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SYNTHESES AND REACTIONS OF IRIDIUM COMPLEXES OF OCTAETHYLPORPHYRIN

HISANOBU OGOSHI*, JUN-ICHIRO SETSUNE and ZEN-ICHI YOSHIDA*
Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Kyoto 606 (Japan)

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Summary

New iridium porphyrin complexes (I-V) have been prepared by the reactions of octaethylporphyrin ($OEPH_2$) or N-methyloctaethylporphyrin (N-Me·OEP-H) with μ-dichloro-hexacarbonyl-diiridium(I) ($[Ir(CO)_3Cl]_2$) or μ-dichloro-bis[π-cyclooctadiene-(1,5)]-diiridium(I) ($[Ir(COD)Cl]_2$). Hydrido- and organo-iridium(III)OEP complexes (VI-XII) have been synthesized by various methods and characterized on the basis of spectroscopic measurements.

Introduction

Recently, new methods have been developed to prepare second- and third-row transition metal complexes of porphyrins [1,2]. Among the group VIII metals, ruthenium [3-6], osmium [7-9], rhodium [10-16] and iridium [10] porphyrins have been synthesized and the axial coordination and redox chemistry of these metalloporphyrins have been shown to be very different from those of iron and cobalt porphyrins. No report on iridium porphyrins has been made since Fleischer and Sadasivan obtained iridium(III) porphyrin by the reaction of meso-porphyrin IX dimethyl ester with $Ir(CO)_3Cl$ or $Ir(cyclooctene)_2(CO)Cl$ [10]. The formation of the porphyrin·Ir(III) has been assumed to proceed *via* the mono-valent iridium complex, [porphyrin·IrCl(CO)], which has not been isolated as yet. Recently we have isolated new rhodium(I) porphyrins, μ-OEP$[Rh(CO)_2]_2$ and N-Me·OEPH$[Rh(CO)_2Cl]_2$, by treatment of porphyrins with $[Rh(CO_2Cl]_2$ [15,16]. Organo-cobalt and -rhodium compoexes of square planar ligands have been prepared as mimetic compounds of coenzyme vitamin B_{12} [16-22]. However, investigation for iridium analogues has not been developed due to difficulty in incorporation of the metal and the high resistance to reduction of the Ir^{III} compoex to the Ir^{I} complex [17]. In this paper, we report facile synthetic methods to obtain the tri- and mono-valent iridium porphyrins. The syntheses and spectroscopic proper-

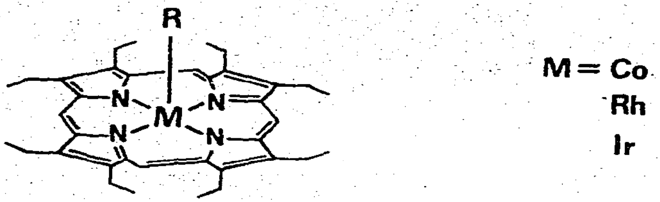


Fig. 1. Organometal(III) octaethylporphyrins

ties of organoiridium(III)OEP compoexes will be discussed in comparison with the corresponding cobalt [20] and rhodium [15] porphyrin complexes.

Results and discussion

New iridium(I) porphyrin complexes

Iridium porphyrin compoexes (I–V) have been generated through the reaction of $OEPH_2$ or N-Me·OEPH with $[Ir(CO)_3Cl]_2$ or $[Ir(COD)Cl]_2$ as summarized in Scheme 1. When iridium carbonyl chloride was used as a metal source, unusual bimetallic mononuclear iridium porphyrins, μ-OEP$[Ir(CO)_3]_2$ (I) and N-Me·OEPH$[Ir(CO)_3Cl]_2$ (IV), were obtained. Unusual metalloporphyrins have been prepared from metal carbonyls and porphyrins and their structures have been elucidated by single crystal X-ray diffraction analyses [24–26]. A crystallographic study of μ-octaethylporphyrinato-bis[dicarbonylrhodium(I)] shows coordination of the porphyrin ligand to two rhodium(I) atoms above and below the macrocyclic plane. Each d^8 rhodium(I) ion is in square planar coordination consisting of two adjacent nitrogens of porphyrin and two carbonyl carbons [24]. In unusual Re^I and Tc^I porphyrin complexes, porphyrin $[M(CO)_3]_2$, two d^6 metal ions have been found to be located in a distorted octahedral coordination of three nitrogens of porphyrin and three carbonyl carbons [25,26] (See Figure 2.). The ir and visible spectrum of (I) are closely akin to those of μ-OEP$[Rh^I(CO)_2]$ (Table 1.). This indicates that the complex (I) has a similar molecular structure to that

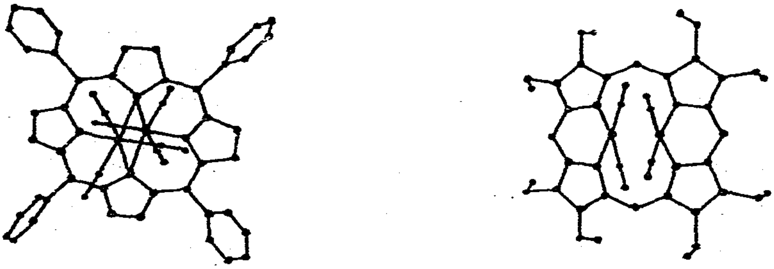


Fig. 2. Structures of μ-TPP$[Re^I(CO)_3]_2$ [25] (left) and μ-OEP$[Rh^I(CO)_2]_2$ [24] (right) determined by X-ray analyses.

of the rhodium complex. There is a slight difference between (I) and the bimetallic porphyrin complexes hitherto reported. No centrosymmetry of (I) is evidenced by existence of six carbonyl absorption bands in the ir spectrum and the splitting of proton signals of peripheral four meso protons and eight ethyl protons of octaethylporphyrinato ligand in the pmr spectrum. The coordination of three carbonyl groups to each iridium ion probably reduces the molecular symmetry.

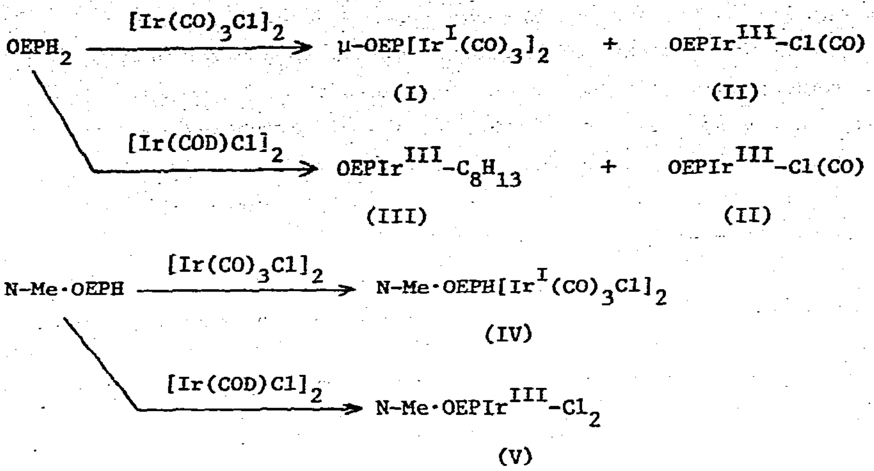
Table 1. Visible spectra of unusual Rh^{I} and Ir^{I} porphyrins.[a]

	$\lambda_{max}(\log\varepsilon)$					
μ-OEP$[Rh(CO)_2]_2$[b]		367 (4.82)	444 (4.59)	516 (4.14)	590 (3.70)	
μ-OEP$[Ir(CO)_3]_2$[c]	350 (sh)	388 (4.92)	445 (4.55)	530 (4.06)		
N-Me•OEPH$[Rh(CO)_2Cl]_2$[d]	398 (4.56)	430 (4.48)	555 (3.70)	570 (3.78)	595 (3.75)	617 (3.54)
N-Me•OEPH$[Ir(CO)_3Cl]_2$[c]	399 (4.71)	428 (4.51)	550 (3.64)	567 (3.79)	599 (3.64)	615 (3.56)

a) measured in $CHCl_3$ in nm unit. b) reference 16. c) this work.
d) reference 15.

The formation of the complex (IV) and (V) is much faster than that of the complex (I). The rate enhancement is probably caused by the distortion of the porphyrin ring due to the N-alkylation of pyrrolic N-H bond [27-29]. The spectroscopic properties of N-Me•OEPH$[Ir(CO)_3Cl]_2$ (IV) are similar to those of N-Me•OEPH$[Rh(CO)_2Cl]_2$ [15]. The pmr spectrum shows four separated singlets for the meso protons and eight resolved triplets for the methyl protons of peripheral ethyl groups. Complex (IV) is considered to have a structure analogous to that of the rhodium(I) complex, where two metal ions of metal carbonyl chloride dimer are bonded to the two adjacent nitrogens of the porphyrinato core. When $[Ir(COD)Cl]_2$ was used as a metal source, no mono-valent iridium porphyrin was formed. A new type of complex, N-Me•OEPIr^{III}-Cl_2 (V), was isolated from the reaction of N-Me•OEPH instead. In complex (V), a tri-valent iridium ion seems to be ligated by two chloride ions in the axial coordination sites because chloride ion could not be exchanged by the other anion such as ClO_4^-.

The monitoring of the reaction of $OEPH_2$ and $[Ir(CO)_3Cl]_2$ by TLC showed that the brownish compound (I) generated at an earlier stage was converted to the reddish compound, OEPIr^{III}-Cl(CO) (II), as is seen in the case of μ-OEP$[Rh(CO)_2]_2$ [16]. Indeed, the complex (I) was obtained as a main product under milder reaction conditions. In contrast to the rhodium porphyrin complex (II) has a carbonyl group as the sixth ligand. OEPIr^{III}-Cl(CO) (II) was afforded in moderate yield when the mixture of $OEPH_2$ and



Scheme 1. Formation of iridium porphyrins

$[Ir(COD)Cl]_2$ was refluxed in xylene. Although the detailed reaction pathway is not known, the carbonyl group is probably derived from the coordinated cyclooctadiene. It is suggested that low-valent metal complexes catalyze the oxidation of olefins to aldehydes *via* intermediate formation of dioxetane [30,31], resulted in the liberation of carbonmonoxide from aldehyde [32,33]. Therefore, a similar scheme may occur in the formation of (II). No low-valent unusual metalloporphyrin has been detected even under milder reaction conditions. An organoiridium(III)OEP (III) was isolated as a minor product. Axial coordination of C_8 ring system to the trivalent iridium was confirmed by the nmr spectrum and microanalysis, but its precise structure and the mechanism of its axial ligation are still not clear.

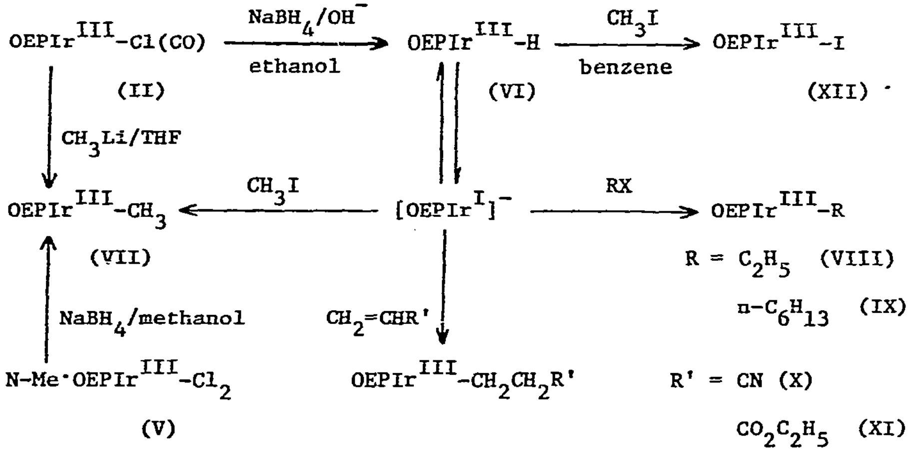
Hydridoiridium(III)OEP and organoiridium(III)OEP complexes

Although many mono- and tri-valent organoiridium complexes are known, no alkyliridium complex has been reported hitherto for square planar macrocyclic systems. Schrauzer reported that treatment of chlorobis-dimethylglyoximatoiridium, $(DMG)_2Ir^{III}$-Cl·HCl, with a reducing agent, followed by the addition of an alkyl halide gave trace amounte of alkyliridoximes [17]. When the complex (II) was treated with $NaBH_4$ in ethanol, hydrido-iridium(III)OEP (VI) was generated. The formation of a covalent Ir-H bond has been confirmed by the absorption at 2330 cm^{-1} in the ir and the signal at δ -40.27 in the pmr spectrum. The proton signals of transition metal hydrides usually appear at high field. In addition, the hydride is subjected to the strong diamagnetic ring current of the porphyrin macrocycle. If deviation of the hydrogen atom from the porphyrin plane is about 2 Å, the up-field shift due to the ring current is expected to be more than 10 ppm [16]. Addition of alkyl halides to (VI) in basic alcoholic solution under argon resulted in the formations of alkyliridium(III)OEP complexes in high yield. The reactions with olefins substituted with electron-withdrawing groups gave β-substituted ethyliridium(III)OEP complexes (X) and (XI).

Hydridocobaloxime liberates its hydrogen as a proton to form an anionic complex through the acid-base equilibrium. The reaction of the anionic

$$(L)_nM^{III}\text{-}H \rightleftharpoons [(L)_nM^{I}]^- + H^+$$

species with ethyl acrylate proceeds through a Michael-Type addition to give the β-substituted ethylcobaloxime, while the hydrido species affords the α-substituted ethylcobaloxime [17,34]. Treatment of complex (VI) with ethyl acrylate in benzene did not give any organoiridium complexes. The addition of methyl iodide to a benzene solution of (VI) did not afford $OEPIr^{III}\text{-}CH_3$ but $OEPIr^{III}\text{-}I$, whereas the hydridocobalt and hydridorhodium complexes have been reported to give alkylmetal complexes in their reactions with alkyl halides [34]. These facts suggest that a small amount of an anionic mono-valent iridium complex, $[OEPIr^{I}]^-$, generated in basic alcoholic medium, reacts as a nucleophile with alkyl halide. We have found that hydridorhodium(III)OEP suspended in ethanol can be dissolved readily by the addition of 1N NaOH solution, and the formation of octaethylporphyrinatorhodium(I) anion is confirmed by the visible spectrum change [16,35]. However, complex (VI) showed extremely low solubility in basic alcoholic solution, probably due to the higher pKa value of $OEPIr^{III}\text{-}H$ than that of $OEPRh^{III}\text{-}H$.

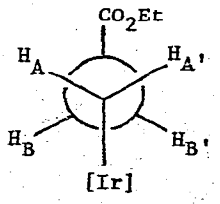


Scheme 2. The reactions of iridium porphyrin complexes

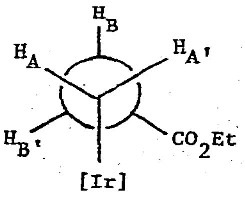
When N-Me·OEPIr^{III}–Cl_2 (V) was treated with $NaBH_4$ in ethanol, a methyl migration from nitrogen to iridium took place to form OEPIr^{III}–CH_3 (VII). The reaction seems to proceed via an intramolecular oxidative addition of the N–CH_3 bond to the Ir^{I} ion of N-Me·OEPIr^{I}. This reaction seems to be initiated by the reduction of (V) to the monovalent complex. Similar trends have been found for the cobalt and rhodium complex as have been described in our previous reports [15,36].

Spectroscopic properties of organoiridium(III)OEP complexes

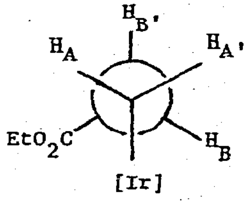
The chemical shifts in the pmr spectra of methyl- (VII), ethyl- (VIII), and β-ethoxycarbonylethyl-iridium(III)OEP (XI) are compared with those of the corresponding cobalt- and rhodium-OEP complexes in Table 2. The protons of the methyl or methylene groups bonded directly to the metals resonate at lower magnetic fields as with electronegativity of the metal increases. The positions of the chemical shifts of the aromatic meso protons of the organoiridium porphyrins are at higher magnetic field by about 0.3 ppm than those of the corresponding cobalt and rhodium porphyrins. This fact can be interpreted in terms of changes in the π-back donation of electrons from the central metal ion to the porphyrin ring. Figure 3. demonstrates the pmr signals of the axially coordinated ethylene group of the OEPIr^{III}–$CH_2CH_2CO_2CH_3$. This spectrum is analyzed as an AA'BB' pattern. In the presence of a stoichiometric excess of pyridine, the line shapes and chemical shifts of these signals changed owing to the coordination of pyridine as the sixth ligand. The up-field shift of the methylene protons directly bonded to iridium can be ascribed to the trans influence of the coordinated pyridine. It is reported that the pattern in the AA'BB' spectrum becomes simpler, as the difference of the vicinal coupling constants, J_{AB} and $J_{AB'}$, is smaller [37,39]. Coordination of a pyridine molecule causes a larger difference between J_{AB} and $J_{AB'}$. Therefore the population of the trans conformer (A) is preferable to those of the gauche conformers (B) and (C). This phenomenon can be interpreted in terms of the increase in the steric interaction between the ethoxycarbonyl group and the porphyrin ligand caused by the shortening of the Ir–C bond on coordination of pyridine or the change in the degree of displacement of iridium from porphyrin plane accompanied by the structural change from five to six coordination [40,41].



(A)



(B)



(C)

Table 2. Pmr data of organometal porphyrins, OEPM^{III}-R[a]

	Ir[b]			Rh[c]			Co[d]		
	equatorial ligand								
R	=CH-	$-CH_2-$	$-CH_3$	=CH-	$-CH_2-$	$-CH_3$	=CH-	$-CH_2-$	$-CH_3$
$-CH_3$	9.55	3.87	1.83	9.94	4.01	1.90	10.08	4.00	1.88
$-C_2H_5$	9.64	3.95	1.86	9.97	4.03	1.40	10.00	4.00	1.89
$-CH_2CH_2R'$[e]	9.73	3.88	1.83	9.94	43.99	1.88	10.01	4.00	1.87

	axial ligand					
	H_α[f]	H_β	H_α	H_β	H_α	H_β
$-CH_3$	-6.97		-6.47		-5.20	
$-C_2H_5$	-6.13	-5.18	-5.55	-4.95	-4.08	-5.47
$-CH_2CH_2R'$	-5.88	-4.16	-5.52	-4.14	-2.7 ∿ 6.7[g]	-4.22

a) δ-value in $CDCl_3$ using TMS as an internal reference. b) this work. c) reference 16. d) reference 20. e) R'= $CO_2C_2H_5$ for Ir and Co, CO_2CH_3 for Rh. f) H_α(H_β) is the proton attached to the carbon of α(β)-position with respect to the metal. g) very broad absorption.

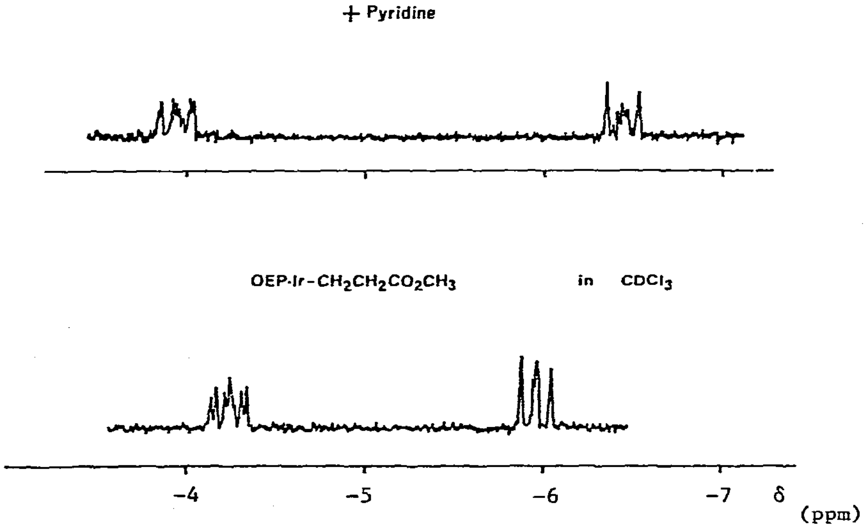


Fig. 3. Pmr spectra of the $-CH_2CH_2-$ group of OEPIr^{III}-$CH_2CH_2CO_2CH_3$ (bottom) and its pyridine adduct (top).

Experimental

Infrared, proton nmr and visible spectra were recorded on a Hitachi EPI-G31 grating spectrophotometer, a Varian HA-100 spectrometer and a Hitachi EPS-3T recording spectrophotometer respectively. Octaethylporphyrin was prepared according to the method of Inhoffen, et al [23].

μ-OEP[$Ir^{I}(CO)_3]_2$ (I) and OEPIr^{III}-Cl(CO) (II)

A mixture of 300 mg (0.482 m mol) of $[Ir(CO)_3Cl]_2$ and 350 mg (0.653 m mol) of $OEPH_2$ was suspended in 700 ml of xylene and refluxed for 15 hr. After removal of the solvent under reduced pressure, the residue was chromatographed on silica gel (Wakogel C-200). The first eluate with benzene afforded 18 mg of brownish red crystals of μ-OEP$[Ir^{I}(CO)_3]_2$ (I) (3.5 % yield based on $OEPH_2$): ir(KBr) 2110, 2050, 2025, 2020, 1965 and 1935 cm^{-1} ν(C≡O); pmr $\delta(CDCl_3)$ 10.44, 10.36, 10.16 and 9.89(s, 4H, $=C\underline{H}-$), 4.05(m, 16H, $-C\underline{H}_2-CH_3$) and 1.90, 1.80, 1.77 and 1.69(t, 24H, $-CH_2C\underline{H}_3$); vis($CHCl_3$) λ_{max}(logε) 350(4.63), 388(4.92), 445(4.55), 520(4.05) and 548 nm(4.08). Anal. Calcd for $C_{42}H_{44}N_4O_6Ir_2$: C, 46.48; H, 4.09; N, 5.16; Cl, 0.00. Found: C, 47.50; H, 4.39; N, 5.56; Cl, 0.00. The second fraction eluted with benzene-acetone (3 : 1) gave violet crystals. Recrystallization of the crude crystals from $CH_2Cl_2-CH_3OH$ gave 132 mg of OEPIr^{III}-Cl(CO) (II) (35 % yield): ir(KBr) 2050 cm^{-1} ν(C≡O); pmr $\delta(CDCl_3)$ 10.27(s, 4H, $=C\underline{H}-$), 4.14(q, 16H, $-C\underline{H}_2CH_3$) and 2.00(t, 24H, $-CH_2C\underline{H}_3$); vis($CHCl_3$) λ_{max}(logε) 402(5.23), 516(4.16) and 547 nm(4.52). Anal. Calcd for $C_{37}H_{44}N_4OClIr\cdot(1/2)CH\ Cl$: C, 54.21; H, 5.34; N, 6.74; Cl, 8.53. Found: C, 53.90; H, 5.60; N, 6.70; Cl, 8.89.

When 750 mg of $[Ir(COD)Cl]_2$ and 544 mg of $OEPH_2$ were refluxed in xylene for 12 hr, complex (II) was isolated in 52 % yield. The organoiridium complex, OEPIr^{III}-C_8H_{13} (III), also was isolated in 5 % yield as the first eluate with benzene from the silica gel column chromatography of the reaction residue: pmr $\delta(C_6D_6)$ 9.79(s, 4H, $=C\underline{H}-$), 3.88(q, 16H, $-C\underline{H}_2CH_3$), 1.86(t, 4H, $-CH_2C\underline{H}_3$) and 0 ∿ -6.5(broad m, 13H, Ir-$C_8\underline{H}_{13}$); vis($CHCl_3$) λ_{max}(logε) 383(5.10), 388(5.17), 498(4.10) and 529 nm(4.55). Anal. Calcd for $C_{44}H_{57}N_4Ir$: C, 63.35; H, 6.89; N, 6.72. Found: C, 63.55; H, 6.78; N, 6.74.

N-Me·OEPH$[Ir^{I}(CO)_3Cl]_2$ (IV) and N-Me·OEPIr^{III}-Cl_2 (V)

A new mono-valent iridium complex (IV) was prepared by stirring a benzene solution of N-Me·OEPH (46 mg) and $[Ir(CO)_3Cl]_2$ (70 mg) at 55°C for 5 hr. The solution was concentrated under reduced pressure. Recrystallization from petroleum ether - benzene (1 : 2) afforded 46 mg of violet crystals (IV) (47 %): ir(KBr) 2070, 2040, 1996 and 1960 cm^{-1} ν(C≡O); pmr $\delta(CDCl_3)$ 10.56, 10.46, 10.45 and 10.21(s, 4H, $=C\underline{H}-$), 4.4 ∿ 3.8(m, 16H, $-C\underline{H}_2CH_3$), 1.95, 1.93, 1.87, 1.83, 1.83, 1.76, 1.74 and 1.73(t, 24H, $-CH_2C\underline{H}_3$), -3.23

(s, 1H, N-$\underline{H}$) and -6.00(s, 3H, N-C$\underline{H}_3$); vis($CHCl_3$) λ_{max}(logε) 399(4.71), 428(4.51), 550(3.64), 567(3.79), 599(3.64) and 615 nm(3.56). Anal. Calcd for $C_{43}H_{48}N_4O_6Cl_2Ir_2$: C, 44.06; H, 4.13; N, 4.77; Cl, 5.95. Found: C, 43.57; H, 4.15; N, 4.78; Cl, 6.05.

A monometallic porphyrin (V) was isolated from the reaction of N-Me·OEPH and $[Ir(COD)Cl]_2$ in CH_2Cl_2 at room temperature for 8 hr. The solvent was removed and the resulting residue was chromatographed on silica gel with $CHCl_3$. The eluate afforded dark crystals of N-Me·OEPIr^{III}-Cl_2 (V) by recrystallization from benzene - n-hexane (1 : 3) (24 % yield): pmr δ($CDCl_3$) 10.13(s, 2H, =C$\underline{H}$-), 10.08(s, 2H, =C$\underline{H}$-), 3.96(m, 16H, -C$\underline{H}_2$CH$_3$), 1.93(t, 12H, -CH$_2$C$\underline{H}_3$), 1.86(t, 6H, -CH$_2$C$\underline{H}_3$), 1.77(t, 6H, -CH$_2$C$\underline{H}_3$) and -1.98(s, 3H, N-C$\underline{H}_3$); vis(C_6H_6) λ_{max}(logε) 416(5.20), 514(3.97), 549(3.97) and 585 nm (3.97). Anal. Calcd for $C_{37}H_{47}N_4Cl_2Ir$: C, 54.80; H, 5.84; N, 6.91; Cl, 8.74. Found: C, 54.82; H, 5.91; N, 6.96; Cl, 8.44.

OEPIr^{III}-CH$_3$ (VII)

(A) To 9.5 mg of N-Me·OEPIr^{III}-Cl_2 in 15 ml of ethanol was added 6 mg of $NaBH_4$ in 1 ml of 0.5*N* NaOH solution under argon. A red precipitate was formed when the dark brown reaction mixture was stirred for 2 hr at 50°C. Chloroform was added to the solution. The organic layer was washed with water, dried over Na_2SO_4 and concentrated under reduced pressure. The resulting residue was chromatographed on silica gel. The first eluate with benzene afforded 6 mg of OEPIr^{III}-CH$_3$ (72 %).

(B) Ten times molar amounts of methyllithium in dry THF was added to a THF solution of OEPIr^{III}-Cl(CO) (II). The progress of the reaction was monitored by the thin layer chromatography (Merck Kiesilgel 60 F_{254}). After it had been refluxed for 5 hr, the reaction mixture was poured into water and extracted with benzene. OEPIr^{III}-CH$_3$ (VII) was obtained in 25 % yield.

OEPIr^{III}-H (VI)

Complex (II) (111 mg), suspended in 45 ml of ethanol, was treated with 40 mg of $NaBH_4$ in 2 ml of aqueous 1*N* NaOH solution for 1 hr at 50°C under argon. An amorphous red precipitate was formed. After adding 30 ml of 0.1*N* HCl, the precipitate was collected by filtration and washed with water and then with methanol. The hydrido complex, OEPIr^{III}-H (VI), was dried over P_2O_5 under vacuum at 80°C (86 % yield): ir(KBr) 2330 cm^{-1} ν(IrH); pmr δ(C_6D_6) 9.85(s, 4H, =C$\underline{H}$-), 3.90(q, 16H, -C$\underline{H}_2$CH$_3$), 1.86(t, 24H, -CH$_2$C$\underline{H}_3$) and -40.27(s, 1H, Ir-$\underline{H}$); vis(C_6H_6) λ_{max}(logε) 393(5.23), 502(4.15) and 531 nm(4.51). Anal. Calcd for $C_{36}H_{45}N_4Ir$: C, 59.56; H, 6.25; N, 7.72. Found: C, 59.85; H, 6.23; N, 7.78.

OEPIr^{III}-R (R = CH_3 (VII), C_2H_5 (VIII), n-C_6H_{13} (IX))

To an ethanol suspension of 37 mg of (II), $NaBH_4$ (7 mg) in 1 ml of aqueous 1*N* NaOH was added under argon. The reaction mixture was stirred for 1 hr at 50°C. Methyl iodide was added to this solution containing the hydridoiridium complex (VI). The solution was stirred for 5 hr at ambient temperature. Benzene was added to the reaction mixture. The benzene extract was washed with water and dried over anhydrous Na_2SO_4. Purification by preparative TLC gave 25 mg of OEPIr^{III}-CH_3 (VII) in 72 % yield. Complex (VII) has the following properties which were coincident with those of the complex prepared through the other two methods as described before: ir(KBr) 1227 cm^{-1} deformation of CH_3; pmr δ($CDCl_3$) 9.55(s, 4H, $=C\underline{H}-$), 3.87(q, 16H, $-C\underline{H}_2CH_3$), 1.83(t, 24H, $-CH_2C\underline{H}_3$) and -6.97(s, 3H, $Ir-C\underline{H}_3$); vis($CHCl_3$) λ_{max}-(logε) 389(5.18), 501(4.10) and 529 nm(4.49). Anal. Calcd for $C_{37}H_{47}N_4Ir$: C, 60.05; H, 6.40; N, 7.57. Found: C, 59.31; H, 6.40; N, 7.57.

OEPIr^{III}-C_2H_5 (VIII) and OEPIr^{III}-n-C_6H_{13} (IX) were prepared by using ethyl iodide and n-hexyl bromide in yields of 85 % and 67 %, respectively, using the procedure described above. The pmr spectrum of (VIII) shows ($CDCl_3$): δ 9.64(s, 4H, $=C\underline{H}-$), 3.95(q, 16H, $-C\underline{H}_2CH_3$), 1.86(t, 24H, $-CH_2C\underline{H}_3$), -5.17 (t, 3H, $Ir-CH_2C\underline{H}_3$) and -6.12(q, 2H, $Ir-CH_2CH_3$). Vis($CHCl_3$) λ_{max}(logε) 388(5.24), 500(4.24) and 530 nm(4.48). Anal. Calcd for $C_{38}H_{49}N_4Ir$: C, 60.52; H, 6.55; N, 7.43. Found: C, 59.95; H, 6.41; N, 6.92. The complex (IX) shows signals in the pmr at δ(C_5D_5N) 9.94(s, 4H, $=C\underline{H}-$), 3.97(q, 16H, $-C\underline{H}_2CH_3$), 1.90(t, 24H, $-CH_2C\underline{H}_3$), -0.01(m, 5H, $Ir-(CH_2)_4C_2\underline{H}_5$), -0.63(m, 2H, $Ir-(CH_2)_3C\underline{H}_2-$), -1.72(m, 2H, $Ir-(CH_2)_2C\underline{H}_2-$), -4.41(m, 2H, $Ir-CH_2C\underline{H}_2-$) and -6.32(m, 2H, $Ir-C\underline{H}_2-$). Vis(C_6H_6) λ_{max}(logε) 391(5.32), 500(4.26) and 530 nm(4.54). Anal. Calcd for $C_{42}H_{57}N_4Ir$: C, 62.27; H, 7.09; N, 6.92. Found: C, 61.78; H, 7.33; N, 6.82.

OEPIr^{III}-CH_2CH_2R (R = CN (X), $CO_2C_2H_5$

The complexes (X) and (XI) were obtained from the reaction of acrylonitrile and ethyl acrylate with iridium porphyrin reduced by $NaBH_4$ in yields of 53 % and 83 %, respectively. The pmr of (X) shows: τ(C_5D_5N) 10.11(s, 4H, $=C\underline{H}-$), 4.06(q, 16H, $-C\underline{H}_2CH_3$), 1.96(t, 24H, $-CH_2C\underline{H}_3$), -3.72(m, 2H, $-C\underline{H}_2CN$) and -5.94(m, 2H, $Ir-C\underline{H}_2-$). The C≡N stretching vibration appeared at 2230 cm^{-1} in the ir spectrum. Vis($CHCl_3$) λ_{max}(logε) 390(5.26), 500(4.12) and 531 nm(4.50). Anal. Calcd for $C_{39}H_{48}N_5Ir$: C, 60.12; H, 6.21; N, 8.99. Found: C, 60.30; H, 6.21; N, 8.87. In the pmr of (XI) in $CDCl_3$, the signals appear at δ 9.73(s, 4H, $=C\underline{H}-$), 3.96(q, 16H, $-C\underline{H}_2CH_3$), 2.83(q, 2H, $-)C\underline{H}_2CH_3$), 1.87(t, 24H, $-CH_2C\underline{H}_3$), 0.34(t, 3H, $-OCH_2CH_3$), -4.16(m, 2H, $Ir-CH_2C\underline{H}_2-$) and -5.88(m, 2H, $Ir-C\underline{H}_2-$). The ir spectrum shows ν(C=O) at 1720 cm^{-1}. Vis(C_6H_6) λ_{max}(logε) 391(5.26), 500(4.04) and 530 nm(4.49). Anal. Calcd for $C_{41}H_{53}N_4O_2Ir$: C, 59.61; H, 6.47; N, 6.78. Found: C, 60.44; H, 6.49; N, 6.82.

OEPIr^{III}-I (XII)

To 22 mg of OEPIr^{III}-H (VI) in 12 ml of dry benzene under argon was added methyl iodide (0.2 ml). After it had been stirred for 15 hr at room temperature, the solution was concentrated and chromatographed on a silica gel column. The eluate with $CHCl_3$ was evaporated and the residue was recrystallized to give 16 mg of OEPIr^{III}-I (XII) in 62 % yield: pmr δ($CDCl_3$) 10.21(s, 4H, =$C\underline{H}$-), 4.13(q, 16H, -$C\underline{H}_2CH_3$) and 1.94(t, 24H, -$CH_2C\underline{H}_3$); vis ($CHCl_3$) λ_{max}(logε) 396(5.22), 512(4.13) and 541 nm(4.39). Anal. Calcd for $C_{36}H_{44}N_4IIr$: C, 50.76; H, 5.21; N, 6.58; I, 14.90. Found: C, 50.21; H, 5.76; N, 6.40; I, 14.56.

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