, 6.0 mM of PPh$_3$ and 1.1 mM of PBu$_3$, respectively.

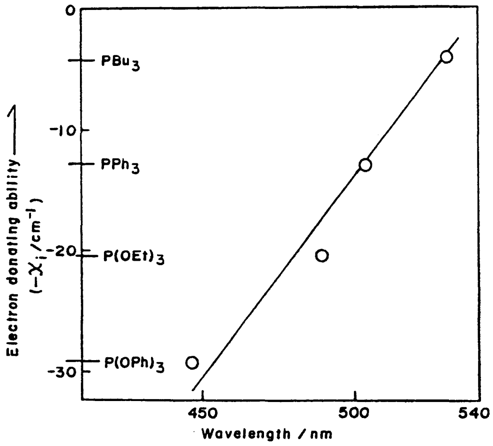

Fig. 5. Relationship between the electron-donating ability ($-X_i$) of PX$_3$ and the wavelength of the absorption band of Co(dmgBF$_2$)$_2$(PX$_3$).

The visible absorption spectra of the methanol solution of Co(dmgBF$_2$)$_2$ showed an absorption band at 462 nm. When PBu$_3$ was added to the parent solution, the band shifted to 530 nm.[3] On the other hand, when PPh$_3$, P(OEt)$_3$, or P(OPh)$_3$ were added to the parent solution, no appreciable amount of the band shift was observed, suggesting that the interaction between these phosphorus ligands and Co(dmgBF$_2$)$_2$ is weak compared with that between PBu$_3$ and Co(dmgBF$_2$)$_2$ in the methanol solution.

The visible absorption spectra of the dichloromethane solution of Co(dmgBF$_2$)$_2$ showed an absorption band at 444 nm. Upon adding the trivalent phosphorus ligands to the parent solution, the band shifted to a longer wavelength while exhibiting isosbestic points. Figure 3 examplifies the spectral change observed upon increasing the amount of P(OEt)$_3$ from zero to $32 \times 10^{-4}$ mol l$^{-1}$ in a $3.3 \times 10^{-4}$ mol l$^{-1}$ of Co(dmgBF$_2$)$_2$

solution (the band at 444 nm shifted to 489 nm while exhibiting three isosbestic points at 408, 467, and 650 nm).

Figure 4 shows the visible absorption spectra (1, 2, 3, 4, and 5) of $Co(dmgBF_2)_2$ in the presence of none, $P(OPh)_3$, $P(OEt)_3$, $PPh_3$, and $PBu_3$, respectively, with the concentration; no more spectral change was observed upon a futher addition of each phosphorus ligand. Sice $Co(dmgBF_2)_2$ forms only 1 : 1 adducts with the phosphorus ligand, it is concluded from Fig. 4 that $Co(dmgBF_2)_2(PBu_3)$, $Co(dmgBF_2)_2(PPh_3)$, $Co(dmgBF_2)_2(P(OEt)_3)$, and $Co(dmgBF_2)_2(P(OPh)_3)$ have an absorption band at 530 nm (18900 $cm^{-1}$), 503 nm (19900 $cm^{-1}$), 489 nm (20400 $cm^{-1}$) and 446 nm (22400 $cm^{-1}$), respectively.

Figure 5 shows a relationship between the wavelength of the absorption band of $Co(dmgBF_2)_2(PX_3)$ and the electron-donating ability of $PX_3$ (the electron-donating ability is represented in units of Tolman $X_i$ parameter).[14] This relationship shows that the absorption band of $Co(dmgBF_2)_2(PX_3)$ shifts to a longer wavelength upon increasing the electron-donating ability of $PX_3$ (namely with decreasing the Tolman $X_i$ parameter of $PX_3$). The electronic configuration of square-pyramidal $d^7$ complexes is $(d_{xz})^2(d_{yz})^2(d_{xy})^2(d_{z^2})^1(d_{x^2-y^2})^0$ in the ground state. If the electron-donating ability of $PX_3$ (as an axial ligand) increases, the energy level of the $d_{z^2}$ orbital would be increased. Thus, from the fact that the absorption bands of $Co(dmgBF_2)_2(PX_3)$ shift to a much longer wavelength upon increasing the electron donating ability of $PX_3$ (Fig. 5), the absorption band in Fig. 4 was assigned to the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition. It was consequently concluded that the order of $d_{z^2}$ $\sigma$-donor orbital mixing is $PBu_3 > PPh_3 > P(OEt)_3 > P(OPh)_3$.

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