second quartet excited state[35] of $Cr(NH_3)_5Cl^{2+}$ is an unattractive postulate, due to the lack of oxygen quenching of the flavin singlet,[2] the low energy of the flavin triplet,[31] and the absence of efficient Cl^- release brought about by direct photolysis of the complex.

Three general implications of these results are stressed. First, while there are several well-documented examples[1a,1f,1g,36] in which coordination compounds do not quench excited singlet states of aromatic molecules, it is clear[1g,h] that energy transfer from organic singlets to "spin-allowed" excited states of metal complexes can be highly efficient. Thus, the application of quenching and sensitization experiments to inorganic photochemistry is not always restricted to "spin-forbidden" excited states. Second, energy transfer quenching of excited organic molecules by metal complexes may in many instances be competitive with quenching processes not producing excited states of the quencher. We presently know virtually nothing about the factors responsible for the greatly varying susceptibility of different photoexcited aromatic molecules to quenching by transition metal complexes or about the detailed nature of "non-energy-transfer" quenching. Finally, the ability of flavins to act as singlet energy donors in metal-containing systems may have important implications for flavin-dependent photobiology.[37] Additional studies of interactions of photoexcited flavins with metal complexes are in progress in this laboratory.

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Spectroscopic and Structural Characterization of Ruthenium(II) Carbonyl–Porphine Complexes

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Abstract: Reaction of $Ru_3(CO)_{12}$ with tetraphenylporphine and tetra-*p*-isopropylphenylporphine affords ruthenium(II) carbonyl–porphine complexes which in past investigations have been formulated as the monocarbonyls Ru(CO)(TPP) and Ru(CO)(*i*-Pr-TPP), respectively. A recent X-ray study of the tetraphenylporphine reaction product recrystallized from chloroform–ethanol has led to reformulation of this product as the *dicarbonyl* $Ru(CO)_2$(TPP), containing markedly bent (154°) Ru–C–O bonds. The nature of these compounds after recrystallization from chloroform–ethanol has been reinvestigated. Chemical and spectroscopic experiments show (i) no CO evolution when monopyridinates are formed with excess pyridine, (ii) no mass spectral peaks due to dicarbonyl ions such as $Ru(CO)_2TPP^+$, (iii) an ABCD pattern of phenyl *o*-H and *m*-H pmr signals (*i*-Pr-TPP complex) which collapses to an AA′BB′ pattern at elevated temperatures, (iv) methyl and methylene pmr signals (*i*-Pr-TPP complex) whose chemical shifts are indicative of axially coordinated ethanol. These observations are incompatible with the dicarbonyl description but are consistent with the formulations Ru(CO)(TPP)(EtOH) and Ru(CO)(*i*-Pr-TPP)(EtOH). The composition and structure of the TPP reaction product has been confirmed by an X-ray determination. The compound Ru(CO)(TPP)(EtOH) crystallizes in space group C_i^1-$P\bar{1}$ of the triclinic system in a cell of dimensions $a = 10.078$ (4), $b = 11.819$ (5), $c = 8.883$ (4) Å; $\alpha = 101.37$ (5), $\beta = 106.12$ (4), and $\gamma = 65.91$ (3)°. A density of 1.416 g cm^{-3} calculated for one molecule in the unit cell agrees with that of 1.39 (1) g cm^{-3} observed by flotation of the crystals in aqueous $ZnCl_2$. The structure has been solved and refined by standard methods, based on 2906 unique reflections collected by counter methods using monochromatized Mo Kα radiation. The final agreement index is 7.5%. The molecule has crystallographically imposed $\bar{1}$ symmetry and hence the CO and EtOH groups are disordered and the RuN_4 portion of the molecule is planar. The overall deviations from planarity of the porphinato core are very small. The distances within the porphinato core are in good agreement with those reported for other metalloporphyrins. The Ru–O(Et) distance is 2.21 (2) Å, and the EtOH group has its expected geometry. The Ru–C (of CO) distance is 1.77 (2) Å and the Ru–C–O bond is essentially linear, the bond angle being 175.8 (1.9)°.

In recent years the range of metalloporphine and porphyrin complexes has been expanded by the synthesis of species containing second- and third-row transition metal ions,[3] including ruthenium(II, III).[4–11] Ruthenium(II) carbonyl–porphine or –porphyrin complexes undergo inter- and intramolecular ligand exchange reactions at rates which allow the study of these

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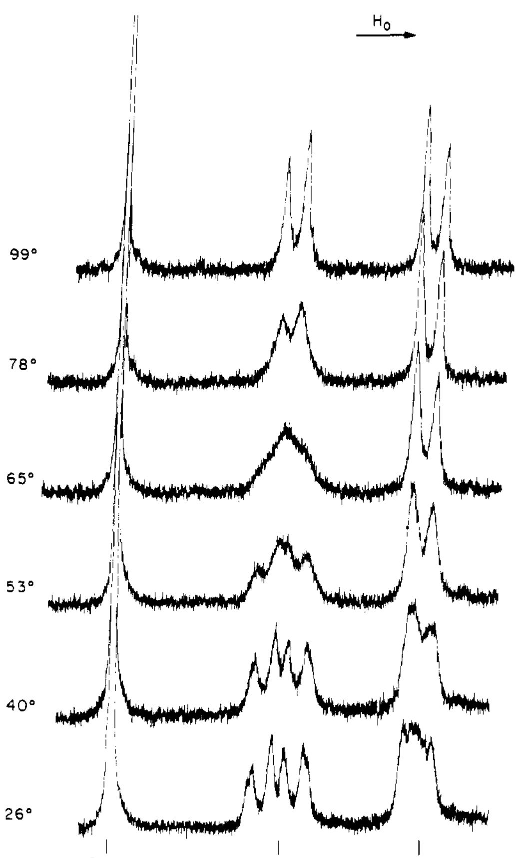
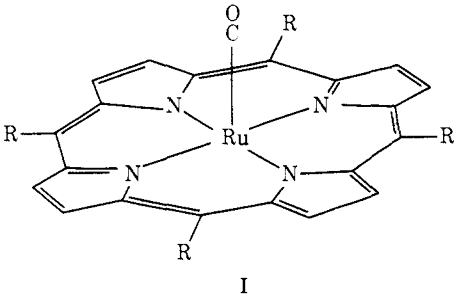


Figure 1. Pmr spectra (100 MHz) of the phenyl resonances of Ru(CO)(*i*-Pr-TPP) in 1,1,2,2-tetrachloroethane solution at various temperatures. Slow-exchange chemical shifts are in ppm downfield from the solvent lock signal. The multiplets centered at −2.14 and −1.60 ppm are assigned to *o*-H and *m*-H, respectively, as discussed elsewhere [F. A. Walker and G. L. Avery, *Tetrahedron Lett.*, 4949 (1971)]. The −2.79 ppm feature is due to the pyrrole protons.

processes by nmr methods.[6-9,12] The unusual lability of these ruthenium(II) complexes has stimulated considerable interest in their structures and properties. Prior to the result of a recent X-ray study,[10] the available evidence for the tetraphenylporphine complex had been interpreted as supporting the formulation Ru(CO)(PP)T[13] (I, R = Ph), considered to contain



I

five-coordinate Ru(II).[5-9,12] Formation of complexes with nitrogenous bases was assumed to involve coordination in the vacant axial position according to reaction 1. Formation of six-coordinate complexes

$$\mathrm{Ru(CO)(TPP)} + \mathrm{L} \rightleftharpoons \mathrm{Ru(CO)(TPP)(L)} \qquad (1)$$

with other bases such as alcohols and water has also been discussed.[5-7] Therefore, the recent conclusions,[10] based on X-ray results, that the compound previously formulated as I is actually the *dicarbonyl* $Ru(CO)_2(TPP)$ and that one of the carbonyl groups is displaced when a base adduct is formed (reaction 2) warrant further

$$\mathrm{Ru(CO)_2(TPP)} + \mathrm{L} \rightleftharpoons \mathrm{Ru(CO)(TPP)(L)} + \mathrm{CO} \qquad (2)$$

scrutiny. This point is further emphasized by the report[10] of *bent* Ru–C–O bonds (154°) in the alleged dicarbonyl. Such a markedly bent bond for a terminal carbonyl is without precedent in metal carbonyls of any type. In this paper we report further characterization of the complexes which result from the reaction of $Ru_3(CO)_{12}$ with tetraphenylporphines.[5-10] Chemical, spectroscopic, and X-ray results demonstrate that the reaction products are in fact monocarbonyls and that the compound studied by Cullen, *et al.*,[10] is Ru(CO)(TPP)(EtOH).

Experimental Section

Preparation of Compounds. $Ru_3(CO)_{12}$ was allowed to react with H_2TPP under the conditions reported by Cullen, *et al.*,[10] and with H_2(*i*-Pr-TPP) as described previously.[8,9] The products, which initially will be referred to as Ru(CO)(TPP) and Ru(CO)(*i*-Pr-TPP), were recrystallized from chloroform–ethanol as in a previous preparation[10] of the former compound. Elemental analyses of both compounds were consistent with formulation as monoethanolates. *Anal.* Calcd for $C_{47}H_{34}N_4O_2Ru$: C, 71.65; H, 4.35; N, 7.11. Found: C, 71.77; H, 4.46; N, 7.19. Calcd for $C_{59}H_{58}N_4O_2Ru$: C, 74.11; H, 6.11; N, 5.86. Found: C, 73.58; H, 6.14; N, 6.15.

Physical Measurements. Infrared spectra were recorded on Perkin Elmer Model 337 and 521 grating spectrometers. Mass spectra were obtained on Hitachi-Perkin Elmer RMU-6D (low resolution) and CEC-21-110B (high resolution) spectrometers operating at 70 eV. Pmr spectra were measured using a Varian HA-100 spectrometer as described previously.[9] Electronic spectra were recorded on a Cary 14 spectrophotometer.

Chemical and Spectroscopic Studies. The studies described in parts (i)–(v) were performed using samples recrystallized from chloroform–ethanol. As described below a single crystal from the bulk sample of Ru(CO)(TPP) was found to possess cell constants near to those reported for $Ru(CO)_2(TPP)$.[10]

(i) **CO Evolution.** (a) **Ru(CO)(TPP).** A solid sample (200 mg, 0.27 mmol) was placed in a 25-ml three-necked flask connected to a 10-cm infrared gas cell with AgCl windows and the system was evacuated. Through a rubber septum closure 1.0 ml (12 mmol) of pyridine was added and the mixture was stirred for *ca.* 10 min. Completion of the reaction was evidenced by a change in color to a more intense red and a change in crystal form. The gas in the reaction vessel was admitted to the cell; no CO absorption was detected in the infrared spectrum. Additional pyridine (1 ml) was added, and again no CO was detected. Injection of 3 ml (0.13 mmol) of CO gas into the system yielded an absorption feature with rotational fine structure centered at 2140 cm^{-1}. The pyridine complex was isolated and recrystallized from trichloroethylene–hexane. Analytical results indicate the formulation Ru(CO)(TPP)(py). *Anal.* Calcd for $C_{44}H_{34}N_5ORu$: C, 72.67; H, 4.23; N, 8.65. Found: C, 72.81; H, 4.38; N, 8.55.

(b) **Ru(CO)(*i*-Pr-TPP).** Using the apparatus described in (a) 305 mg (0.34 mmol) of the complex was allowed to react with 1.0 ml (12 mmol) of pyridine. No CO was detected. Addition of 1 ml of CO gas yielded the strong absorption feature at 2140 cm^{-1}. The monopyridine complex was isolated and recrystallized from trichloroethylene–hexane in the presence of a small amount of pyridine. *Anal.* Calcd for $C_{62}H_{57}N_5ORu$: C, 75.28; H, 5.81; N, 7.08. Found: C, 74.82; H, 5.73; N, 6.91.

(ii) **Pmr Spectra.** At ambient temperature in tetrachloroethane solution, signals of the phenyl protons of Ru(CO)(*i*-Pr-TPP) occur as an ABCD pattern. As the temperature is raised the resonances broaden and coalesce to an AA′BB′ pattern which appears as a simple AB spectrum (Figure 1). The temperature-dependent spectra are quite similar to those observed for Ru(CO)(*i*-Pr-TPP)-

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[12] J. W. Faller and J. W. Sibert, *J. Organometal. Chem.*, 31, C5 (1971).

[13] The following abbreviations are used: TPP, tetraphenylporphinate dianion; *i*-Pr-TPP, tetrakis(*p*-isopropylphenyl)porphinate dianion; TTP, tetrakis(*p*-tolyl)porphinate dianion; 4,5-DMPD, 4,5-dimethylpyridazine; py, pyridine; EtOH, ethanol.

(4,5-DMPD)[9] and In(TPP)Cl.[14] The slow-exchange spectra must result from slow rotation about the *meso* carbon to phenyl carbon bond causing the pairs of ortho and meta protons to be nonequivalent due to differences between the axial ligands on the two sides of the Ru–TPP mean plane. No attempt has been made to obtain accurate kinetic parameters for the rotation process. An approximate treatment[15] yields *ca.* 28 sec^{-1} for the rate of rotation and $\Delta G^{\ddagger} \sim 18$ kcal/mol at the coalescence temperature of *ca.* 65° for *o*-H. Coordinated ethanol has unambiguously been detected by pmr (Figure 2). In a 0.035 *M* solution of Ru(CO)(*i*-Pr-TPP) in tetrachloroethane at 30° a quartet and triplet were observed at 6.39 and 7.21 ppm upfield of the solvent lock signal. Assignment of these peaks to coordinated ethanol was verified by adding an equimolar amount of ethanol, which caused a downfield shift of the signals to 4.94 (broad) and 6.35 ppm (broadened triplet). When the temperature was raised to 51°, the peaks sharpened to a quartet and triplet, respectively.

(iii) Mass Spectra. The spectra of Ru(CO)(TPP) showed peaks for $Ru(CO)(TPP)^+$ (calcd for $^{12}C_{45}{}^1H_{28}{}^{14}N_4{}^{16}O^{102}Ru$, 742.1300; found, 742.12) and $Ru(TPP)^+$ (calcd for $^{12}C_{44}{}^1H_{28}{}^{14}N_4{}^{102}Ru$, 714.1353; found, 714.1220),[16] but not for $Ru(CO)_2(TPP)^+$ as reported previously.[10] A metastable peak corresponding to

$$Ru(CO)(TPP)^+ \xrightarrow{-CO} Ru(TPP)^+$$

and a doubly charged ion pattern for $Ru(TPP)^{2+}$ were also observed. The high mass region of the spectrum was identical for Ru(CO)(TPP) recrystallized from either chloroform–ethanol or chloroform–methanol and for Ru(CO)(TPP)(py), indicating that any axial ligand (*e.g.*, py, EtOH) is removed in the vaporization process. Additional peaks which exhibited ruthenium and carbon isotope patterns were also found in the high mass region. Their increase in relative intensity with time and their lack of correspondence to any clear mass increment above $Ru(CO)(TPP)^+$, such as CO, H_2O, or C_2H_5OH, indicates that they arise from decomposition products. The sample recovered from the spectrometer at the end of a run showed color changes indicative of decomposition. The mass spectrum of Ru(CO)(*i*-Pr-TPP) was also examined and peaks corresponding to $Ru(i\text{-}Pr\text{-}TPP)^+$ (calcd for $^{12}C_{56}{}^1H_{52}{}^{14}N_4{}^{102}Ru$, 882.323; found, 882.331) were observed,[16] but none for $Ru(CO)(i\text{-}Pr\text{-}TPP)^+$ or $Ru(CO)_2(i\text{-}Pr\text{-}TPP)^+$ were found. This sample was also found to be extensively decomposed at the end of the run.

(iv) Infrared Spectra. Due to solubility limitations solution spectra were obtained only in chlorinated solvents, some of which are known to cause broadening or shifting of CO bands in metal carbonyls.[17] Single bands of about 40 cm^{-1} half-width were observed for the following species in tetrachloroethane: Ru(CO)(TPP), 1934 cm^{-1}; Ru(CO)(TPP)(py), 1939 cm^{-1}; Ru(CO)(*i*-Pr-TPP), 1931 cm^{-1}; Ru(CO)(*i*-Pr-TPP)(py), 1936 cm^{-1} (all ±4 cm^{-1}). Narrower bands were found for the same species in Kel-F mulls at 1945, 1965, 1950, and 1955 cm^{-1}, respectively. The solid-phase spectra of Ru(CO)(TPP) and Ru(CO)(*i*-Pr-TPP) recrystallized from chloroform and ethanol or methanol exhibited shoulders or in some instances slightly resolved peaks within 5–10 cm^{-1} of the principal CO band. Similar additional peaks were observed in samples which had never contacted alcohols but had been exposed to humid air. When these samples were freshly prepared and exposed to rigorously dried solvents, only a single CO band was found. The additional peaks are attributed to species such as unsolvated Ru(CO)(TPP) and Ru(CO)(TPP)(H_2O), depending on the history of the sample.

(v) Electronic Spectra. Visible spectra of the two carbonyl porphines and their pyridine complexes have been measured in chloroform solution in the 400–650-nm region. Results are summarized in Table I. Complex formation with pyridine results in a small red shift of bands below 600 nm. Bands above 600 nm observed in the *p*-*i*-Pr species were not clearly discernible in the spectra of the TPP complexes. The data for Ru(CO)(TPP) are in satisfactory agreement with those reported for the compound originally given this formulation[5-7] and for that formulated as $Ru(CO)_2(TPP)$.[10]

Table I. Visible Spectral Data for Ruthenium(II) Carbonyl–Porphines in Chloroform Solution

Complex	λ_{max}, nm (log ϵ_M)
Ru(CO)(TPP)[a]	563 (3.44), 528 (4.32), 490 sh (3.64), 412 (5.36)
Ru(CO)(TPP)(py)	566 (3.57), 532 (4.25), 495 sh (3.71), 413 (5.45)
Ru(CO)(*i*-Pr-TPP)	610 (2.77), 564 (3.62), 531 (4.34), 492 sh (3.68), 412 (5.42)
Ru(CO)(*i*-Pr-TPP)(py)	603 (3.08), 568 (3.75), 534 (4.28), 495 sh (3.74), 415 (5.42)

[a] Literature values: 530 (4.23), 410 (5.36),[5] 561 (weak), 529, 412.[10]

X-Ray Study. Examination of crystals of Ru(CO)(TPP)(EtOH) by precession methods using Mo Kα radiation failed to reveal the presence of any symmetry elements other than the center of symmetry imposed by Friedel's law. Cell constants, determined in the manner described below, are given in Table II. Based on a calculated volume of 923.6 Å^3 and one formula unit in the cell, the calculated density of 1.416 g cm^{-3} and the density of 1.39 (1) g cm^{-3} observed by flotation in aqueous $ZnCl_2$ are in good agreement. The density calculated for the formulation of the complex as $Ru(CO)_2(TPP)$ is 1.389 g cm^{-3}. Because of the inherent inaccuracy of density measurements (reliable to perhaps 1–2% at best), a density determination cannot distinguish between these two formulations.

Table II. Crystal Data

Quantity	Present work $C_{47}H_{34}N_4O_2Ru$	Ref 10 $C_{46}H_{28}N_4O_2Ru$
M	787.89	769.8
Space group	$P\bar{1}$ or $P1$	$P\bar{1}$ or $P1$
a, Å	10.078 (4)[a]	10.097 (3)
b, Å	11.819 (5)	11.849 (3)
c, Å	8.883 (4)	8.865 (4)
α, deg	101.37 (5)	101.30 (3)
β, deg	106.12 (4)	105.89 (4)
γ, deg	65.91 (3)	65.82 (4)
V, Å^3	923.6	926.3
ρ (obsd), g cm^{-3}	1.39 (1)	1.38
ρ (calcd), g cm^{-3}	1.416	1.380

[a] Numbers in parentheses here and in succeeding tables are estimated standard deviations in the least-significant figures.

The cell constants and corresponding standard deviations determined here were obtained from a least-squares refinement[18,19] of the setting angles of reflections centered on a FACS-1 computer controlled diffractometer. The hand centering procedure employs a small takeoff angle (in this instance, 1.0°), a top-bottom beam splitter for the determination of the diffractometer angle χ, and a narrow vertical slit for the determination of the angles Φ and 2θ. Because of the use of this narrow vertical slit, difficulties arising from the dispersion of the α_1,α_2 doublet as a function of 2θ are eliminated, and one centers on the α_1 line. Three separate determinations of cell constants were made in this study: (1) Mo Kα radiation (λ = 0.70930 Å), monochromatized from the (002) face of a highly mosaic graphite crystal, employing 12 strong reflections in the range $31 \leq 2\theta \leq 36°$; (2) Mo Kα radiation filtered through a Zr foil using these same reflections; and (3) Ni-filtered, Cu Kα radiation (λ = 1.54056 Å) employing 12 strong reflections in the range $46 \leq 2\theta \leq 57°$. The resultant least-squares refinements did not yield significant differences among the derived cell constants, and those constants given in Table II are the weighted averages of the three determinations. The crystal selected for data collection was a parallelepiped with bounding faces of the forms $\{100\}$, $\{010\}$, and $\{01\bar{1}\}$. The distances between the faces of these forms are 0.097, 0.253, and 0.258 mm. The crystal was mounted with $[\bar{1}23]$ approximately along the spindle axis.

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[15] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, p 223.

[16] Peaks for the indicated ions corresponding to the presence of the other ruthenium and carbon isotopes were also observed.

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[19] R. J. Doedens and J. A. Ibers, *ibid.*, **6**, 204 (1967).

Table IV. Atomic Parameters for Ru(TPP)(CO)(C_2H_5OH)

Atom	x	y	z	B, Å^2, or β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ru	0	0	0	0.0093 (1)	0.0048 (1)	0.0071 (1)	−0.0021 (1)	−0.0008 (1)	0.0008 (1)
N(1)	0.1286 (6)	−0.0767 (5)	0.2052 (6)	0.0119 (8)	0.0054 (5)	0.0092 (8)	−0.0026 (5)	−0.0004 (7)	0.0013 (5)
N(2)	−0.0308 (6)	0.1751 (5)	0.1111 (6)	0.0117 (8)	0.0063 (5)	0.0077 (8)	−0.0025 (5)	−0.0007 (6)	0.0007 (5)
C(1)	0.1976 (8)	−0.2007 (6)	0.2255 (8)	0.0110 (10)	0.0058 (6)	0.0107 (10)	−0.0019 (6)	−0.0011 (8)	0.0025 (6)
C(2)	0.2732 (8)	−0.2142 (7)	0.3888 (8)	0.0135 (11)	0.0070 (7)	0.0104 (10)	−0.0021 (7)	−0.0021 (9)	0.0026 (7)
C(3)	0.2535 (9)	−0.0992 (7)	0.4596 (8)	0.0153 (11)	0.0078 (7)	0.0086 (10)	−0.0027 (7)	−0.0022 (9)	0.0017 (7)
C(4)	0.1622 (8)	−0.0120 (6)	0.3478 (8)	0.0113 (10)	0.0061 (6)	0.0089 (9)	−0.0029 (6)	−0.0002 (8)	0.0011 (6)
C(5)	0.1198 (8)	0.1171 (6)	0.3741 (7)	0.0112 (10)	0.0077 (7)	0.0073 (9)	−0.0032 (7)	0.0002 (8)	0.0000 (6)
C(6)	0.0274 (8)	0.2029 (6)	0.2673 (8)	0.0113 (10)	0.0060 (6)	0.0103 (10)	−0.0022 (6)	0.0011 (8)	−0.0004 (6)
C(7)	−0.0245 (9)	0.3374 (6)	0.2974 (9)	0.0184 (13)	0.0058 (6)	0.0113 (11)	−0.0037 (7)	−0.0009 (10)	−0.0001 (7)
C(8)	−0.1114 (9)	0.3856 (6)	0.1669 (9)	0.0172 (12)	0.0045 (6)	0.0129 (11)	−0.0017 (7)	−0.0005 (10)	0.0009 (7)
C(9)	−0.1174 (8)	0.2858 (6)	0.0474 (8)	0.0127 (10)	0.0055 (6)	0.0105 (10)	−0.0022 (6)	−0.0006 (8)	0.0013 (6)
C(10)	−0.1943 (8)	0.2984 (6)	−0.1103 (8)	0.0118 (10)	0.0062 (6)	0.0120 (11)	−0.0026 (6)	−0.0004 (9)	0.0013 (6)
O(Et)	0.1927 (18)	−0.0057 (13)	−0.0791 (17)	4.1 (3)					
C(α,Et)	0.3350 (23)	−0.0464 (20)	−0.0183 (27)	0.0154 (29)	0.0117 (22)	0.0179 (36)	−0.0042 (21)	0.0063 (28)	−0.0008 (23)
C(β,Et)	0.3876 (23)	0.0367 (21)	0.1208 (24)	0.0196 (34)	0.0156 (27)	0.0227 (34)	−0.0095 (26)	0.0008 (27)	0.0040 (24)
C(CO)	−0.1658 (25)	0.0182 (21)	0.0515 (27)	4.1 (5)					
O(CO)	−0.2712 (25)	0.0336 (18)	0.0940 (22)	7.3 (5)					

Group	x_c[b]	y_c	z_c	δ	ϵ	η
Ring 1	0.2499 (4)	0.2139 (3)	0.6793 (5)	−1.208 (5)	2.568 (3)	−1.334 (4)
Ring 2	−0.3628 (4)	0.5462 (4)	−0.2111 (4)	−1.055 (3)	2.901 (4)	0.211 (4)

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] The various group parameters have been defined previously. See ref 24, 25.

Data were collected in shells of 2θ by the θ–2θ scan method using Mo Kα radiation monochromatized from graphite. The scan speed was 2 deg in 2θ/min from 1.2° below the Kα_1 peak to 1.2° above the Kα_2 peak. The takeoff angle was 2.8° and the receiving counter aperture was 5 mm high by 6.5 mm wide. The counter was positioned 32 cm from the crystal. The pulse height analyzer was set to admit about 90% of the Kα peak. Initially background counts were taken for 10 sec at each end of the scan range. Past 2θ of 31° these counts were increased to 20 sec and finally between 2θ of 45 and 50° to 40 sec. Examination of the data collected between 49 and 50° revealed that less than 50% were above background (3σ), and hence data collection was terminated at 50°.

During the course of the data collection six standard reflections from diverse regions of reciprocal space were measured every 60 reflections. The deviations of these reflections from their averages were all within counting statistics.

The data were processed in the normal manner[18,19] using a value of p of 0.04. Of the 3461 reflections obtained, 3259 are unique. (Data were collected with $h \geq 0$, so that there are some Friedel pairs among the $0kl$ reflections. The average deviation among these 202 Friedel pairs is a remarkable 0.6%. The averaged values of these Friedel pairs were included in the data set.) Of the unique reflections 2906 have $F^2 > 3\sigma(F^2)$ and only these reflections were included in subsequent refinements.

The structure was solved by standard Patterson and Fourier methods and refined by full-matrix least-squares techniques.[20] The quantity minimized is $\Sigma w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes and where the weights w are taken as $4F_o^2/\sigma^2(F_o^2)$. The agreement indices are defined as $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2}$. Values of the atomic scattering factors[21] and the anomalous terms[22] were from the usual sources and the effects of anomalous dispersion were included in F_c.[23]

Initially it was assumed that the correct space group is the centrosymmetric one, $P\bar{1}$, rather than its noncentrosymmetric subgroup $P1$. With this assumption the molecule has a crystallographically imposed center of symmetry. From the Patterson function the Ru atom and the atoms of the porphine ring were located, and on a subsequent difference Fourier map the carbon atoms of the phenyl rings were found. In subsequent least-squares refinements these phenyl rings were treated as rigid groups[24,25] using a C–C distance of 1.392 Å and idealized symmetry D_{6h}. A least-squares refinement of the Ru(TPP) portion of the molecule, involving isotropic thermal parameters for the nongroup atoms and overall group thermal parameters, led to values of R and R_w of 0.17 and 0.22. An additional cycle in which the nongroup atoms were allowed anisotropic vibrations and individual, variable isotropic thermal parameters were assigned to each of the carbon atoms of the ring led to values of R and R_w of 0.13 and 0.19. A subsequent difference Fourier map clearly revealed features interpretable as a superposition (because of $\bar{1}$ symmetry) of a CO and a C_2H_5OH group.

At this point sample calculations for an absorption correction were made. Based on a linear absorption coefficient of 4.03 cm^{-1} the resultant transmission factors were found to range from 0.91 to 0.97 indicating that corrections for absorption were unnecessary.

In the next cycle, the disordered CO and C_2H_5OH groups (H atoms omitted) were included with occupancy factors of 0.5. The C_2 portion of the C_2H_5OH was refined anisotropically, the O atom of the C_2H_5OH was refined isotropically, and the positions of the C and O atoms of the CO group were idealized and not varied. This refinement converged to values of R and R_w of 0.09 and 0.12. The four independent H atoms of the porphyrin ring, together with the ten independent H atoms of the phenyl rings, were idealized (C–H = 0.95 Å, B(H) = B(C) + 1) and added as fixed contributions in

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(20) In addition to local programs for the CDC 6400, local modifications of the following programs were employed: Zalkin's FORDAP Fourier program, Cahen's AGNOST absorption program, Johnson's ORTEP II thermal ellipsoid plotting program, Busing and Levy's ORFFE error function program. Our least-squares program, NUCLS, in its nongroup form closely resembles the Busing and Levy ORFLS program.

(21) D. T. Cromer and J. T. Waber, "International Tables for X-ray Crystallography," Volume 4, Kynoch Press, Birmingham, England, 1973, Table 2.2A, in press.

(22) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 53, 1891 (1970).

(23) J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, 17, 781 (1964).

(24) S. J. La Placa and J. A. Ibers, *ibid.*, 18, 511 (1965).

(25) R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, 4, 773 (1965).

a subsequent refinement which converged to R and R_w values of 0.08 and 0.10. The idealized CO group was omitted from the next cycle ($R = 0.092$, $R_w = 0.123$) and on a subsequent difference Fourier map the positions of the C and O atoms of the CO group were the major features. These positions were included as variables in the next cycle of refinement, each atom being assigned a variable, isotropic thermal parameter. The values of R and R_w were now 0.077 and 0.100. In the next difference Fourier map the positions of the methyl H atoms were clearly visible. These were idealized, as were the positions of the methylene H atoms, but no attempt was made to idealize the position of the H atom on the hydroxy group of EtOH. All of the H contributions were included as fixed contributions in a final cycle of refinement. This cycle converged to values of R and R_w of 0.075 and 0.097. An analysis of $\Sigma w(|F_o| - |F_c|)^2$ as a function of $|F_o|$, the setting angles, and Miller indices shows as the only trend a decrease with increasing scattering angle. Such a trend could result from insufficiencies in the model for disorder, for example in the assignment of isotropic thermal motion to some of the atoms of the CO and C_2H_5OH groups, or from imposition of rigid geometry on the phenyl rings. A final difference Fourier map shows a maximum electron density of 1.2 (2) e/Å^3 and some peaks of the order of 0.8 (2) e/Å^3 associated with the benzene rings. These peaks are approximately 15–20% of the heights of typical light-atom peaks on earlier Fourier maps. Thus the final difference Fourier map is essentially featureless. A structure factor calculation for the 353 reflections having $F_o^2 < 3\sigma(F_o^2)$, which were omitted from the refinement, indicates that only seven reflections have $|F_o^2 - F_c^2| > 3\sigma(F_o^2)$. Consequently these 353 reflections were omitted from Table III,[26] where we present the values of $10|F_o|$ and $10|F_c|$ for those reflections used in the refinements.

In Table IV we present the atomic and group parameters, together with their standard deviations as derived from the inverse matrix. In Table V we present the positions of the C atoms of the phenyl rings which may be derived from the data of Table IV. In Table VI we present the positions of the H atoms used in the various calculations. Table VII lists the root-mean-square amplitudes of vibration for those atoms refined anisotropically.

Table V. Derived Parameters for the Phenyl Carbon Atoms

Ring 1	x	y	z	B, Å^2
C(11)	0.1864 (6)	0.1664 (5)	0.5339 (5)	3.3 (1)
C(12)	0.3236 (6)	0.1763 (6)	0.5559 (6)	6.4 (2)
C(13)	0.3871 (5)	0.2239 (7)	0.7013 (8)	7.8 (3)
C(14)	0.3134 (7)	0.2614 (6)	0.8248 (6)	5.5 (2)
C(15)	0.1763 (6)	0.2514 (6)	0.8028 (5)	4.9 (2)
C(16)	0.1128 (5)	0.2040 (5)	0.6573 (6)	5.1 (2)
Ring 2				
C(17)	−0.2813 (5)	0.4282 (4)	−0.1597 (6)	3.6 (1)
C(18)	−0.2087 (4)	0.4956 (5)	−0.1922 (7)	5.5 (2)
C(19)	−0.2901 (6)	0.6135 (5)	−0.2437 (8)	5.9 (2)
C(20)	−0.4442 (6)	0.6641 (4)	−0.2626 (8)	5.4 (2)
C(21)	−0.5169 (4)	0.5968 (5)	−0.2301 (8)	6.0 (2)
C(22)	−0.4354 (6)	0.4788 (5)	−0.1786 (7)	5.4 (2)

Table VI. Idealized Positions of the Hydrogen Atoms

Atom	x	y	z
H(2)	0.331	−0.295	0.438
H(3)	0.296	−0.079	0.573
H(7)	0.001	0.385	0.400
H(8)	−0.162	0.477	0.154
H(12)	0.374	0.150	0.472
H(13)	0.481	0.231	0.717
H(14)	0.356	0.295	0.924
H(15)	0.126	0.278	0.888
H(16)	0.019	0.197	0.643
H(18)	−0.104	0.461	−0.179
H(19)	−0.241	0.660	−0.266
H(20)	−0.500	0.745	−0.298
H(21)	−0.622	0.632	−0.243
H(22)	−0.485	0.433	−0.156
H(1)C(α,Et)	0.391	−0.065	−0.105
H(2)C(α,Et)	0.366	−0.136	0.017
H(1)C(β,Et)	0.343	0.042	0.216
H(2)C(β,Et)	0.499	0.005	0.162
H(3)C(β,Et)	0.352	0.124	0.093

Table VII. Root-Mean-Square Amplitudes of Vibration (Å)

Atom	Min	Inter	Max	Angle Γ,[a] deg
Ru	0.148 (1)	0.168 (1)	0.225 (1)	8 (1)
N(1)	0.168 (8)	0.182 (8)	0.246 (8)	7 (6)
N(2)	0.159 (9)	0.191 (8)	0.248 (8)	6 (6)
C(1)	0.158 (10)	0.203 (9)	0.249 (9)	14 (8)
C(2)	0.161 (11)	0.215 (9)	0.281 (10)	7 (4)
C(3)	0.159 (11)	0.216 (10)	0.291 (9)	5 (5)
C(4)	0.171 (10)	0.189 (9)	0.236 (9)	7 (8)
C(5)	0.158 (10)	0.210 (9)	0.236 (9)	20 (16)
C(6)	0.177 (10)	0.196 (9)	0.244 (10)	17 (8)
C(7)	0.174 (10)	0.202 (10)	0.307 (10)	4 (3)
C(8)	0.162 (11)	0.207 (10)	0.306 (10)	4 (4)
C(9)	0.173 (10)	0.190 (9)	0.262 (9)	7 (5)
C(10)	0.185 (9)	0.198 (10)	0.255 (10)	15 (7)
C(α,Et)	0.223 (25)	0.266 (24)	0.281 (25)	
C(β,Et)	0.248 (25)	0.274 (26)	0.329 (24)	

[a] Γ is the angle that the maximum axis of the vibrational ellipsoid makes with the normal to the porphine plane. The fact that Γ is generally near 0 emphasizes the fact that the major vibrations of these atoms are normal to the porphyrin plane.

Several additional calculations were made to settle various questions that arose during the solution of the structure. (1) All nonhydrogen atoms of the CO and C_2H_5OH groups were allowed to vibrate anisotropically. In the resultant refinement there were some expected high correlations, but the atomic shifts were small and there was no significant improvement in the agreement indices. (2) With the assumption of space group $P\bar{1}$ there is no necessity that the ratio EtOH:CO be 1:1. Thus with suitable account taken of the derivatives involved an additional cycle of least-squares refinement was carried out in which the occupancy of the CO group was varied. This calculation resulted in a value for the occupancy factor of 0.49 (2) and in no improvement in the agreement indices. (3) A more difficult question to settle is the assignment of the correct space group. In space group $P1$ the CO and C_2H_5OH groups need not be disordered. Structure factor calculations based on the two possible enantiomorphs in $P1$ indicated that the breakdown of Friedel's law would be undetectable for data collected with Mo Kα radiation and would be very difficult to detect (maximum differences between $I(hkl)$ and $I(\bar{h}\bar{k}\bar{l}) \approx 3\%$) with Cu K$\alpha$ radiation. These calculations were based on the assumption that the only deviation from symmetry $\bar{1}$ is brought about by the differences between CO and EtOH. Presumably variations in Friedel pairs would be larger if the Ru(TPP) portion of the molecule were significantly noncentrosymmetric. But there are several factors that suggest the space group $P\bar{1}$, used in our calculations, is the correct one. (a) A sensitive test for piezoelectricity was negative. (b) Although the final R value of 0.075 is rather high for structures done in this laboratory, it seems typical of R values on carefully studied metalloporphyrin structures,[27–30] as is our data/parameter ratio of 17. Hence, the agreement indices do not point to an improper model. (c) The vibrational ellipsoids of the Ru(TPP) portion of the molecule seem quite normal (Table VII), and, as expected, the major axes of the various vibrational ellipsoids are ap-

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[26] Table III will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-73-2141. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

(27) J. L. Hoard, *Science*, 174, 1295 (1971), and references contained therein.

(28) D. M. Collins, R. Countryman, and J. L. Hoard, *J. Amer. Chem. Soc.*, 94, 2066 (1972).

(29) L. J. Radonovich, A. Bloom, and J. L. Hoard, *ibid.*, 94, 2073 (1972).

(30) A. B. Hoffman, D. M. Collins, V. W. Day, E. B. Fleischer, T. S. Srivastava, and J. L. Hoard, *ibid.*, 94, 3620 (1972).

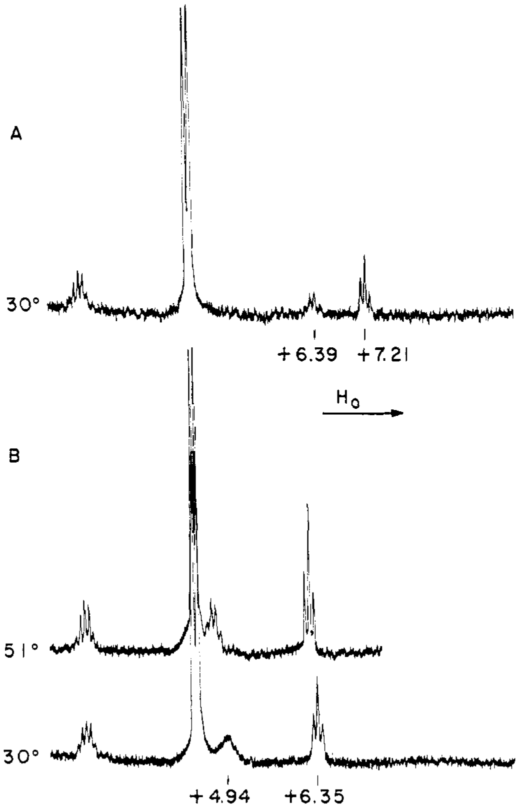

Figure 2. (A) A 100-MHz pmr spectrum of Ru(CO)(*i*-Pr-TPP) in 1,1,2,2-tetrachloroethane. The features at +6.39 and +7.21 ppm are assigned as the methylene and methyl resonances, respectively, of coordinated ethanol. (B) Ru(CO)(*i*-Pr-TPP) plus equimolar ethanol. Chemical shifts are in ppm upfield of the solvent lock signal. The low field doublet and multiplet are due to the methyl and methine protons, respectively, of the *p*-*i*-Pr groups.

proximately normal to the porphine plane. These would be more excessive if the true space group were $P1$. (d) The fact that the phenyl H atoms *and* the methyl H atoms could be located on difference Fourier maps is perhaps the strongest evidence that the correct structure has been found. There is no reason to believe that the phenyl rings would retain their centrosymmetric relationships nor would one expect to find the H atoms of the CH_3 group if the correct space group were $P1$.

Results and Discussion

The reaction of $Ru_3(CO)_{12}$ with H_2TPP yields a ruthenium carbonyl porphine, the properties of which have been the subject of a number of investigations.[5-10,12] Except for the recent X-ray results,[10] the available evidence was interpreted as indicating formation of a monocarbonyl with probable structure I. The same compound has been reported to result from the reaction of H_2TPP with $[Ru(CO)_3Cl_2]_2$ and, after recrystallization from chloroform–ethanol, was characterized as a monoethanolate on the basis of elemental analysis and mass spectral results.[5] The principal purpose of this investigation has been to accumulate evidence which permits a clear distinction between the monocarbonyl (I) and the dicarbonyl[10] as the reaction product from $Ru_3(CO)_{12}$ and tetraphenylporphines. Because of the possibility of inconclusive results from our X-ray study, chemical and spectroscopic experiments were carried out simultaneously with the structure determination, which was confined to the tetraphenylporphine reaction product. All of our results indicate that with H_2TPP or H_2(*i*-Pr-TPP) only a monocarbonyl species is obtained as the principal product.

Reaction of H_2TPP and H_2(*i*-Pr-TPP) with $Ru_3(CO)_{12}$ afforded red crystalline solids with very similar properties. Both compounds were recrystallized from chloroform–ethanol. Elemental analyses of both complexes suggested formulation as the monoethanolates Ru(CO)(TPP)(EtOH) and Ru(CO)(*i*-Pr-TPP)(EtOH). Cell constants of the TPP complex obtained in this manner are near to those given for $Ru(CO)_2(TPP)$ (Table II). Analytical data are insufficiently sensitive to exclude the dicarbonyl formulation and additional experiments were performed on Ru(CO)(TPP) and Ru(CO)(*i*-Pr-TPP). Neither compound liberated CO on treatment with excess pyridine and analyses of the reaction products were consistent with the formulations Ru(CO)(TPP)(py) and Ru(CO)(*i*-Pr-TPP)(py). The infrared spectra of these products further support the monocarbonyl description inasmuch as only one carbonyl stretching band was observed in solid samples or in tetrachloroethane solution. Two carbonyl bands should arise from any seven-coordinate species such as $Ru(CO)_2(TPP)(py)$ and it is unlikely that their frequency difference would not be resolvable under the conditions of our measurements. No molecular ions corresponding to $Ru(CO)_2(TPP)^+$ or $Ru(CO)_2$(*i*-Pr-TPP)$^+$ were observed in the high-resolution mass spectra. Cullen, *et al.*,[10] reported a peak at m/e 770 which they assigned to $Ru(CO)_2(TPP)^+$ and peaks at m/e 742 and 714. We also observe the latter two peaks, which are assigned to $Ru(CO)(TPP)^+$ and $Ru(TPP)^+$, respectively. The *p*-*i*-Pr analog yielded Ru(*i*-Pr-TPP)$^+$ as the only identifiable fragment in the high mass region.

The more soluble complex Ru(CO)(*i*-Pr-TPP) was examined by pmr in tetrachloroethane solutions. The observation of pairwise nonequivalence of ortho and meta protons at ambient temperature (Figure 1), together with the collapse of the spectrum to an AA′BB′ pattern at elevated temperatures, can only be rationalized in terms of restricted phenyl group rotation in a species which does not possess a centrosymmetric structure such as described for $Ru(CO)_2(TPP)$.[10] The room temperture nonequivalencies and the temperature-dependent spectral changes are quite similar to those observed for Ru(CO)(*i*-Pr-TPP)(4,5-DMPD)[9] and In(TTP)Cl.[14] No controversy attends the nature of the latter species and the difference in magnetic environments of phenyl protons above and below the metal-porphine mean plane is apparent. Similar environmental differences are considered responsible for the spectral features in Figure 1. The presence of axially coordinated ethanol in Ru(CO)(*i*-Pr-TPP) is evident from the spectral results in Figure 2. The methylene quartet and methyl triplet of ethanol (Figure 2A) are displaced *upfield* by 4.71 and 3.13 ppm, respectively, compared to the shifts of free ethanol in tetrachloroethane. These shifts are caused by the magnetic anisotropy of the porphine ring. The larger shift of the methylene resonance is consistent with coordination through oxygen, placing the methylene group closer to the ring and causing a larger diamagnetic shift than for the more remote methyl protons.[31] Addition of excess ethanol produced spectral features

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[31] For related examples, *cf.* J. E. Maskasky and M. E. Kenney, *J. Amer. Chem. Soc.*, **93**, 2060 (1971).

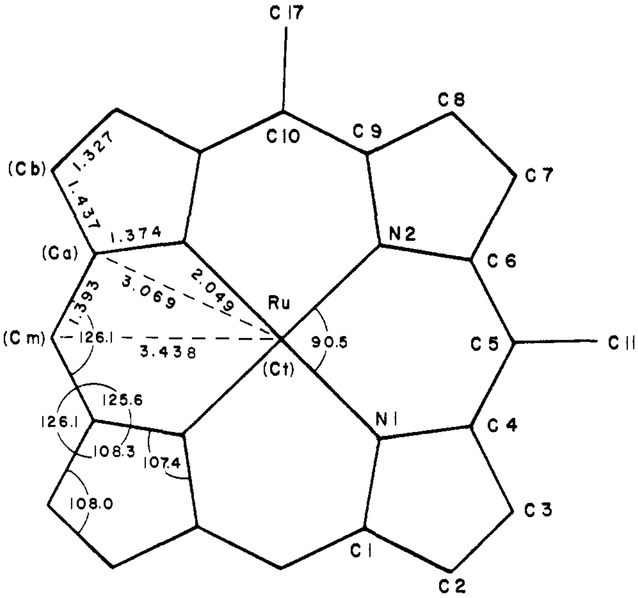

Figure 3. A sketch of the Ru(TPP) portion of the Ru(CO)(TPP)(EtOH) molecule showing the labeling scheme and principal distances and angles. The notation Ct, C_a, C_b, and C_m is that of Hoard.[27]

indicative of exchange between coordinated ethanol and that in the bulk solution. If the $Ru_3(CO)_{12}$–H_2(*i*-Pr-TPP) reaction product was recrystallized from THF–hexane instead of chloroform–ethanol, no proton resonances at higher fields than that of the *i*-Pr methyl doublet (Figure 2) were observed. Samples of Ru(CO)(*i*-Pr-TPP) which had not been exposed to alcohols were employed in our study of intra- and intermolecular ligand exchange reactions.[8,9]

The chemical and spectroscopic results just described are entirely consistent with the formulations Ru(CO)(TPP)(EtOH) and Ru(CO)(*i*-Pr-TPP)(EtOH). To provide definitive characterization the X-ray structure of the former has been determined.

Description of the Structure of Ru(CO)(TPP)(EtOH). On the basis of the analysis of the diffraction data described above there is no doubt that the material studied here is Ru(CO)(TPP)(EtOH). This formulation is completely consistent with the analytical and spectroscopic data as well.

Figure 3 is a sketch of the Ru(TPP) portion of the molecule, displaying the numbering scheme as well as principal bond distances and angles. Figure 4 is a drawing of the molecule with omission of the phenyl rings, and Figure 5 is a stereoscopic view of the entire molecule. Figure 5 illustrates very well the fact that the CO and C_2H_5OH portions of the molecule are shielded from intermolecular contacts by the phenyl rings, which are nearly perpendicular to the porphyrin plane. This provides a convenient rationale for the disorder between CO and EtOH in space group $P\bar{1}$. There are no unusual intermolecular contacts in the structure, the shortest being H···H contacts of the order of 2.4 Å.

Table VIII lists important distances and angles in the molecule, while Table IX presents details on the least-squares plane through the porphine skeleton. Hoard[27] has admirably summarized the geometries of the porphyrin core in a number of metalloporphyrins.

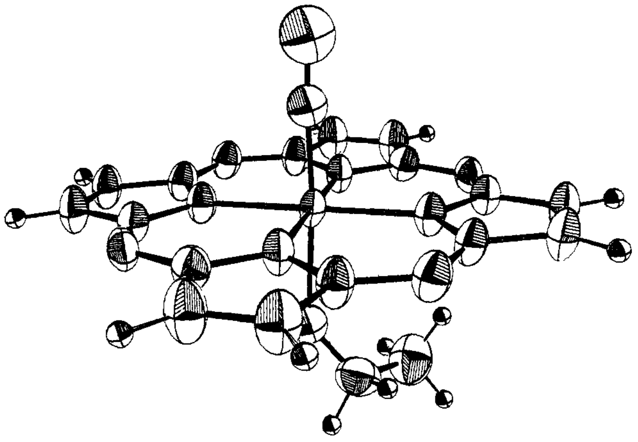

Figure 4. A drawing of the Ru(CO)(TPP)(EtOH) molecule with the phenyl rings omitted for the sake of clarity. Nonhydrogen atoms are drawn at their 50% probability ellipsoids. The hydrogen atoms have been drawn artificially small.

With the possible exception of the C_b–C_b distance found here, the distances presented in Figure 3 and Table VIII all fall within the range described by Hoard.[27] The C_b–C_b distance appears to be about 0.03 Å shorter than previously found. The Ru–N (or Ct···N) distance of 2.049 (5) Å is within the range of 1.960–2.099 Å discussed by Hoard.[27] This Ru(II)–N distance is significantly shorter than that of 2.144 (4) Å found earlier[32] in $[Ru(NH_3)_6]^{2+}$.

The deviations from planarity of the porphyrin skeleton (Table IX), though significant, are comparable with those found in (piperidine)$_2$ Fe(TPP)[29] and are small compared with the deviations found in some metalloporphyrins.[27]

The errors on the Ru–CO and Ru–EtOH portions of the molecule are large, as a result of the disorder of the CO and EtOH groups and the difficulty of describing this disorder in a completely adequate manner. Nevertheless, the results seem very reasonable. The Ru–O(Et) distance of 2.21 (2) Å may be compared with the corresponding Ni(II)–O(Et) distance of 2.099 (9) Å in the six-coordinate Ni(II) complex $[Ni(OMe)(sal)(EtOH)]_4$ (sal = *o*-O·C_6H_4·CHO).[33] The bond distances in the C_2H_5OH moiety and the bond angles in the Ru–O–C–C portion of the molecule do not differ significantly from those in the Ni structure.[33] It is particularly pleasing to find experimentally the expected staggering of the methylene and methyl hydrogen atoms of the ethanol group.

The Ru–C(CO) distance of 1.77 (2) Å seems reasonable. For example, the comparable distance in $Cs_2[RuCl_4(H_2O)(CO)]$ is 1.804 (15) Å.[34] The fact that the Ru–C–O bond angle is 175.8 (1.9)° is comforting, for it is in marked contrast to the most unusual "bent" Ru–C–O bond angle of 153.3 (9)° found by Cullen, *et al.*[10]

One might have expected the Ru atom, bonded as it is strongly to CO and weakly to EtOH, to be out of the plane of the porphyrin ring. In the present instance it is restricted to the plane by the imposed crystallographic symmetry, and so possible deviations from

(32) H. C. Stynes and J. A. Ibers, *Inorg. Chem.*, 10, 2304 (1971).

(33) J. E. Andrew and A. B. Blake, *J. Chem. Soc. A*, 1456 (1969).

(34) J. A. Stanko and S. Chaipayungpundhu, *J. Amer. Chem. Soc.*, **92**, 5580 (1970).

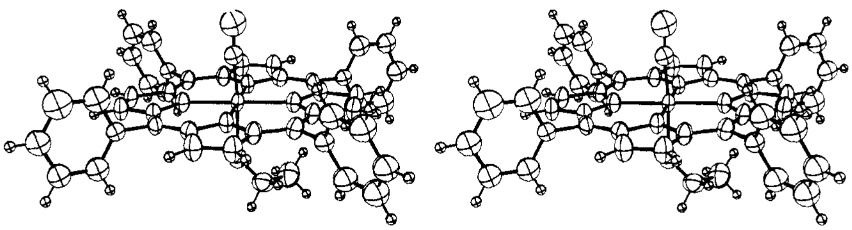

Figure 5. A stereoview of the Ru(CO)(TPP)(EtOH) molecule with nonhydrogen atoms drawn at their 50% probability ellipsoids and hydrogen atoms drawn artificially small.

Table VIII. Selected Bond Distances (Å) and Angles (deg)

Ru–N(1)	2.051 (5)	Ct···N[a]	2.049 (5)[b]	C(1)–C(2)	1.445 (9)	C_a–C_b	1.437 (13)
Ru–N(2)	2.048 (5)			C(3)–C(4)	1.420 (9)		
Ru–C(1)	3.068 (7)	Ct···C_a	3.069 (7)	C(6)–C(7)	1.450 (9)		
Ru–C(4)	3.069 (7)			C(8)–C(9)	1.432 (10)		
Ru–C(6)	3.065 (7)			C(2)–C(3)	1.339 (10)	C_b–C_b	1.327 (12)
Ru–C(9)	3.072 (7)			C(7)–C(8)	1.314 (10)		
Ru–C(5)	3.426 (6)	Ct···C_m	3.438 (11)	C(1)–C(10′)[c]	1.388 (10)	C_a–C_m	1.393 (10)
Ru–C(10)	3.449 (7)			C(4)–C(5)	1.396 (9)		
Ru–C(CO)	1.77 (2)			C(5)–C(6)	1.383 (9)		
Ru–O(Et)	2.21 (2)			C(9)–C(10)	1.404 (10)		
Ru–C(α,Et)	3.24 (2)			C(5)–C(11)	1.506 (9)		
Ru–C(β,Et)	3.93 (2)			C(10)–C(17)	1.506 (9)		
N(1)–C(1)	1.366 (8)	N–C_a	1.374 (8)	C(CO)–O(CO)	1.16 (3)		
N(1)–C(4)	1.377 (8)			O(Et)–C(α,Et)	1.30 (3)		
N(2)–C(6)	1.380 (8)			C(α,Et)–C(β,Et)	1.53 (3)		
N(2)–C(9)	1.371 (8)						
Ru–N(1)–C(1)	126.6 (4)	Ct···N–C_a	126.3 (4)	N(1)–Ru–N(2)	90.5 (2)	N···Ct···N	90.0 (5)
Ru–N(1)–C(4)	126.0 (4)			N(1)–Ru–N(2′)	89.5 (2)		
Ru–N(2)–C(6)	125.7 (4)			C(9)–C(10)–C(1′)	125.4 (6)	C_a–C_m–C_a	126.1 (6)
Ru–N(2)–C(9)	126.8 (4)			C(4)–C(5)–C(6)	126.7 (6)		
N(1)–C(1)–C(2)	108.6 (6)	N–C_a–C_b	108.3 (6)	C(3)–C(4)–C(5)	126.3 (6)	C_m–C_a–C_b	126.1 (7)
N(1)–C(4)–C(3)	108.4 (6)			C(2)–C(1)–C(10′)	125.1 (6)		
N(2)–C(6)–C(7)	107.5 (6)			C(5)–C(6)–C(7)	126.8 (6)		
N(2)–C(9)–C(8)	108.6 (6)			C(8)–C(9)–C(10)	126.0 (6)		
C(1)–N(1)–C(4)	107.5 (5)	C_a–N–C_a	107.4 (5)	N(1)–Ru–C(CO)	91.7 (8)		
C(9)–N(2)–C(6)	107.4 (6)			N(1′)–Ru–C(CO)	88.3 (8)		
C(6)–C(7)–C(8)	108.2 (6)	C_a–C_b–C_b	108.0 (8)	N(2)–Ru–C(CO)	86.2 (7)		
C(7)–C(8)–C(9)	108.3 (6)			N(2′)–Ru–C(CO)	93.8 (7)		
C(1)–C(2)–C(3)	106.8 (6)			N(1)–Ru–O(Et)	93.7 (4)		
C(2)–C(3)–C(4)	108.7 (6)			N(1′)–Ru–O(Et)	86.3 (4)		
N(1)–C(1)–C(10′)	126.2 (6)	N–C_a–C_m	125.6 (6)	N(2)–Ru–O(Et)	91.0 (4)		
N(1)–C(4)–C(5)	125.2 (6)			N(2′)–Ru–O(Et)	89.0 (4)		
N(2)–C(6)–C(5)	125.7 (6)			Ru–C(CO)–O(CO)	175.8 (1.9)		
N(2)–C(9)–C(10)	125.4 (6)			Ru–O(Et)–C(α,Et)	132.6 (1.4)		
Ru–N(1)–N(2)/C(11)–C(12)–C(13)[d]	−87.9			O(Et)–C(α,Et)–C(β,Et)	115.8 (1.7)		
Ru–N(1)–N(2)/C(17)–C(18)–C(19)[d]	−77.6						

[a] The designations Ct, C_a, C_b, and C_m are adopted from ref 27. [b] The number in parentheses is the standard deviation of *a single observation* and is the larger of that estimated from the individual errors or from the deviations of the individual values from the mean on the assumption that the values averaged are from the same population. The general agreement between these two estimates is a strong indication that the standard deviations derived from the least-squares procedure are reasonable. [c] Primed atoms are related to unprimed atoms by the center of inversion. [d] These are vectors between the normals formed from the planes defined by the two groups of three atoms.

Table IX. Weighted Least-Squares Plane through the Porphyrin Ring

Plane Equation: $9.781x + 4.637y - 4.435z = 0$ (triclinic coordinates)

Atom	Deviation, Å	Atom	Deviation, Å
N(1)	−0.008 (7)	C(5)	0.056 (9)
N(2)	0.019 (7)	C(6)	0.024 (9)
C(1)	0.002 (9)	C(7)	0.006 (10)
C(2)	−0.045 (10)	C(8)	−0.042 (10)
C(3)	−0.019 (10)	C(9)	−0.033 (9)
C(4)	−0.011 (9)	C(10)	−0.028 (9)

the plane must take the form of excessive vibrations normal to the plane. The root-mean-square amplitude of vibration of the Ru atom in this direction, 0.225 (1) Å, is not excessive. This suggests that any genuine deviation of the Ru atom from the porphyrin plane is quite small.

Comparison with the Results of Cullen, *et al.*[10] Chemical and analytical evidence strongly suggests that the present structure investigation has been carried out on crystalline material of the same composition as that studied by Cullen, *et al.*[10] The unit cell data, presented in Table II, show deviations that are significant when compared with the results of Cullen, *et al.*[10] Without further details on their determination of cell parameters, it is difficult to do more than speculate on a possible reason why the cells are not in better agreement. If Cullen, *et al.*,[10] used the standard Syntex software logic for the determination of their cell constants on a Datex-Syntex diffractometer, then possibly significant differences could arise. Because that software employs a scan technique with wide-open counter aperture to obtain the setting angles for a given reflection, one does not isolate the Kα_1 line, but rather uses some mixture of the Kα_1 and Kα_2 lines, depending upon the angle 2θ. It is thus possible to introduce small, but systematic, errors into the cell determination carried out in this way because of the dispersion of the α_1,α_2 doublet.

Perhaps an indication that the two structure determinations were carried out on the same material can be obtained by asking what results we would have obtained if we had failed to find the β-C atom of the C_2H_5OH group. We then would have determined a Ru–C(of CO) distance which would be the weighted average of the Ru–C(of CO) distance of 1.77 Å and the Ru–O(of Et) distance of 2.21 Å. If we weight these two distances in the ratio of 6 to 8, corresponding roughly to the relative scattering powers of C and O, we obtain an "Ru–C" distance of 2.03 Å, which compares favorably with that of 2.04 (1) Å found by Cullen, *et al.*[10] Similarly if we assume that the position of the O atom of the CO will be such as to account both for the O atom of the CO and for the α-C atom of the EtOH, we would expect an "Ru–C–O" angle that is approximately the average of the true Ru–C–O angle of 176° and of the Ru–O(Et)–C(α,Et) angle of 133°, namely 154°, almost exactly the 153.3(9)° angle found by Cullen, *et al.*, for their unprecedented "bent Ru–C–O." Of course, a crystallographic proof of our contention that Cullen, *et al.*,[10] determined the structure of the same material but failed to find the β-C atom of the EtOH group must come from their diffraction data, which are, as yet, unpublished.

The collective evidence from the chemical, spectroscopic, and diffraction studies described here leaves no doubt, in our opinion, that the products of the reactions between $Ru_3(CO)_{12}$ and tetraphenylporphines recrystallized from chloroform–ethanol are authentic monocarbonyls. The claim[10] of the existence of $Ru(CO)_2$(TPP), obtained in this manner, is considered incorrect. The compound identified in this work as Ru(CO)(TPP)(EtOH) is apparently the same as that prepared from $[Ru(CO)_3Cl_2]_2$ by Chow and Cohen.[5] We conclude that the Ru(CO)(*i*-Pr-TPP) species employed in our previous nmr studies[8,9] of ligand exchange was not a dicarbonyl and did not contain ethanol, for it had not been exposed to this solvent at any point during preparation or purification. There remain the possibilities that the species was five-coordinate or that the sixth coordination position was occupied by water or some other adventitious impurity. If the latter situation obtained, the ligand exchange process (reaction 1) would presumably involve initial displacement of an axial ligand with a nitrogenous base L. However, the kinetic results[8,9] for exchange of L are unaffected.

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