Syntheses of Tervalent Iridium Complexes of Octaethylporphyrin; Influence of Axial Ligands on their Ultra-violet–Visible, Infrared, and Nuclear Magnetic Resonance Spectra, and Redox Potentials

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Tervalent iridium complexes of 2,3,7,8,12,13,17,18-octaethylporphyrin (oep), $[Ir^{III}(oep)(CO)X]$ (X = Cl, ClO_4, BF_4, CN, Br, or CH_3), and $[Ir^{III}(oep)(L)CH_3]$ [L = none, *N*-methylimidazole (mim), pyridine (py), NH_3, or CN] were isolated or generated *in situ*. For the carbonyl complexes $[Ir^{III}(oep)(CO)X]$ the carbonyl stretching frequencies [ν(CO)] and the wavenumbers of the absorption peaks of electronic spectra are both found to be approximately in the order of decreasing electron-donating tendency of the axial ligand, *i.e.* CH_3^-, $Br^- \sim Cl^-$, $ClO_4^- \sim BF_4^-$, except in the case of the cyanide ion, where various types of complexity are conceivable. Throughout the whole series there is a good linear correlation between the chemical shift of the *meso* protons and the reversible redox potential Ir^I–Ir^{III} as shown in cyclic voltammetry in the range *ca.* +0.4—+1.3 V depending on the axial ligands. These results are explained in terms of the change of the electron density caused by chelation of the axial ligands depending on their electron-donating tendency, and the order of such tendency is inferred to be: CO < none < py < NH_3 < mim < CN^- < $ClO_4^- \sim BF_4^-$ < $Cl^- \sim Br^-$ < CH_3^-.

ALTHOUGH cobalt and iridium have the same number of outer shell ($d + s$) electrons, their chemical properties often show subtle differences. For example whereas tervalent cobalt porphyrins are rather unstable and readily reduced to the bivalent complex under various conditions, no bivalent iridium complexes have yet been reported. On the other hand, Ogoshi *et al.*[1] widely investigated the synthesis of ter- and uni-valent iridium complexes of octaethylporphyrin and nucleophilic reactions of the monovalent complex with halides to form the metal–carbon bond, providing a plausible model for the coenzyme vitamin B_{12}.

Recently, we revealed the influence of the axial ligand to the central cobalt atom for the porphyrin complexes both chemically and electrochemically by using tervalent cobalt porphyrins having various types of axial ligands in connection with the bio-inorganic study for vitamin B_{12}.[2] It seems, therefore, interesting and valuable from the bio-inorganic point of view to investigate the influence of the axial ligand to the central iridium atom of porphyrin complexes and to compare it with that in cobalt porphyrins.

In this paper we wish to report the syntheses of various tervalent iridium porphyrins having different types of axial ligands and the evaluation of the influence of these axial ligands to the central iridium atom from the results of u.v.–visible, i.r., ^1H n.m.r., and cyclic voltammetry.

EXPERIMENTAL

Syntheses of Compounds.—The starting complex $[Ir^{III}(oep)(CO)Cl]$ (1) was prepared according to the procedure previously reported.[1,3]

$[Ir^{III}(oep)(CO)ClO_4]$ (2). To complex (1) (100 mg) in dry benzene (50 cm^3) was added anhydrous $AgClO_4$ (100 mg). The reaction mixture was gently refluxed for 1 h. The mixture was cooled to room temperature and the precipitate of AgCl removed by filtration. The residual solution was slowly condensed with an evaporator until fine crystals appeared. The crystals thus obtained were collected, washed with water several times, and dried over P_2O_5 under vacuum to give fine dark red crystals (70 mg) (Found: C, 53.6; H, 5.65; N, 6.65. Calc. for $C_{37}H_{44}ClIrN_4O_5$: C, 52.15; H, 5.20; N, 6.55%).

$[Ir^{III}(oep)(CO)BF_4]$ (3). A dichloromethane solution of (2) was washed several times with 10% tetrafluoroboric acid. The solution was then washed with water and dried over anhydrous Na_2SO_4. After removal of solvent, the residual solid was recrystallized from benzene–light petroleum (1:1 v/v) to afford (3) in an almost quantitative yield as fine dark red crystals (Found: C, 52.3; H, 5.55; N, 6.65. Calc. for $C_{37}H_{44}BF_4IrN_4O$: C, 52.9; H, 5.30; N, 6.65%).

$[Ir^{III}(oep)(CO)CN]$ (4). A dichloromethane solution of (2) was shaken with 5% KCN several times at *ca.* 10 °C. The solution was then washed with water and dried over anhydrous Na_2SO_4. After removal of solvent, the residual solid was recrystallized from dichloromethane–diethyl ether (1:1 v/v) to give (4) in *ca.* 70% yield as dark red crystals (Found: C,57.3; H, 5.75; N, 8.75. Calc. for $C_{38}H_{44}IrN_5O\cdot H_2O$: C, 57.25; H, 5.55; N, 8.80%).

$[Ir^{III}(oep)(CO)Br]$ (5). A dichloromethane solution of (2) was treated with 10% KBr. The solution was washed with water several times and dried over anhydrous Na_2SO_4. After removal of solvent, the residual solid was recrystallized from benzene to afford (5) in an almost quantitative yield as dark red crystals (Found: C, 53.3; H, 5.45; N, 6.65. Calc. for $C_{37}H_{44}BrIrN_4O$: C, 53.35; H, 5.30; N, 6.75%).

$[Ir^{III}(oep)CH_3]$ (6). This compound was prepared by the method previously reported.[1]

$[Ir^{III}(oep)(CO)CH_3]$ (7). Into a dichloromethane solution of (6) carbon monoxide gas was bubbled for several minutes until the absorption band at 529 nm was completely shifted to 554 nm. After removal of solvent, the residual solid was recrystallized from benzene to give (7) in an almost quantitative yield as dark red crystals (Found: C, 58.55; H, 6.15; N, 7.20. Calc. for $C_{38}H_{47}IrN_4O\cdot 0.5H_2O$: C, 58.75; H, 6.10; N, 7.20%).

$[Ir^{III}(oep)(mim)CH_3]$ (8). To complex (6) (100 mg) in dry benzene (100 cm^3) was added mim (0.5 cm^3) and the solution was heated to about 50 °C for 1 h. The solution was condensed to a small volume and allowed to stand overnight at room temperature. The resulting dark red crystals were filtered off, washed with ether, and dried under vacuum (80 mg) (Found: C, 60.75; H, 6.95; N, 9.75. Calc. for $C_{41}H_{53}IrN_6\cdot\frac{1}{3}C_6H_6$:† C, 60.45; H, 6.60; N, 9.85%).

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† The ^1H n.m.r. spectra of (8) in CD_2Cl_2 revealed the existence of the calculated amount of benzene.

$[Ir^{III}(oep)(CN)CH_3]^-$ (9). A dichloromethane solution of (6) was shaken with aqueous KCN several times. The organic layer was separated and dried over anhydrous Na_2SO_4, and used for spectroscopic measurements and cyclic voltammetry.

$[Ir^{III}(oep)(py)CH_3]$ (10). To a dichloromethane solution of (6) was added an excess amount of pyridine. The reaction was monitored by u.v.–visible spectra, and the solution used for spectroscopic measurements and cyclic voltammetry.

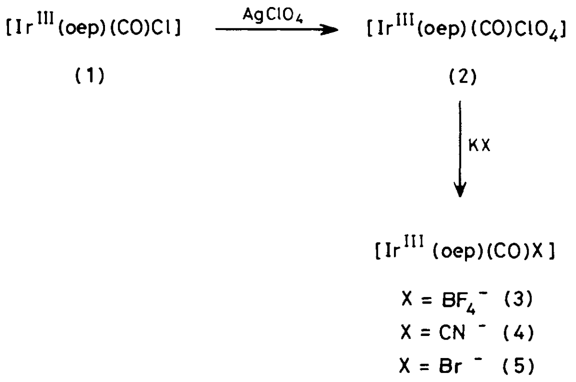
$[Ir^{III}(oep)(NH_3)CH_3]$ (11). Ammonia gas was bubbled through a dichloromethane solution of (6). The reaction was monitored by u.v.–visible spectra, and the resulting solution used for spectroscopic measurements and cyclic voltammetry.

Spectral Measurements.—Absorption spectra were measured on a Hitachi model 200-10 spectrophotometer. Infrared spectra were obtained on a JASCO A-102 spectrophotometer and ^1H n.m.r. spectra on a JEOL HM-100 spectrometer.

Cyclic Voltammetry.—Dichloromethane as the solvent was dried and distilled over CaH_2 before use. As a supporting electrolyte tetrabutylammonium perchlorate was used after being subjected twice to crystallization from benzene. Cyclic voltammograms were obtained on a HA-104 potentiostat (Hokuto Denko) in combination with a HB-107A function generator (Hokuto Denko). A three electrode system was used which consisted of platinum working and counter electrodes and a commercial saturated calomel electrode (s.c.e.) separated from the bulk of solution by a bridge filled with solvent and supporting electrolyte. The bridge had its solution changed periodically to avoid aqueous contaminants from entering the cell *via* the s.c.e. All solutions were purged of oxygen by passing purified nitrogen through them for 10 min just before taking cyclic voltammograms. After the degassing a blanket of nitrogen was kept over the solution. The half-wave potentials ($E_{\frac{1}{2}}$) were taken as that potential lying midway between the oxidation and reduction for a given couple. All experiments were carried out at room temperature (20 °C) and the potentials reported refer to the s.c.e. The cell for the spectroelectrochemical investigation was similar to that reported previously by Lexa *et al.*[4] with a platinum grid working electrode and a platinum wire counter electrode. It was fitted in a Hitachi 556 spectrophotometer.

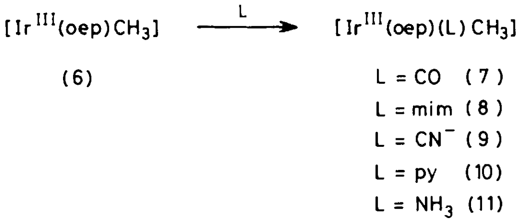
RESULTS AND DISCUSSION

Formation.—A series of carbonyl porphyrin complexes of the type $[Ir^{III}(oep)(CO)X]$ could be obtained as shown in Scheme 1. Thus, by use of anhydrous $AgClO_4$ the axial chloride ion in the starting complex (1) could be replaced by the ClO_4^- ion which was expected to be one of the weakest axial ligands. This ClO_4^- ion could be easily replaced further by various types of ligands without dissociation of the carbonyl group simply by shaking the complex with aqueous solutions of electrolyte. Derivative (4) having the cyanide group which is probably the strongest axial ligand, could also be obtained by this method. On the other hand, a series of methyl derivatives $[Ir^{III}(oep)(L)CH_3]$ were derived from the methyl derivative (6) previously described by Ogoshi *et al.*,[1] according to Scheme 2. Of these, derivatives (7) and (8) were isolated, whereas (9)—(11) were generated *in situ* and submitted to various physicochemical measurements. The above preparative investigation suggests that the total electron-donating ability of the two axial ligands must lie within a certain range in order that the complex should exist in a stable form. This point will be considered later in connection with the redox potentials.



SCHEME 1

Carbonyl Stretching Frequencies and Electronic Absorption Peaks of Iridium Porphyrins.—The results of some of the physicochemical measurements are given in the Table. One of the most characteristic features of the iridium chemistry seems to be the frequent occurrence of carbonyl groups in various complexes, doubtless reflecting general stability of the iridium–carbon bond which often survives replacement of other ligand molecules [complexes (1)—(5), (7); *cf.* preceding section]. The influence of the axial counter ion on the central iridium ion in such complexes may be evaluated by comparison of carbonyl stretching frequencies [ν(CO)]. It is well known that[5] ν(CO) are widely dependent on the strength of π-back donation from the filled metal *d*π-orbitals to empty π*-orbitals of CO. If the counter ion is a good σ-donor the effective electron density on the metal is increased, and the filled *d*π-orbitals would be expected to expand, facilitating overlap between the metal and CO, and thereby reducing ν(CO). The ν(CO) measured in dichloromethane moved to higher wavenumber in the order of anions $CH_3^- < Cl^-, Br^- < CN^- < ClO_4^- < BF_4^-$, as shown in the Table. The order is approximately that of the decreasing σ-donating strength of the anion in conformity with the above argument except in the case of CN^-. The considerably higher values of the cyanide derivative (4) (2 075 cm^{-1}) than those of the halogeno derivatives (2 056—2 057 cm^{-1}) is probably due to the



SCHEME 2

strong π-back donation from the metal to cyanide orbitals. The CN^- will compete with CO for the metal $d\pi$-orbitals, reducing M–CO π-back bonding.

An analogous ordering of the axial ligands, $CH_3^- <$ Cl^-, $Br^- < BF_4^- < ClO_4^- < CN^-$ was observed with the increasing wavenumber of the u.v. (Soret band) and visible (α,β bands) light absorption of these carbonyl porphyrin complexes. This also seems to be accounted for qualitatively, in terms of the different degree of σ-donation. Thus the σ-donation from the axial ligand should destabilize the filled π-orbitals (a_{2u}) from which transition occurs in light absorption by decreasing the degree of the interaction of the latter with the empty $6p$ orbitals of the iridium atom. It is not, therefore, surprising that an approximately linear relationship is observed between the wavenumbers of these absorption maxima and the wavenumbers of the carbonyl stretching frequencies.

Absorption, i.r., ^1H n.m.r. data, and half-wave potentials for tervalent iridium complexes of octaethylporphyrin

Compound	U.v.-visible [a] $\lambda_{max.}$/nm	I.r.[b] ν(CO)/cm^{-1}	^1H N.m.r. [c] δ/p.p.m.				$E_{\frac{1}{2}}$/V *versus* s.c.e.[d]
			meso	α-CH_2	β-CH_3	Axial-CH_3	
(1) $[Ir^{III}(oep)(CO)Cl]$	402 (5.23) 516 (4.16) 547 (4.52)	2 056	10.27	4.14	2.00		+1.18
(2) $[Ir^{III}(oep)(CO)ClO_4]$	393 (4.70) 512 (3.51) 545 (3.86)	2 077	10.46	4.18	1.96		
(3) $[Ir^{III}(oep)(CO)BF_4]$	393 (4.69) 512 (3.52) 545 (3.85)	2 084	10.52	4.20	1.98		+1.33
(4) $[Ir^{III}(oep)(CO)CN]$	388 (4.81) 515 (3.70) 547 (3.90)	2 075	*e*				+1.27
(5) $[Ir^{III}(oep)(CO)Br]$	404 (5.30) 517 (4.21) 549 (4.50)	2 057	*e*				
(6) $[Ir^{III}(oep)CH_3]$	390 (5.18) 499 (4.10) 529 (4.49)		9.70	3.92	1.82	−7.00	+0.68
(7) $[Ir^{III}(oep)(CO)CH_3]$	406 (4.85) 523 (4.02) 554 (4.02)	2 022	9.90	4.02	1.91	−7.84	+0.90
(8) $[Ir^{III}(oep)(mim)CH_3]$	400 (4.84) 506 (3.77) 533 (3.92)		9.56	3.96	1.78	−7.72	+0.56
(9) $[Ir^{III}(oep)(CN)CH_3]^-$	422 (4.7) 522 (3.5) 546 (3.8)		9.24	3.64	1.64	−8.44	$< +0.43$
(10) $[Ir^{III}(oep)(py)CH_3]$	402 (5.0) 506 (3.8) 546 (3.8)		*e*				+0.65
(11) $[Ir^{III}(oep)(NH_3)CH_3]$	398 (5.0) 506 (3.8) 534 (3.9)		*e*				+0.58

[a] In CH_2Cl_2, values in parentheses refer to log ϵ. [b] In CH_2Cl_2. [c] In CD_2Cl_2, $SiMe_4$ as internal standard. [d] In CH_2Cl_2–$[NBu^t{}_4][ClO_4]$. [e] ^1H N.m.r. spectra could not be measured due to its insolubility in CD_2Cl_2.

Within the series having a methyl group, on the other hand, the order of the other axial ligands that cause the increase of wavenumbers of the light absorption is: none $< CN^- < NH_3 <$ mim $<$ py $<$ CO. This order also seems to be that of decreasing σ-donating ability except in the case of ' none ' which means absence of the second axial ligand so that the complex is thought to have a considerably different electronic structure. Here, the cyanide ion, which is considered to be electron withdrawing among the anions, is still regarded as more electron-donating compared with neutral ligands.

Proton N.M.R. Spectra and Cyclic Voltammetry.—Another important criterion for the influence of axial ligands could be obtained from various ^1H n.m.r. parameters such as the chemical shifts of the *meso* protons (*cis*-influence) and the axial methyl protons (*trans*-influence) of the porphyrin ligand (*cf.* Table). The chemical shifts of *meso* protons vary from δ 9.24 for (9) to 10.52 for (3), and those of the axial methyl protons are distributed from −7.00 to −8.44 p.p.m. When the absorption maxima of the Soret band and visible bands are plotted against the chemical shifts of the *meso* protons, we find that a series of carbonyl porphyrin complexes again forms a fairly straight line but that the methyl porphyrin complexes having no carbonyl group make another straight line which is considerably far apart from that formed by the carbonyl complexes (Figure 1). These results seem to indicate that within a series of complexes having similar constitution, the σ-donating ability of the axial ligand is again a dominant factor which effects the chemical shifts of the *meso* protons probably reflecting the effect of the σ-donation to the electron density on the *meso* protons.

The chemical shifts of the methyl protons for $[Ir^{III}(oep)(L)CH_3]$ (L = none, mim, CO, or CN^-) were −7.00, −7.72, −7.84, and −8.44 p.p.m., respectively. Although all of these figures represent abnormally high field shift due to the well known large diamagnetic ring current of the porphyrin ring,[1] their comparison shows that the methyl resonance moved to higher field in the order of compounds: (6) < (8) < (7) < (9). This order is somewhat different from that of the chemical shifts of the *meso* protons. These results indicate that the chemical shifts of *meso* protons and/or axial methyl protons of the iridium complexes cannot be explained on a single basis, and implies possible participation of the change in the bond length, second order Zeeman effects, and direct deshielding by non-bonding electrons of the iridium(III) atom in addition to the σ-donation discussed above. Therefore, it cannot be unequivocally decided from the data discussed above which is the simpler barometer for the change of electron density on the metal, the chemical shifts of *meso* protons or those of the axial methyl protons.

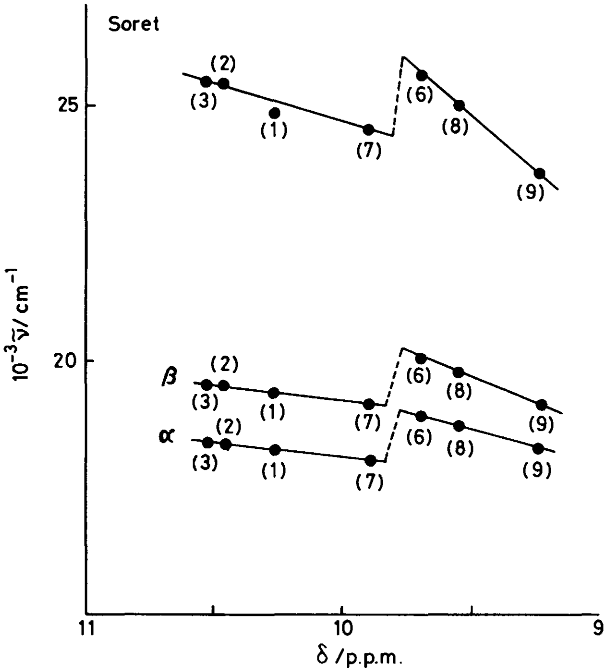


FIGURE 1 The correlation between the wavenumbers of electronic absorption maxima and the chemical shifts of the *meso* protons for compounds [Ir^{III}(oep)(CO)X] [X = Cl (1), ClO$_4$ (2), or BF$_4$ (3)] and [Ir^{III}(oep)(L)CH$_3$] [L = none (6), CO (7), mim (8), or CN (9)]

In order to settle the problem discussed above and evaluate more quantitatively the effect of axial ligands, the redox potentials of the complexes were measured. In spite of many electrochemical investigations of cobalt porphyrins,[6] there has been no report about the electrochemistry of the iridium porphyrins. As seen from the typical cyclic voltammogram obtained with (1), most of the present complexes showed one distinct quasi-reversible redox couple in the range between *ca.* +0.4 and +1.3 V, and an obscure couple appeared in a more negative region (Figure 2). Half-wave potentials of these complexes in the positive region are summarized in the Table. For cobalt complexes, bivalent species are quite stable, and two quasi-reversible redox couples, Co^{I}–Co^{II} and Co^{II}–Co^{III}, are usually observed.[6] On the other hand, bivalent iridium species are scarcely known so far, and tervalent iridium porphyrins are directly reduced to the univalent species by various reductants.[1,3] In order to assign the redox couple at the positive region, a spectroelectrochemical investigation of the reduction of (1) was carried out on a platinum-grid electrode. The reduction at −0.5 V * gave a smooth spectral change as shown in Figure 3. This visible spectrum showed satisfactory coincidence with that of the univalent species [Ir^{I}(oep)]$^-$ chemically generated by the reduction with

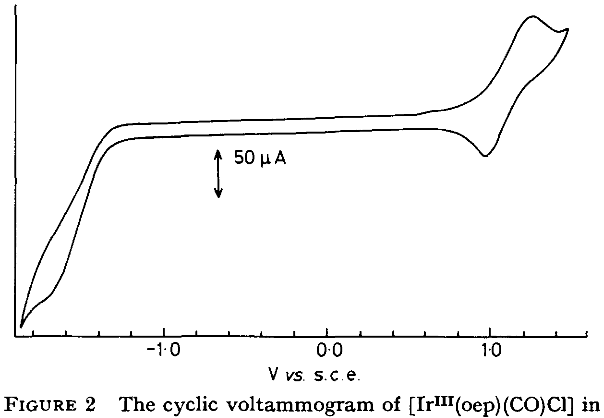


FIGURE 2 The cyclic voltammogram of [Ir^{III}(oep)(CO)Cl] in CH$_2$Cl$_2$

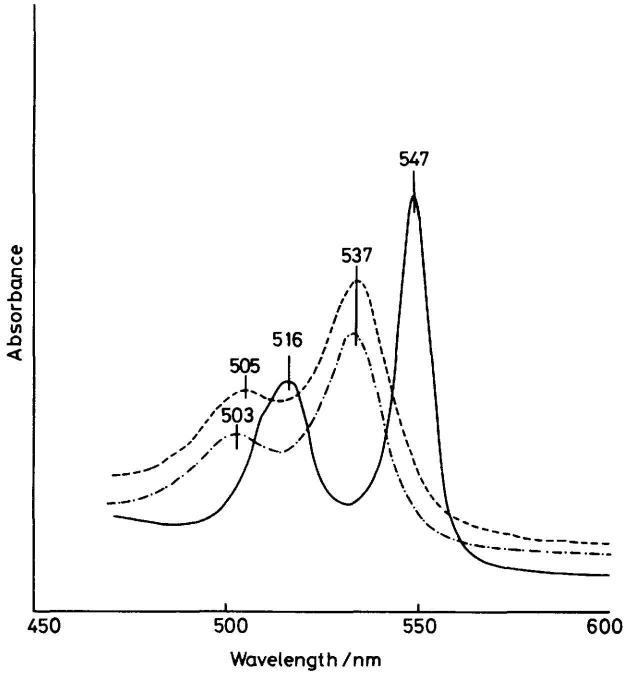


FIGURE 3 Visible spectra of: [Ir^{III}(oep)(CO)Cl] in dichloromethane (——); electrochemically reduced species at −0.5 V (– – – –); and chemically reduced species by NaBH$_4$ (— · — · —)

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* The reduction at +0.5 V gave the same spectral change, but required a long time to complete it.

$NaBH_4$ in ethanol.[1] The number of electrons required for the complete reduction was determined to be *ca.* two by the controlled potential coulometry.* From these results, the redox couple can be unambiguously assigned to the Ir^I–Ir^{III} couple. This kind of single two-electron step for the Ir^I–Ir^{III} redox couple is generally observed for other organometallic compounds such as $[Ir(CO)(R)(PPh_3)_2]$(R = alkyl or aryl).[7] Thus the situation is largely different from that of cobalt complexes having two one-electron steps for Co^I–Co^{II} and Co^{II}–Co^{III}.

The half-wave potentials for the Ir^I–Ir^{III} redox couple are seen to be in the order (9) < (8) < (11) < (10) < (6) < (7) < (1) < (3), which suggests that they assume a more negative value as the axial ligand has stronger σ-donating ability. The oxidation peak of the cyano methyl derivative (9) was observed at +0.43 V, but the corresponding reduction peak was not, probably because the negatively charged species (9) resists the reduction to a more electron rich species $[Ir^I(oep)(CN)CH_3]^{3-}$.

In the foregoing section, it was pointed out that although the ordering of the ^1H n.m.r. chemical shifts of *meso* protons and those of axial methyl protons both reflect the σ-donating ability of the axial ligands, a certain discrepancy was noted between the orderings of these two kinds of chemical shift. When the values of these chemical shifts are plotted against the redox potentials estimated from cyclic voltammetry ($E_{\frac{1}{2}}$), the chemical shifts of the *meso* protons are seen to be in a better parallelism with the redox values (Figure 4). This seems to indicate that the chemical shifts of *meso* protons reflect the electron density of the complex in a more straightforward way than that of the axial methyl protons. This is probably due to the absence of any significant change of bond length of the porphyrin ring due to its high rigidity. On the other hand, the chemical shift of the axial methyl protons would be affected by the change of metal–carbon bond length or other factors in addition to the change of the electron density on the metal atom by the co-ordination of axial ligands.

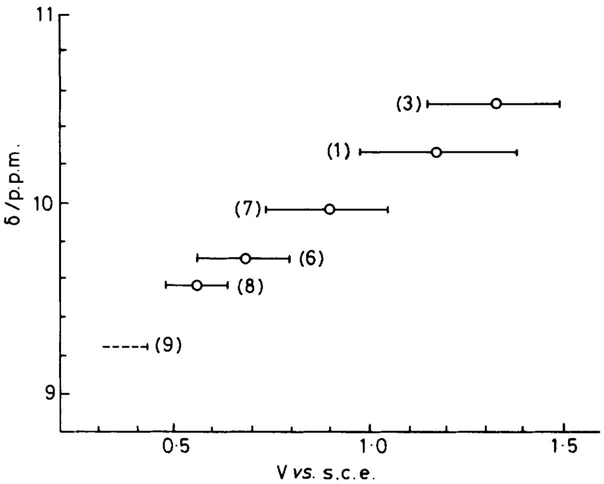

FIGURE 4 The correlation between the half-wave potentials and the chemical shifts of the *meso* protons of compounds $[Ir^{III}(oep)(CO)X]$ [X = Cl (1) or BF_4 (3)] and $[Ir^{III}(oep)(L)CH_3]$ [L = none (6), CO (7), mim (8), or CN (9)]

An influence of the axial ligand on the redox values similar to the above case of Ir^I–Ir^{III} was observed in the Co^{II}–Co^{III} redox potentials of cobalt complexes.[6] For various reasons, however, the series was much less complete. For example, there exists no carbon monoxide adduct of methyl–cobalt porphyrin comparable to the iridium complex, and co-ordination of amine to the methyl–cobalt porphyrin makes the Co^{II}–Co^{III} redox couple irreversible and ambiguous as shown in Figure 5.

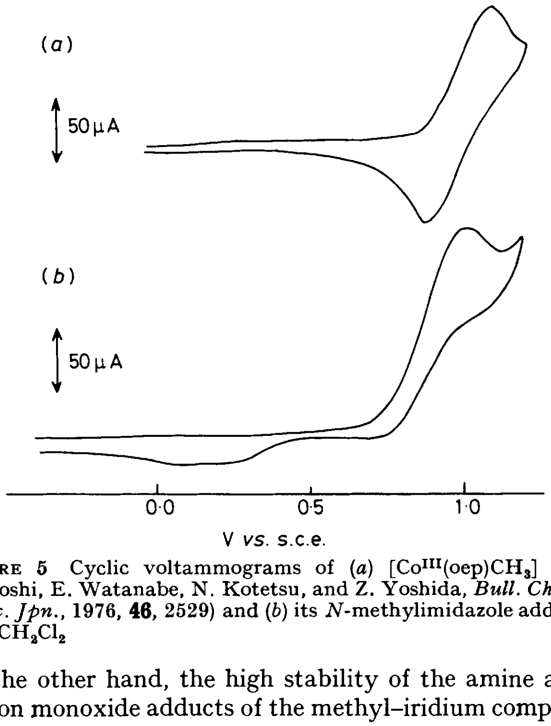

FIGURE 5 Cyclic voltammograms of (*a*) $[Co^{III}(oep)CH_3]$ (H. Ogoshi, E. Watanabe, N. Kotetsu, and Z. Yoshida, *Bull. Chem. Soc. Jpn.*, 1976, **46**, 2529) and (*b*) its *N*-methylimidazole adduct in CH_2Cl_2

On the other hand, the high stability of the amine and carbon monoxide adducts of the methyl–iridium complex enabled us to evaluate the influence of these axial ligands to the central metal, and revealed a straightforward dependence as described above. However, such stability of iridium complexes does not necessarily mean that they are suited as catalysts, because stability in many cases means insensitivity to various reagents. Thus the somewhat unstable and in a sense erratic nature of cobalt porphyrins or related compounds seems to be rather a prerequisite for many such compounds to exhibit biologically versatile catalytic activities.[8]

It may be of some value to make a quantitative estimation of the influence of donation tendency of the axial ligands to the redox potentials. A simple way of doing this would be assigning a certain characteristic quantity to every ligand so that the observed half-wave potentials of an iridium porphyrin may be expressed as the sum of these quantities. The redox values in the Table are thus reproduced fairly well by assuming the following values: CH_3^-, 0.02; Cl^-, 0.30; CN^-, 0.40; BF_4^-, 0.45;

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* Values of *n* were calculated after measuring the total area under current *versus* time curves for complete electrolysis. Reactions were judged to be complete when the current had fallen below 1% of its initial value.

mim, 0.54; NH_3, 0.56, py, 0.63; none, 0.66; and CO, 0.88. It should be noted that these quantities are of a complex nature which is composite of various factors, and are applicable only to octaethylporphyrin complexes of iridium. However, the order at least is seen to reflect the electron donating tendency fairly well. Here the anions are naturally arranged in the order of Hamett σ which is a well accepted measure of the electron-donating or withdrawing tendency of an atom or group which, when bound to a metal, is usually formulated as a negative group. A new significance seems to be that neutral ligands are included in the series. The fact that the cyanide ion which is known to be electron-withdrawing still lies ahead of neutral ligands seems to imply the importance of charge in this situation.

It should be noted that there is a certain limit of the potential of the Ir^{I}–Ir^{III} couple beyond which either the oxidation or the reduction of oep itself occurs. This means that a hypothetical compound having the Ir^{I}–Ir^{III} potentials beyond this limit cannot exist in a stable form, or that two strongly electron-withdrawing or donating groups cannot coexist as axial ligands. Thus the above type of parameters have a possibility of being utilized as a kind of criterion in predicting the stability of members of a series of compounds.

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