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Synthesis and Crystal Structure of (2,7,12,17-Tetrapropylporphycenato)bis-[tricarbonylrhenium(I)]

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Introduction

Since the first synthesis of porphycene[1] in 1986, the chemistry of metalloporphycenes[2] has attracted our interest. Studies by Vogel and co-workers[1,2] showed that the cavity of a porphycene is smaller than that of a porphyrin and is rectangular in shape. This would suggest that the reactivities of metalloporphycenes, especially those containing large metal ions, could be quite different from those of their porphyrin counterparts. We have reported that the relatively large Os(II) and Ru(II) ion can be accommodated in the "small" cavity of 2,7,12,17-tetrapropylporphycene.[3] Herein are described the preparation and crystal structure of the first Re(I) porphycene complex.

Experimental Section

Reagent and Materials. $Re_2(CO)_{10}$ was purchased from Strem Chemicals Inc. 2,7,12,17-Tetrapropylporphycene was prepared by the literature method.[4] All other chemicals were reagent grade and were used as received.

Synthesis of (2,7,12,17-Tetrapropylporphycenato)bis[tricarbonylrhenium(I)], (TPrPc)[Re(CO)$_3$]$_2$. A solution of 2,7,12,17-tetrapropylporphycene (32 mg) and $Re_2(CO)_{10}$ (80 mg) in decalin (10 mL) was refluxed with stirring under a nitrogen atmosphere for 30 min. The solution slowly changed from purple-red to green. Decalin was then distilled off under reduced pressure, the residue was redissolved in chloroform (3 mL), and the solution was chromatographed on a silica gel column using toluene as eluent. The green band was collected and concentrated to ca. 3 mL. Addition of *n*-hexane precipitated the product as a deep green solid (yield: 83%). Green needle crystals were obtained by slow evaporation of a 1:1 dichloromethane−*n*-hexane solution the complex. Anal. Calcd for $Re_2C_{38}H_{36}N_4O_6$: C, 44.87; H, 3.57; N, 5.51. Found: C, 44.77; H, 3.59; N, 5.49. IR (KBr pellet): ν_{CO} 1892, 1908, and 2018 cm^{-1}. UV−visible ($CHCl_3$) [λ_{max}/nm (log ϵ)]: 350 (4.26) sh, 385 (4.61), 411 (4.04) sh, 532 (3.84) sh, 618 (3.97). ^{1}H NMR (270 MHz, $CDCl_3$): δ 10.13 (s, H-9,10,19,20, 4H), 9.50 (s, H-3,6,13,16, 4H), 4.17(t, α-CH_2, 8H), 2.41 (m, β-CH_2, 8H), 1.38 (m, CH_3, 12H).

Physical Measurement. ^{1}H NMR spectra were recorded on a JEOL JNM-GSX 270 FT NMR spectrometer (270 MHz), and the chemical shifts (δ ppm) were reported relative to tetramethylsilane (TMS). UV−visible spectra were recorded on a Milton Roy Spectronic 3000 diode array spectrophotometer. Infrared spectra were obtained as KBr pellets on a Nicolet 20 SXC FT-IR spectrometer. Cyclic voltammetry was performed with a Princeton Applied Research Model 273A potentiostat and an X-Y recorder.

Table 1. Crystallographic Data for (TPrPc)[Re(CO)$_3$]$_2$

mol formula	$Re_2C_{38}H_{36}N_4O_6$
M_r	1017.13
space group	monoclinic $P2_1/c$
a/Å	8.598(4)
b/Å	18.554(4)
c/Å	22.463(9)
β/deg	94.69(4)
V/Å^3	3571(2)
Z	4
D_{calcd} (g cm^{-3})	1.892
μ/cm^{-1}	36.3
λ(Mo Kα)/Å	0.7107
R[a]	0.054
R_w[b]	0.049
goodness-of-fit	2.33
temp/K	298
F(000)	1412

[a] $R = \sum|F_o| - |F_c|/\sum|F_o|$. [b] $R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$.

X-ray Structure Determinations. Intensity data were collected at room temperature on an Enraf-Nonius diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.7107 Å). The dimensions of the crystal were 0.50 × 0.15 × 0.05 mm^3. A total of 4650 unique reflections were measured, 2540 of which with $I_o > 2\sigma(I_o)$ were used in structure solution and refinement. The structure was solved by the heavy-atom method and refined by least squares. The final least-squares cycle, calculated with 452 parameters, gave R = 0.054 and R_w = 0.049. The goodness of fit is 2.33. The final difference Fourier map showed no unusual feature with residuals in the range −1.35 to +5.20 e Å^{-3}. The crystal data are summarized in Table 1. Table 2 lists the atomic coordinates of non-hydrogen atoms. Selected bond distances and bond angles are summarized in Table 3.

Molecular Orbital Calculation. The electronic structure of the title compound was studied by the EHMO method. The geometric configuration was taken from the X-ray crystal data described in this work. The parameters for Re were taken from the literature,[9] and those for other atoms are standard values;[10] 86 atoms and 246 valence orbitals, of which 129 were occupied, were involved in the calculation. The calculated molecular orbital energies and compositions of the frontier molecular orbitals are summarized in Table 4.

Results and Discussion

Coordination of Re(I) to tetraphenylporphyrin (TPP) was reported previously by Tsutsui and co-workers.[5] In this work, the similar reaction of H_2TPrPc with $Re_2(CO)_{10}$ gave the air-stable (TPrPc)[Re(CO)$_3$]$_2$ complex, which has been shown by X-ray crystal analysis to be isostructural with its porphyrin analogue.

Figure 1 shows a perspective view of the molecule with the atomic numbering scheme. The structure features the first example of metalloporphycene with two metal ions concurrently bound to the porphycene ligand. Like (TPP)[Re(CO)$_3$]$_2$, the

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(1) Vogel, E.; Köcher, M.; Schmickler, H.; Lex, J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 257.

(2) Vogel, E. *Pure Appl. Chem.* **1990**, *62*, 557.

(3) Li, Z. Y.; Huang, J. S.; Che, C. M.; Chang, C. K. *Inorg. Chem.* **1992**, *31*, 2670.

(4) Vogel, E.; Balci, M.; Pramod, K.; Koch, P.; Lex, J.; Ermer, O. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 928.

(5) Cullen, D.; Meyer, E.; Srivastava, T. S.; Tsutsui, M. *J. Am. Chem. Soc.* **1972**, *94*, 7603.

(6) Tsutsui, M.; Ostfeld, D.; Hoffman, L. M. *J. Am. Chem. Soc.* **1971**, *93*, 1820.

(7) Gisselbrecht, J. P.; Gross, M. *J. Am. Chem. Soc.* **1990**, *112*, 8618.

(8) Louati, A.; Gross, M.; Jordan, J. *J. Electroanal. Chem. Interfacial Electrochem.* **1978**, *86*, 301.

(9) Deng, H. B.; Hoffmann, R. *Inorg. Chem.* **1993**, *32*, 1991.

(10) Albright, T. A.; Hoffmann, R.; Thibeault, J. C.; Thorn, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 3801.

0020-1669/95/1334-0984$09.00/0

Table 2. Atomic Positional and Isotropic Thermal Parameters[a]

	x	*y*	*z*	$B_{eq}{}^{b}$/Å^2
Re(1)	0.89216(14)	0.36529(5)	0.29781(5)	2.30(4)
Re(2)	0.60082(14)	0.32973(5)	0.19840(5)	2.32(4)
N(1)	0.6332(24)	0.3980(9)	0.2908(9)	2.8(10)
N(2)	0.7139(23)	0.4297(9)	0.1785(8)	2.4(9)
N(3)	0.8565(22)	0.2976(9)	0.2080(8)	2.0(9)
N(4)	0.7809(23)	0.2640(9)	0.3201(9)	2.6(10)
C(1)	0.556(3)	0.3994(13)	0.3430(12)	4.2(16)
C(2)	0.473(3)	0.4618(14)	0.3438(14)	5.4(16)
C(3)	0.514(3)	0.5045(14)	0.3019(12)	4.3(15)
C(4)	0.595(3)	0.4688(12)	0.2691(12)	3.3(14)
C(5)	0.660(3)	0.4864(12)	0.2098(13)	3.5(15)
C(6)	0.682(3)	0.5535(12)	0.1841(10)	2.7(13)
C(7)	0.765(3)	0.5368(12)	0.1347(11)	3.1(13)
C(8)	0.791(3)	0.4579(12)	0.1343(12)	3.3(14)
C(9)	0.877(3)	0.4204(13)	0.1014(11)	3.2(13)
C(10)	0.936(3)	0.3485(13)	0.1101(12)	3.4(14)
C(11)	0.934(3)	0.2973(12)	0.1540(11)	2.4(12)
C(12)	1.011(3)	0.2305(12)	0.1477(10)	2.6(12)
C(13)	0.981(3)	0.1870(13)	0.1946(12)	3.2(13)
C(14)	0.896(3)	0.2265(13)	0.2299(11)	3.0(13)
C(15)	0.834(3)	0.2088(12)	0.2865(13)	3.3(15)
C(16)	0.812(3)	0.1428(12)	0.3161(12)	2.7(13)
C(17)	0.727(3)	0.1586(12)	0.3649(11)	2.4(11)
C(18)	0.710(3)	0.2361(13)	0.3664(10)	2.5(12)
C(19)	0.616(3)	0.2771(14)	0.3993(12)	3.4(14)
C(20)	0.554(3)	0.3479(12)	0.3883(11)	2.9(13)
C(21)	0.389(3)	0.4856(14)	0.3989(15)	5.2(18)
C(22)	0.325(3)	0.5618(16)	0.3961(13)	5.1(17)
C(23)	0.249(4)	0.5846(16)	0.4522(14)	5.8(18)
C(24)	0.833(3)	0.5871(13)	0.0919(11)	3.4(15)
C(25)	0.800(4)	0.6636(15)	0.1000(15)	6.0(19)
C(26)	0.859(4)	0.7139(15)	0.0552(14)	6.3(19)
C(27)	1.107(3)	0.2071(14)	0.0965(11)	3.7(14)
C(28)	1.178(4)	0.1332(14)	0.1018(12)	4.6(16)
C(29)	1.251(4)	0.1111(15)	0.0477(15)	5.4(17)
C(30)	0.670(3)	0.1063(13)	0.4093(12)	3.8(15)
C(31)	0.707(4)	0.0279(14)	0.3966(14)	4.9(17)
C(32)	0.638(4)	−0.0214(15)	0.4406(14)	5.9(19)
C(33)	0.928(3)	0.4037(13)	0.3757(11)	3.3(13)
C(34)	1.096(3)	0.3357(14)	0.3079(12)	3.8(14)
C(35)	0.992(3)	0.4581(15)	0.2692(11)	4.0(16)
C(36)	0.387(3)	0.3612(12)	0.1909(11)	2.8(12)
C(37)	0.569(3)	0.2927(15)	0.1198(13)	5.2(16)
C(38)	0.511(3)	0.2438(13)	0.2279(12)	3.3(14)
O(1)	0.9473(25)	0.4280(11)	0.4231(9)	6.0(12)
O(2)	1.2264(21)	0.3130(10)	0.3134(9)	5.0(12)
O(3)	1.054(3)	0.4986(12)	0.2435(11)	8.4(15)
O(4)	0.2616(20)	0.3830(10)	0.1833(9)	5.0(11)
O(5)	0.5424(24)	0.2722(11)	0.0736(9)	6.0(12)
O(6)	0.4595(21)	0.1895(9)	0.2401(9)	4.6(11)

[a] Esd's refer to the last digit printed. [b] B_{eq} is the mean of the principal axes of the thermal ellipsoid.

complex has one Re(I) above and the other below the porphycene plane. The average displacement of Re(I) from the porphycene plane is 1.50(1) Å. Each Re(I) is coordinated to three CO groups and to three nitrogen atoms of the porphycene ligand. Not surprisingly, those Re−N distances with the N atom bonded to only one Re(I) are considerably shorter than those with the N atom bonded to two Re(I) atoms. The average Re−C(CO) distance is 1.92(3) Å, which is slightly longer than that of 1.88 Å in (TPP)[Re(CO)$_3$]$_2$.

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for (TPrPc)[Re(CO)$_3$]$_2$

Bond Distances			
Re(1)−N(1)	2.301(21)	C(1)−C(2)	1.36(4)
Re(1)−N(3)	2.375(18)	C(1)−C(20)	1.40(3)
Re(1)−N(4)	2.185(18)	C(2)−C(3)	1.30(4)
Re(1)−C(33)	1.890(23)	C(2)−C(21)	1.55(4)
Re(1)−C(34)	1.83(3)	C(3)−C(4)	1.24(4)
Re(1)−C(35)	2.05(3)	C(4)−C(5)	1.52(4)
Re(2)−N(1)	2.428(20)	C(5)−C(6)	1.39(4)
Re(2)−N(2)	2.157(18)	C(6)−C(7)	1.40(4)
Re(2)−N(3)	2.271(19)	C(7)−C(8)	1.48(3)
Re(2)−C(36)	1.922(3)	C(7)−C(24)	1.49(4)
Re(2)−C(37)	1.89(3)	C(8)−C(9)	1.29(4)
Re(2)−C(38)	1.92(2)	C(9)−C(10)	1.43(4)
N(1)−C(1)	1.39(3)	C(10)−C(11)	1.37(4)
N(1)−C(4)	1.43(3)	C(33)−O(1)	1.16(3)
N(2)−C(5)	1.37(3)	C(34)−O(2)	1.20(3)
N(2)−C(8)	1.35(3)	C(35)−O(3)	1.11(4)

Bond Angles			
N(1)−Re(1)−N(3)	91.4(7)	C(33)−Re(1)−C(34)	85.2(12)
N(1)−Re(1)−N(4)	78.6(7)	C(33)−Re(1)−C(35)	86.1(10)
N(1)−Re(1)−C(33)	92.7(10)	C(34)−Re(1)−C(35)	82.5(11)
N(1)−Re(1)−C(34)	176.1(10)	Re(1)−N(1)−Re(2)	87.9(6)
N(1)−Re(1)−C(35)	100.7(9)	Re(1)−N(1)−C(1)	118.2(17)
N(3)−Re(1)−N(4)	73.2(7)	Re(1)−N(1)−C(4)	117.3(15)
N(3)−Re(1)−C(33)	170.2(9)	Re(1)−N(3)−Re(2)	89.9(7)
N(3)−Re(1)−C(34)	90.2(1)	Re(1)−N(3)−C(11)	133.3(14)
N(3)−Re(1)−C(35)	101.9(8)	Re(1)−N(3)−C(14)	100.6(14)
N(4)−Re(1)−C(33)	98.9(9)	Re(1)−C(33)−O(1)	178(3)
N(4)−Re(1)−C(34)	98.4(9)	Re(1)−C(34)−O(2)	176.6(22)
N(4)−Re(1)−C(35)	175.0(9)	Re(1)−C(35)−O(3)	164.3(25)

Table 4. Calculated Molecular Orbital Energies and Compositions

			% compn		
no.	level/(eV)		2Re(I)	TPrPc^{2-}	6CO
135	−8.5153		4.23	5.31	90.46
134	−8.6897		8.09	22.84	69.07
133	−8.9489		9.41	64.10	26.49
132	−9.1409		22.26	27.38	50.37
131	−9.8855	NLUMO	5.22	92.85	1.93
130	−10.3393	LUMO	0.14	99.57	0.28
129	−11.4071	HOMO	1.08	98.53	0.40
128	−11.7825	NHOMO	3.88	93.54	2.58
127	−12.2349		26.83	57.08	16.09
126	−12.3541		9.82	83.61	6.57
125	−12.4258		28.69	56.98	14.34
124	−12.5030		3.25	94.94	1.81
123	−12.6102		13.91	78.89	7.19
122	−12.6637		4.77	92.88	2.35
121	−12.6983		7.01	90.15	2.84
120	−12.7462		4.02	94.14	1.84
119	−12.8313		47.67	34.51	17.83
118	−12.8916		36.84	46.63	16.53

	transn energy/eV	
transition	calcd	obsd
128 → 131	1.897	2.006 (618 nm)
127 → 131	2.349	2.330 (532 nm)
126 → 131	2.469	
127 → 132	3.094	3.017 (411 nm)
126 → 132	3.213	3.220 (385 nm)
125 → 132	3.285	
123 → 132	3.469	
122 → 132	3.523	3.542 (350 nm)

It is interesting to compare the N···N separations in (TPrPc)[Re(CO)$_3$]$_2$ with those in [Ni(TPrPc)][4] and in H$_2$TPrPc. The mean value of the N(1)···N(2) and N(3)···N(4) separation is 2.72(3) Å, which lies between the related values of 2.554(4) Å in Ni(TPrPc) and 2.831(3) Å in H$_2$TPrPc. Interestingly, the mean value of the N(2)···N(3) and N(1)···N(4) separations is 2.82(3) Å, and this is not much different from that of 2.801(4) Å in Ni(TPrPc). Worthy of note is the fact that the difference between the two mean values is only 0.09 Å, suggesting that the arrangement of the four pyrrole nitrogens is close to a square.

The results of extended Hückel molecular calculations on the title compound are summarized in Table 4. The HOMO, NHOMO, LUMO, and NLUMO mainly consist of TPrPc^{2-} ligand-centered atom orbitals (at least 93%). Two molecular orbitals labeled 127 and 125 are of lower energy than the HOMO and NHOMO and contain contributions from the Re(I)

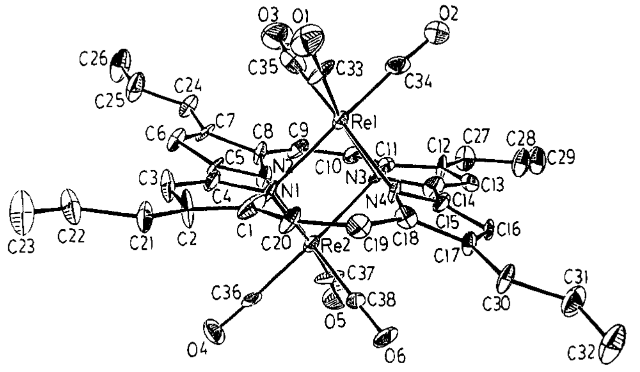

Figure 1. Perspective drawing of (TPrPc)[Re(CO)$_3$]$_2$ with atomic numbering scheme.

5d orbitals and porphycene atom orbitals. The Re(I) 5d orbitals lie in the energy range −12.70 to −13.49 eV.

The calculated electronic configurations of Re(I) are $5d^{6.20}6s^{0.41}6p^{0.88}$ and $5d^{6.22}6s^{0.41}6p^{0.90}$. The Re−N(1), Re−N(2), and Re−N(3) bond orders are 0.333, 0.428, and 0.260. The Re−N(2) bond order has the largest value since N(2) only coordinates to one Re(I).

The IR spectrum of (TPrPc)[Re(CO)$_3$]$_2$ shows three intense bands at 1892, 1908, and 2018 cm^{-1} assignable to ν(CO) stretches. This agrees with the X-ray data in that three slightly different CO distances are found. Our calculation also shows that, for each Re(CO)$_3$ unit, the three CO bond orders are slightly different from each other and the calculated average values are 1.140, 1.196, and 1.295.

The UV−vis absorption spectrum of the complex is depicted in Figure 2. There are two near-UV bands at 350 and 385 nm and three visible bands at 411, 532, and 618 nm. The 618 nm band appears to correspond to the 612 nm band of Ru(TPrPc)(CO).[3] The 411 and 532 nm bands can be considered as additional bands. It was reported that (TPP)[Re(CO)$_3$]$_2$ also shows more UV−vis absorption bands [411 (Soret), 483 and 514 (β) nm] than Ru(TPP)(CO) [412 (Soret), 528 (β) nm].[6] Table 4 compares some of the calculated electronic transition energies based on EHMO calculations with the measured UV−vis spectral data. The lowest energy absorption band at 618 nm is essentially due to the intraligand transition of the porphycene ligand. The 532 nm band, on the other hand, could contain some MLCT Re → π^*(porphycene) character. It is interesting to note that the 411 nm band, being the most intense one, closely matches the difference in energies between orbital 127 and orbital 132. Because orbital 132 has a substantial contribution from the atom orbitals of CO and orbital 127 from the Re(I) 5d orbitals, the transition between these two orbitals may have both intraligand and Re → π^*(CO) character.

The ^{1}H NMR spectrum of (TPrPc)[Re(CO)$_3$]$_2$ recorded at room temperature is shown in Figure 3. Both the 9,10,19,20- and 3,6,13,16-protons appear as sharp singlets at 10.13 and 9.50 ppm, respectively. The α-CH$_2$, β-CH$_2$, and methyl protons of the *n*-propyl groups appear as a triplet, a sextet, and a triplet, respectively, is similar to those of Os(TPrPc)(O)$_2$.[3] Cooling the sample down to −50 °C does not affect these spectroscopic findings.

The geometry of the Re$_2$N$_4$(CO)$_6$ moiety in (TPrPc)[Re(CO)$_3$]$_2$ can be described as two distorted octahedra sharing an edge, with an inclined center-to- center axis with respect to the plane of the porphycene macrocycle. The molecular symmetry of (TPrPc)[Re(CO)$_3$]$_2$ depends on the direction in which the Re−Re axis is inclined. Figure 4 shows three extreme cases. For structures **I** and **II**, the molecule has a C_{2h} symmetry. In such structures, the four 9,10,19,20-protons are identical and so are the 3,6,13,16-protons. In **III**, the molecule has C_i symmetry and the 9,10,19,20- and 3,6,13,16-protons are not identical. If the (TPrPc)[Re(CO)$_3$]$_2$ complex had structure **III** in solution, the 9,10,19,20- and 3,6,13,16-protons would have appeared as a doublet in the ^{1}H NMR spectrum. Thus the ^{1}H NMR data suggest that the structure of (TPrPc)[Re(CO)$_3$]$_2$ in solution could be either **I** or **II**. Alternatively, the ^{1}H NMR data can be interpreted by a rapid tautomerization reaction. If this is the case, the tautomerization has to be very rapid since only one set of the 9,10,19,20-protons and 3,6,13,16-protons is observed even at a temperature of −50 °C.

The cyclic voltammogram of (TPrPc)[Re(CO)$_3$]$_2$ in 1,2-dichloroethane with 0.1 M tetrabutylammonium tetrafluoroborate as supporting electrolyte shows two reversible reduction waves at −1.16 and −1.51 V and two reversible oxidation waves at 0.69 and 0.89 V vs the ferrocenium/ferrocene couple. The reduction and oxidation waves indicate ligand-centered redox reactions of the porphycene on the basis of comparison with H$_2$TPrPc and other metalloporphycene.[7] It is interesting

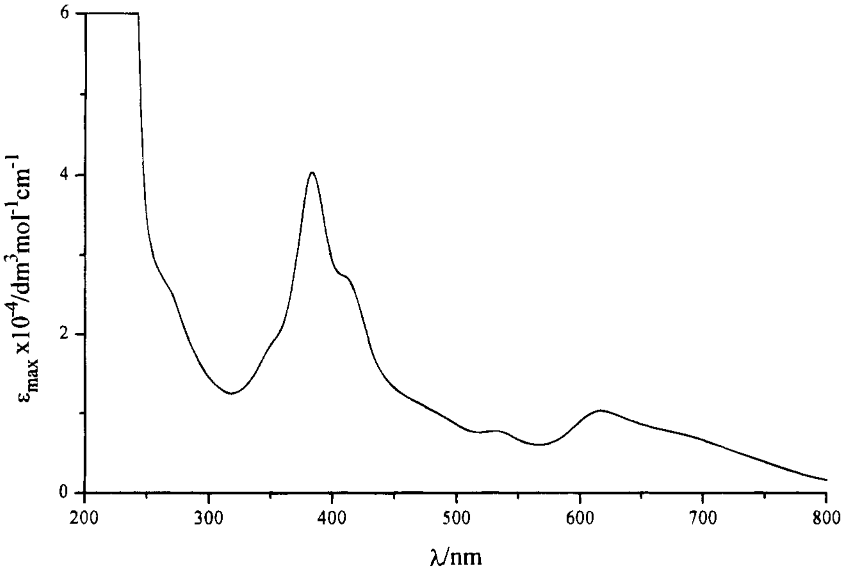

Figure 2. UV−visible spectrum of (TPrPc)[Re(CO)$_3$]$_2$ in CHCl$_3$.

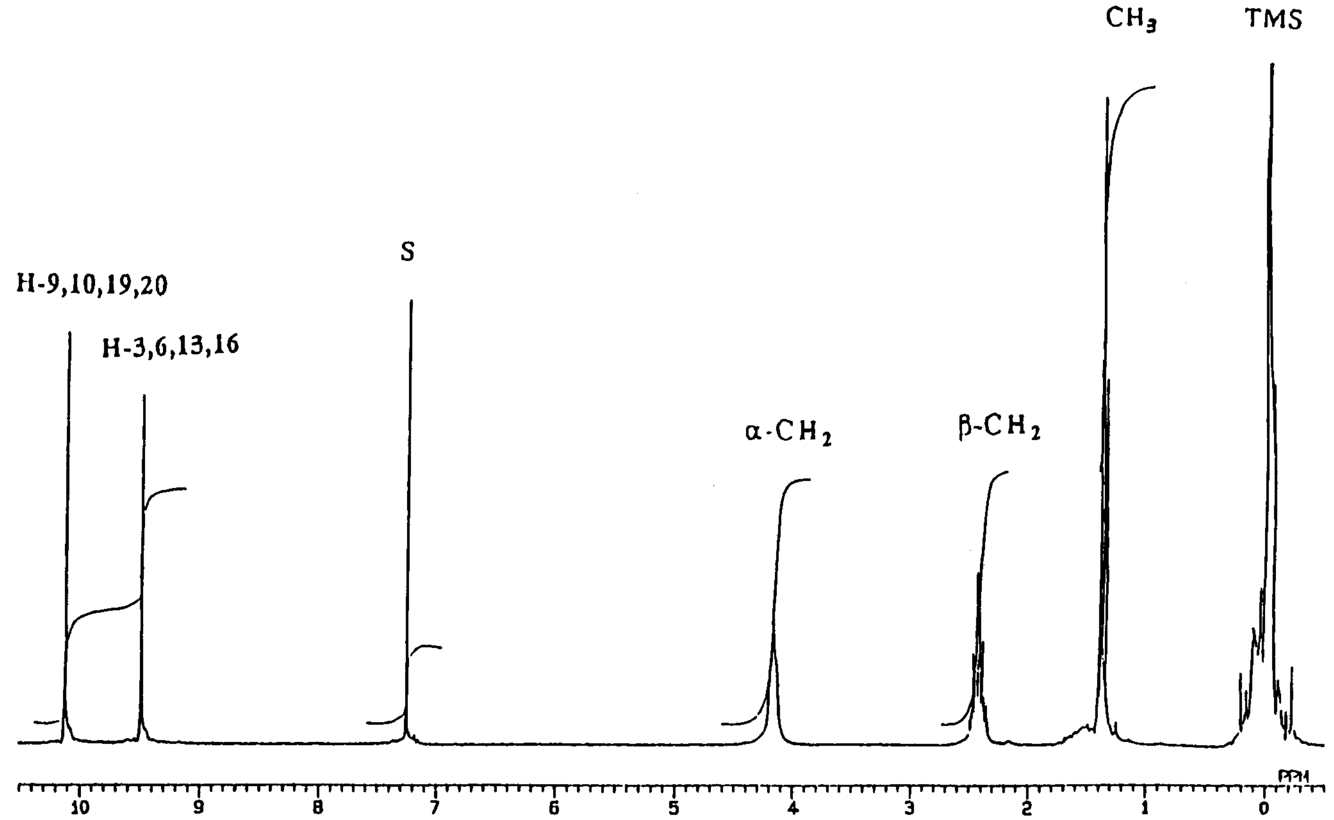

Figure 3. ^{1}H NMR spectrum of (TPrPc)[Re(CO)$_3$]$_2$ in CDCl$_3$.

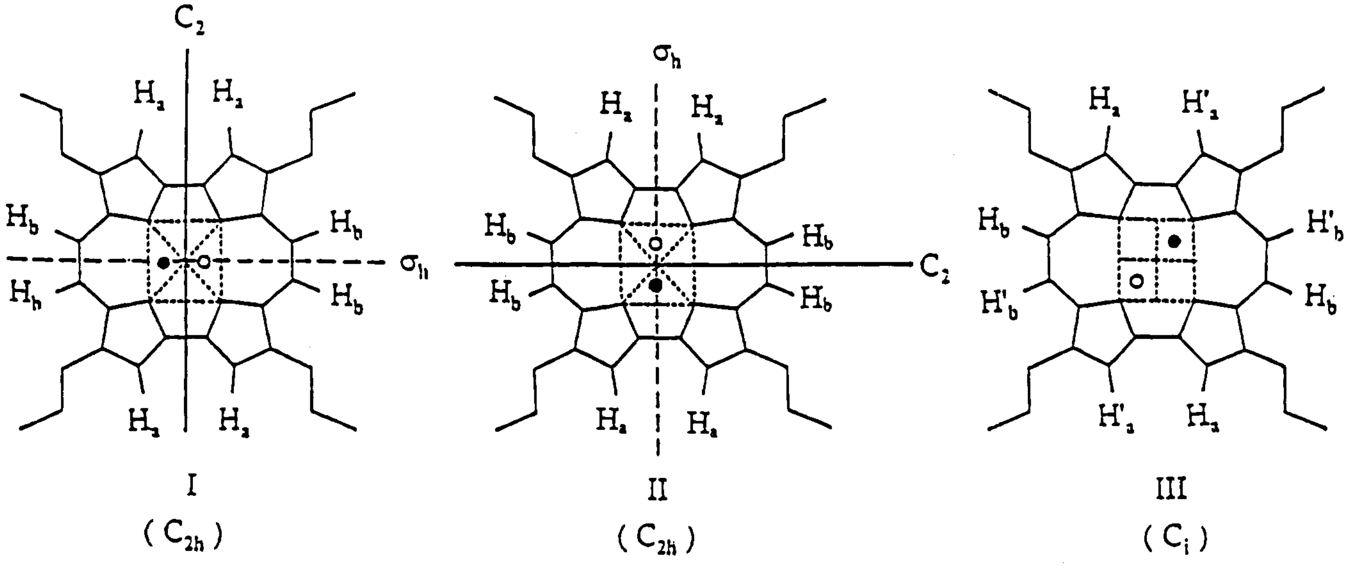

Figure 4. Schematic diagram of possible structures for (TPrPc)[Re(CO)$_3$]$_2$ with the atomic numbering scheme: •, Re(CO)$_3$ moiety above the porphycene plane; ∘, Re(CO)$_3$ moiety below the porphycene plane.

to note that similar electrochemistry has been found for the analogous (TPP)[Re(CO)$_3$]$_2$.[8]

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Supplementary Material Available: Tables giving crystal data and details of the structure determination, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom coordinates (7 pages). Ordering information is given on any current masthead page.

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