stretching frequencies are high, indicating that π back-bonding may be minor, a similar argument may be used. On replacing the platinum methyl group trans to the carbonyl by a chloro substituent, ν(CO) increases from 2085 to 2104 cm^{-1} while $\delta_{C(carbonyl)}$ changes from 178.7 to 159.3 ppm. Concomitant with the increased carbon–oxygen bond order is an increased paramagnetic screening of the carbon nucleus.

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Structure of (Tetraphenylporphinato)(carbonyl)(pyridine)ruthenium(II)–1.5-Toluene

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Abstract: The crystal structure of Ru(CO)(py)(TPP) has been determined from three-dimensional X-ray diffraction data. The compound crystallizes in the triclinic space group C_i^1-$P\bar{1}$ (a = 11.665 (1), b = 19.667 (2), c = 10.758 (2) Å; α = 92.22 (1), β = 93.32 (1), γ = 96.50 (1)°; Z = 2), with three toluene molecules of crystallization. Least-squares refinement has led to a final value of the conventional R factor (on F) of 0.065 for the 4617 reflections having $F_o^2 > 3\sigma(F_o^2)$. The Ru(II) atom is 0.079 Å out of the porphyrin plane toward the carbonyl carbon atom. The Ru–C–O angle is 178.4 (7)° and the Ru–CO distance is 1.838 (9) Å. The Ru–N(pyridine) distance is 2.193 (4) Å, compared with the average Ru–N(porphyrin) distance of 2.052 (9) Å. The long axial Ru–N(py) bond length is attributed to a trans effect of the carbonyl group. The bond lengths and angles within the porphyrin compare well with those observed previously in Ru(CO)(EtOH)(TPP).

This study of carbonyl complexes of metalloporphyrins is of general importance with respect to the carbonyl complexes of the corresponding Fe hemes. The position of the metal relative to the mean plane of the porphyrin and the effect, if any, of the carbonyl group on the distance of the trans ligand from the metal are of import in developing models for conformational changes that may occur in hemoglobin on carbonylation. Although compounds of the type Fe(CO)(base)(porphyrin) have been prepared,[1,2] no crystal structures of these systems have yet appeared.

Although the chemistry of Ru and Fe porphyrins shows marked differences, both the Ru and Fe complexes of the type M(CO)(base)(porphyrin) are presumably pseudooctahedral low-spin diamagnetic complexes. Accordingly, studies of these systems, when M = Ru, are not totally unrelated to the biological models. Recently the structure of Ru(CO)(EtOH)(TPP)[3] was reported. In that study the linearity of the Ru–C–O linkage was demonstrated, but because of disorder problems the metrical details were necessarily inaccurate. The present study of Ru(CO)(py)(TPP) was undertaken to provide more reliable results on the relation of the metal to the mean porphine plane and on the trans labilizing effect of the CO on the axial base.

Experimental Section

A sample of Ru(CO)(py)(TPP), [$RuC_{49}H_{32}N_5O$], was prepared according to literature methods[3,4] and was kindly supplied by Professor R. H. Holm. Suitable crystals were obtained by dissolving this material in boiling toluene, diluting with ether, and then allowing this solution to evaporate slowly over a period of months. On the basis of the present structural study, the compound thus obtained is Ru(CO)(py)(TPP)·1.5toluene. Preliminary precession photographs taken with Cu Kα radiation showed only the required center of symmetry and hence the space group is either $P1$ or $P\bar{1}$. The crystal selected for data collection was a pseudoparallelepiped with major bounding faces of the forms {110}, {010}, {001}, and minor faces, {100}. The distances between the faces of these forms are 0.116, 0.198, 0.553, and 0.205 mm. The crystal was mounted with the c^* axis approximately along the spindle axis.

The lattice parameters, obtained as previously described[6] by hand centering of 13 reflections with Cu Kα_1 radiation in the range $60 \leq 2\theta \leq 65°$, are a = 11.665 (1) Å, b = 19.667 (2) Å, c = 10.758 (2) Å, α = 92.22 (1)°, β = 93.32 (1)°, and γ = 96.50 (1)°. The calculated density, based on two molecules of porphyrin complex and three of toluene per unit cell, is 1.29 g/cm^3 and agrees well with an observed value of 1.30 (1) g/cm^3, as measured by flotation in aqueous zinc chloride solution.

Data were collected in shells of 2θ by the θ–2θ scan method using Cu Kα radiation prefiltered with Ni foil. The scan range in 2θ was from 0.9° below the Cu Kα_1 peak to 0.9° above the Cu Kα_2 peak. The takeoff angle was 3.0° and the receiving counter was positioned 32 cm from the crystal with an aperture 5.0 mm high and 5.0 mm wide. The pulse height analyzer was set to admit about 90% of the Cu Kα peak. Initially background counts of

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[4] The compound Ru(CO)(py)(OEP) (OEP = octaethylporphyrin) has also been prepared.[5] We have found that it crystallizes in the triclinic space group $P1$ or $P\bar{1}$: a = 9.85, b = 10.82, c = 7.54 Å; α = 97.7, β = 106.9, γ = 93.2°; Z = 1 (precession photographs).

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Table II. Atomic Parameters for Ru(CO)(py)(TPP)–1.5-Toluene

Atom	x	y	z	B, Å^2 or β_{11}^{a}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ru	0.17458 (4)^b	−0.23931 (3)	0.11858 (5)	651 (5)	197 (2)	835 (7)	50 (2)	84 (4)	38 (2)
N(1)	0.2201 (5)	−0.3281 (3)	0.0378 (6)	75 (5)	22 (2)	96 (7)	5 (2)	6 (5)	2 (3)
N(2)	0.2530 (5)	−0.1842 (3)	−0.0179 (5)	76 (5)	22 (2)	93 (7)	4 (2)	7 (5)	8 (3)
N(3)	0.1370 (5)	−0.1497 (3)	0.2037 (5)	69 (5)	21 (2)	91 (7)	8 (2)	6 (5)	3 (3)
N(4)	0.1100 (5)	−0.2933 (3)	0.2620 (5)	71 (5)	26 (2)	86 (7)	6 (2)	6 (5)	6 (3)
N(5)	0.3422 (3)	−0.2259 (2)	0.2251 (4)	3.9 (1)					
O	−0.0555 (5)	−0.2545 (3)	−0.0212 (6)	80 (5)	42 (2)	163 (8)	8 (3)	−31 (5)	2 (3)
C(1)	0.1991 (6)	−0.3920 (4)	0.0826 (7)	72 (6)	21 (2)	105 (9)	5 (3)	7 (6)	4 (4)
C(2)	0.2420 (7)	−0.4398 (4)	−0.0035 (8)	101 (8)	22 (2)	123 (10)	9 (3)	6 (7)	−1 (4)
C(3)	0.2873 (7)	−0.4054 (4)	−0.0966 (8)	107 (8)	24 (3)	116 (10)	14 (4)	23 (7)	−1 (4)
C(4)	0.2735 (6)	−0.3334 (4)	−0.0716 (7)	77 (7)	27 (3)	91 (9)	10 (3)	9 (6)	−0 (4)
C(5)	0.3120 (6)	−0.2800 (4)	−0.1445 (7)	77 (7)	27 (3)	87 (8)	9 (3)	10 (6)	0 (4)
C(6)	0.3041 (6)	−0.2105 (4)	−0.1189 (7)	80 (7)	26 (3)	81 (8)	8 (3)	19 (6)	3 (4)
C(7)	0.3446 (7)	−0.1545 (4)	−0.1932 (7)	93 (8)	30 (3)	98 (9)	10 (4)	23 (6)	9 (4)
C(8)	0.3185 (7)	−0.0972 (4)	−0.1392 (7)	91 (7)	25 (3)	107 (9)	4 (3)	18 (7)	14 (4)
C(9)	0.2602 (6)	−0.1151 (4)	−0.0278 (7)	67 (6)	24 (2)	94 (8)	5 (3)	5 (6)	7 (4)
C(10)	0.2179 (6)	−0.0681 (3)	0.0545 (7)	62 (6)	20 (2)	111 (9)	4 (3)	−2 (6)	8 (4)
C(11)	0.1605 (6)	−0.0856 (4)	0.1610 (7)	65 (6)	25 (2)	88 (8)	4 (3)	0 (6)	4 (4)
C(12)	0.1169 (7)	−0.0370 (4)	0.2462 (8)	84 (7)	22 (2)	113 (9)	10 (3)	5 (6)	−1 (4)
C(13)	0.0689 (6)	−0.0730 (4)	0.3373 (7)	81 (7)	29 (3)	91 (8)	9 (3)	7 (6)	−3 (4)
C(14)	0.0816 (6)	−0.1441 (4)	0.3116 (7)	68 (6)	23 (2)	87 (8)	6 (3)	1 (6)	−3 (3)
C(15)	0.0455 (6)	−0.1977 (4)	0.3873 (7)	67 (6)	29 (3)	84 (8)	6 (3)	5 (6)	2 (4)
C(16)	0.0602 (6)	−0.2668 (4)	0.3634 (7)	71 (6)	27 (3)	90 (8)	5 (3)	5 (6)	5 (4)
C(17)	0.0249 (7)	−0.3222 (4)	0.4409 (8)	95 (8)	33 (3)	106 (9)	4 (4)	25 (7)	12 (4)
C(18)	0.0520 (7)	−0.3805 (4)	0.3886 (8)	103 (8)	27 (3)	106 (9)	6 (4)	14 (7)	7 (4)
C(19)	0.1072 (6)	−0.3629 (4)	0.2746 (7)	74 (7)	23 (2)	103 (9)	1 (3)	1 (6)	13 (4)
C(20)	0.1474 (6)	−0.4094 (3)	0.1914 (7)	72 (6)	17 (2)	110 (9)	1 (3)	1 (6)	5 (4)
C(50)	0.0332 (7)	−0.2493 (3)	0.0312 (7)	87 (8)	19 (2)	98 (9)	4 (3)	24 (7)	6 (3)
C(21)^c	0.1326 (5)	−0.4830 (2)	0.2224 (5)	4.2 (2)					
C(22)	0.2214 (4)	−0.5099 (3)	0.2892 (6)	7.7 (2)					
C(23)	0.2121 (5)	−0.5796 (3)	0.3111 (6)	9.0 (3)					
C(24)	0.1140 (6)	−0.6223 (2)	0.2661 (6)	6.5 (2)					
C(25)	0.0253 (5)	−0.5954 (3)	0.1992 (6)	7.7 (2)					
C(26)	0.0346 (4)	−0.5258 (3)	0.1774 (5)	6.6 (2)					
C(27)	0.3705 (5)	−0.2980 (3)	−0.2588 (5)	4.6 (2)					
C(28)	0.3056 (4)	−0.3234 (3)	−0.3666 (6)	6.8 (2)					
C(29)	0.3608 (6)	−0.3418 (4)	−0.4720 (5)	9.0 (3)					
C(30)	0.4810 (6)	−0.3349 (4)	−0.4696 (5)	8.6 (3)					
C(31)	0.5459 (4)	−0.3095 (4)	−0.3617 (7)	8.4 (3)					
C(32)	0.4907 (5)	−0.2911 (3)	−0.2563 (5)	6.4 (2)					
C(33)	0.2363 (4)	0.0058 (2)	0.0236 (5)	3.9 (1)					
C(34)	0.3387 (4)	0.0463 (3)	0.0625 (5)	6.0 (2)					
C(35)	0.3548 (4)	0.1148 (3)	0.0328 (6)	7.0 (2)					
C(36)	0.2684 (5)	0.1429 (2)	−0.0358 (6)	6.0 (2)					
C(37)	0.1661 (4)	0.1025 (3)	−0.0748 (5)	5.7 (2)					
C(38)	0.1500 (3)	0.0339 (2)	−0.0451 (5)	4.8 (2)					
C(39)	−0.0085 (5)	−0.1814 (3)	0.5050 (4)	4.0 (1)					
C(40)	−0.1274 (4)	−0.1799 (3)	0.5057 (5)	7.2 (2)					
C(41)	−0.1777 (4)	−0.1668 (3)	0.6170 (6)	8.3 (3)					
C(42)	−0.1092 (5)	−0.1552 (3)	0.7276 (5)	6.0 (2)					
C(43)	0.0098 (5)	−0.1567 (3)	0.7269 (4)	7.4 (2)					
C(44)	0.0601 (3)	−0.1698 (3)	0.6156 (5)	6.3 (2)					
C(45)	0.3568 (4)	−0.1893 (3)	0.3337 (5)	6.0 (2)					
C(46)	0.4621 (5)	−0.1766 (3)	0.4038 (4)	7.9 (3)					
C(47)	0.5583 (4)	−0.2033 (3)	0.3592 (6)	7.3 (2)					
C(48)	0.5447 (4)	−0.2416 (3)	0.2463 (6)	6.8 (2)					
C(49)	0.4355 (4)	−0.2513 (3)	0.1835 (4)	5.7 (2)					
C(51)	0.4192 (13)	0.4828 (8)	−0.3488 (15)	13.1 (4)					
C(52)	0.3806 (8)	0.4421 (4)	−0.2485 (7)	9.6 (3)					
C(53)	0.4481 (5)	0.4351 (4)	−0.1396 (9)	8.7 (3)					
C(54)	0.4024 (7)	0.3965 (5)	−0.0447 (7)	10.5 (3)					
C(55)	0.2892 (8)	0.3648 (4)	−0.0585 (8)	10.0 (3)					
C(56)	0.2218 (5)	0.3718 (4)	−0.1673 (9)	10.1 (3)					
C(57)	0.2675 (7)	0.4104 (4)	−0.2623 (7)	10.2 (3)					
C(58)	0.2744 (7)	0.0151 (8)	−0.4045 (15)	9.8 (3)					
C(59)	0.3925 (3)	0.0072 (4)	−0.4545 (7)	10.9 (7)					
C(60)	0.4876 (7)	0.0031 (5)	−0.3721 (1)	12.6 (4)					
C(64)	0.4049 (4)	0.0041 (5)	−0.5824 (6)	10.6 (4)					

Group^d	x_c	y_c	z_c	δ	ϵ	η
Phenyl 1	0.1233 (4)	−0.5527 (2)	0.2442 (4)	−1.562 (4)	−2.683 (4)	−2.946 (4)
Phenyl 2	0.4257 (4)	−0.3165 (2)	−0.3642 (4)	1.730 (4)	2.690 (4)	1.213 (4)
Phenyl 3	0.2524 (3)	0.0744 (2)	−0.0061 (3)	−1.594 (3)	−2.705 (3)	0.265 (4)
Phenyl 4	−0.0588 (3)	−0.1683 (2)	0.6163 (4)	1.527 (4)	2.693 (3)	−1.753 (4)
Pyridine	0.4500 (3)	−0.2147 (2)	0.2918 (3)	−2.516 (5)	2.320 (4)	2.407 (5)
Toluene 1	0.3350 (4)	0.4034 (3)	−0.1535 (4)	−0.989 (15)	2.719 (5)	2.601 (15)
Toluene 2	0.5000	0.0	−0.5000	1.351 (17)	1.992 (6)	1.578 (17)

Table II (*Footnotes*)

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}lk)]$. All of the anisotropic thermal parameters have been multiplied by 10^4, except those of the metal atom, which have been multiplied by 10^5. [b] Numbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant figures. [c] From C(21) on (except for C(51)), these atoms were treated as parts of groups. [d] The various group parameters have been defined previously. See S. J. La Placa and J. A. Ibers, *Acta Crystallogr.*, **18**, 511 (1965); R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965).

10 sec were taken at the end of each scan range. Past a 2θ of 49° this was increased to 20 sec, and finally it was increased to 40 sec for 2θ greater than 80°. A scan rate of 2° in 2θ per minute was used. Attenuators were automatically inserted if the intensity of the diffracted beam exceeded approximately 7000 counts per second during a scan. The attenuators were of Cu foil and gave attenuator factors of about 2.3. Data were collected in the range $0 < 2\theta \leq 103°$. Data collection was terminated when less than 30% of the measured reflections were statistically observable. During the course of data collection six standard reflections from diverse regions of reciprocal space were measured every 100 reflections. The deviations of these standards were all within counting statistics.

The data were processed as previously described[6] using a value of 0.04 for p. Of the 5697 reflections measured, 5338 are unique and of these 4617 have $F_o^2 > 3\sigma(F_o^2)$ and were used in subsequent refinements. Data were collected with $l > 0$, so Friedel pairs of the type $hk0$ were measured. Since these pairs of reflections deviate by only 1.1% from their average values, the centrosymmetric space group $P\bar{1}$ seems most probable. Sample calculations[7] for an absorption correction were made using a linear absorption coefficient of 30.02 cm^{-1}. The transmission factors calculated ranged from 0.44 to 0.73, and an absorption correction was therefore applied.

Solution and Refinement of the Structure. Normalized structure factors ($|E|$'s) scaled such that $\langle E^2\rangle = 1.0$ were calculated from the measured structure amplitudes. The statistical distribution of the $|E|$'s was examined and compared with the theoretical distributions for acentric and centric cases. The distribution found closely resembled that for a centric crystal, again suggesting that the correct space group is $P\bar{1}$.

Using the quantities $|E^2 - 1|$ a sharpened, origin removed Patterson map was calculated, and the positions of the ruthenium atom, the five ligand nitrogen atoms, and the carbonyl carbon atom were obtained. A subsequent difference Fourier map phased on these atomic positions revealed the position of the porphyrin molecule and toluene 1. The structure was refined as follows. The four phenyl groups of the porphyrin, the pyridine, and the toluene were idealized as groups. The dimensions of the pyridine were those reported by Bak, *et al.*[8] Least-squares refinement of the 28 independent atoms and the six groups, using isotropic temperature factors and a random half of the data, reduced R and R_w to 0.143 and 0.187.

The structure was refined by full-matrix least-squares techniques. 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 and the anomalous terms were taken from the usual sources.[9]

The H atoms of the phenyl groups and the pyrrole C_b-positions were idealized (C–H = 0.95 Å, B(H) = B(C) + 1.0 Å^2) and added as fixed contributions in subsequent refinements. One cycle of isotropic refinement and one of anisotropic refinement using all the data reduced R and R_w to 0.095 and 0.158. Examination of a difference Fourier map revealed a second toluene molecule disordered on a center at $^1/_2$, 0, $-^1/_2$. The second toluene molecule was then included as a six-atom group (four C atoms and two phenyl H atoms). Three cycles of anisotropic, full-matrix least-squares refinement of the 30 nongroup atoms and isotropic treatment of the seven groups (individual, isotropic temperature factors for the group atoms), converged with R and R_w equal to 0.065 and 0.089, respectively. Refinement was terminated at this point since the last cycle led to insignificant shifts in the atomic coordinates.

An analysis of $\Sigma w(|F_o| - |F_c|)^2$ as a function of setting angles, magnitude of $|F_o|$, and Miller indices showed no unusual trends. The standard deviation of an observation of unit weight is 3.23 e. A final difference Fourier map revealed the position of the methyl hydrogen atoms on toluene 1. Other peaks on the map (0.73–0.39 e/Å^3) were associated with the phenyl groups on the TPP.

A structure factor calculation for the 722 reflections having $F_o^2 < 3\sigma(F_o^2)$, which were omitted from the refinement, showed only 37 reflections having $|F_o^2 - F_c^2| > 3\sigma(F_o^2)$, and of these only ten having $\Delta F^2 > 4\sigma(F_o^2)$. These 722 reflections were omitted from Table I[10] where the values of $10|F_o|$ and $10|F_c|$ are given.

The final atomic parameters and their errors are listed in Table II. The calculated atomic parameters for the hydrogen atoms are given in Table III.[10] Table IV presents the root-mean-square amplitudes of thermal vibration.

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

Atom	Min	Inter	Max	Angle Γ,[a] deg
Ru	0.1937 (10)	0.2072 (9)	0.2232 (9)	38
N(1)	0.206 (9)	0.226 (8)	0.237 (9)	53
N(2)	0.198 (10)	0.228 (8)	0.238 (9)	61
N(3)	0.194 (9)	0.219 (8)	0.231 (8)	53
N(4)	0.213 (9)	0.218 (8)	0.232 (8)	53
O	0.211 (8)	0.284 (8)	0.328 (8)	85
C(1)	0.202 (11)	0.221 (10)	0.248 (10)	56
C(2)	0.203 (11)	0.262 (10)	0.269 (11)	71
C(3)	0.200 (12)	0.252 (12)	0.283 (10)	8
C(4)	0.209 (11)	0.234 (10)	0.239 (10)	53
C(5)	0.212 (11)	0.231 (10)	0.236 (10)	44
C(6)	0.201 (11)	0.223 (11)	0.245 (10)	12
C(7)	0.218 (11)	0.233 (11)	0.270 (10)	23
C(8)	0.197 (11)	0.246 (10)	0.267 (10)	35
C(9)	0.207 (11)	0.214 (10)	0.238 (10)	61
C(10)	0.192 (10)	0.203 (10)	0.260 (10)	71
C(11)	0.208 (10)	0.218 (11)	0.230 (11)	80
C(12)	0.201 (11)	0.241 (10)	0.259 (11)	70
C(13)	0.217 (11)	0.235 (10)	0.247 (11)	86
C(14)	0.204 (11)	0.213 (10)	0.234 (11)	96
C(15)	0.213 (10)	0.221 (11)	0.236 (11)	79
C(16)	0.219 (10)	0.223 (11)	0.235 (11)	70
C(17)	0.214 (12)	0.259 (11)	0.274 (10)	26
C(18)	0.224 (11)	0.247 (11)	0.268 (10)	4
C(19)	0.192 (12)	0.224 (10)	0.261 (11)	80
C(20)	0.178 (11)	0.222 (10)	0.256 (11)	73
C(50)	0.188 (11)	0.218 (10)	0.263 (11)	13

[a] Γ is the angle that the major axis of the vibrational ellipsoid makes with the normal to the least-squares plane through the porphyrin.

Description and Discussion of the Structure

The crystal structure consists of two discrete molecules of Ru(CO)(py)(TPP) and three toluene molecules of crystallizaton (see Figure 1). A single Ru(CO)(py)(TPP) molecule is illustrated in Figure 2, and Figure 3 presents the numbering scheme used through-

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(7) 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, Dewar's program FAME for Wilson statistics and generation of normalized structure factors. Our least-squares program, NUCLS, in its nongroup form, closely resembles the Busing and Levy ORFLS program. Final calculations were carried out by remote hook-up with the CDC 7600 at Lawrence Berkeley Laboratory. Programs used were very minor modifications of the above.

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Table V. Bond Distances (Å) and Angles (deg) in Ru(CO)(py)(TPP)

Ru-N(1)	2.057 (6)	Ru-N 2.052 (9)[a]	C(2)-C(3)	1.332 (11)	C_b-C_b 1.333 (9)
Ru-N(2)	2.055 (6)		C(7)-C(8)	1.322 (10)	
Ru-N(3)	2.058 (5)		C(12)-C(13)	1.343 (11)	
Ru-N(4)	2.038 (6)		C(17)-C(18)	1.335 (10)	
Ru-N(5)	2.193 (4)		C(1)-C(20)	1.385 (10)	C_a-C_m 1.395 (8)
Ru-C(50)	1.838 (9)		C(4)-C(5)	1.385 (10)	
O-C(50)	1.141 (10)		C(5)-C(6)	1.398 (10)	
N(1)-C(1)	1.365 (9)	N-C_a[b] 1.370 (8)	C(9)-C(10)	1.403 (10)	
N(1)-C(4)	1.369 (9)		C(10)-C(11)	1.395 (10)	
N(2)-C(6)	1.380 (9)		C(14)-C(15)	1.398 (10)	
N(2)-C(9)	1.361 (8)		C(15)-C(16)	1.406 (10)	
N(3)-C(11)	1.362 (9)		C(19)-C(20)	1.393 (10)	
N(3)-C(14)	1.368 (9)		C(20)-C(21)	1.491 (8)	C_m-C_{phenyl} 1.491 (6)
N(4)-C(16)	1.378 (9)		C(5)-C(27)	1.490 (10)	
N(4)-C(19)	1.378 (9)		C(10)-C(33)	1.499 (8)	
C(1)-C(2)	1.443 (10)	C_a-C_b 1.446 (8)	C(15)-C(39)	1.485 (9)	
C(3)-C(4)	1.459 (10)		C(51)-C(52)	1.432 (18)	
C(6)-C(7)	1.440 (10)				
C(8)-C(9)	1.448 (10)				
C(11)-C(12)	1.451 (10)				
C(13)-C(14)	1.441 (10)				
C(16)-C(17)	1.435 (10)				
C(18)-C(19)	1.453 (11)				
N(1)-Ru-N(2)	89.8 (2)		C(1)-N(1)-C(4)	108.4 (6)	C_a-N-C_a 107.8 (4)
N(1)-Ru-N(3)	177.2 (2)		C(6)-N(2)-C(9)	107.4 (6)	
N(1)-Ru-N(4)	89.8 (2)		C(11)-N(3)-C(14)	107.9 (6)	
N(2)-Ru-N(3)	89.8 (2)		C(16)-N(4)-C(19)	107.6 (6)	
N(2)-Ru-N(4)	175.2 (2)		N(1)-C(1)-C(2)	107.8 (6)	N-C_a-C_b 108.3 (8)
N(3)-Ru-N(4)	90.3 (2)		N(1)-C(4)-C(3)	108.2 (6)	
N(5)-Ru-N(1)	88.7 (2)		N(2)-C(6)-C(7)	108.2 (6)	
N(5)-Ru-N(2)	87.5 (2)		N(2)-C(9)-C(8)	108.6 (6)	
N(5)-Ru-N(3)	88.5 (2)		N(3)-C(11)-C(12)	108.6 (6)	
N(5)-Ru-N(4)	87.7 (2)		N(3)-C(14)-C(13)	108.6 (6)	
C(50)-Ru-N(1)	92.3 (3)		N(4)-C(16)-C(17)	108.2 (6)	
C(50)-Ru-N(2)	90.5 (3)		N(4)-C(19)-C(18)	108.4 (7)	
C(50)-Ru-N(3)	92.7 (3)		C(1)-C(2)-C(3)	108.8 (7)	C_a-C_b-C_b 107.8 (8)
C(50)-Ru-N(4)	92.1 (3)		C(2)-C(3)-C(4)	106.7 (7)	
C(50)-Ru-N(5)	178.9 (3)		C(6)-C(7)-C(8)	108.2 (7)	
Ru-C(50)-O	178.4 (7)		C(7)-C(8)-C(9)	107.7 (7)	
N(1)-C(1)-C(20)	127.2 (7)	N-C_a-C_m 126.4 (5)	C(11)-C(12)-C(13)	107.1 (6)	
N(1)-C(4)-C(5)	126.5 (6)		C(12)-C(13)-C(14)	107.7 (7)	
N(2)-C(6)-C(5)	125.7 (7)		C(16)-C(17)-C(18)	108.9 (7)	
N(2)-C(9)-C(10)	126.5 (7)		C(17)-C(18)-C(19)	108.9 (7)	
N(3)-C(11)-C(10)	126.6 (7)		C(4)-C(5)-C(6)	126.0 (7)	C_a-C_m-C_a 125.0 (6)
N(3)-C(14)-C(15)	126.4 (6)		C(9)-C(10)-C(11)	124.8 (6)	
N(4)-C(16)-C(15)	126.3 (7)		C(14)-C(15)-C(16)	124.8 (7)	
N(4)-C(19)-C(20)	126.3 (7)		C(19)-C(20)-C(1)	124.6 (6)	
			C(51)-C(52)-C(57)	116.2 (9)	
			C(51)-C(52)-C(53)	123.7 (9)	

[a] The figure in parentheses following mean values of bond distances in this table is the standard deviation of an *individual* distance as calculated on the assumption that the values averaged are from the same population. With the possible exception of the Ru-N distances, the agreement between the two estimates of standard deviations of individual distances supports the hypotheses that (1) the distances averaged are indeed equivalent and (2) that the standard deviations estimated from the inverse matrix are reasonable. [b] The notation C_a, C_b, C_m, and Ct is that of Hoard.[12]

out this paper. Bond distances and angles are given in Table V.

In the porphyrin complex the geometry of the TPP moiety is very similar to that found in other metalloporphyrins.[11,12]

The averaged bond distances and angles for the four, crystallographically nonequivalent pyrrole rings are presented in Figure 4. They agree within experimental error with those found previously for Ru(CO)(EtOH)(TPP).[3] The porphyrin ring is slightly puckered, as is shown in Figure 5. The puckering has a C_2 distribution and manifests itself in distortions about the methine (C_m) carbons. As shown by the data in Table VI the individual pyrroles are strictly planar, but adjacent methine carbon atoms deviate from these planes by 0.01–0.04 Å.

The C_b-C_b bond distance of 1.333 (9) Å is marginally shorter than the average C_b-C_b bond distance of 1.358 Å given by Hoard,[12] but agrees with that of 1.327 (12) Å found in Ru(CO)(EtOH)(TPP).[3] Similarly short C_b-C_b bond lengths have been reported in Fe(PP-IX)Cl,[13] 1.334 (8) Å, and in Cu(TPP),[14] 1.337 (14) Å. The short bond length in Ru(CO)(py)(TPP) may, however, be an artifact of the data set used in the refinement of the structure. Hoard, *et al.*,[15] have demonstrated that a limited data set, or alternatively an inadequate treatment of the low order data, can significantly affect experimentally determined bond lengths.

The environment of the central metal atom is that

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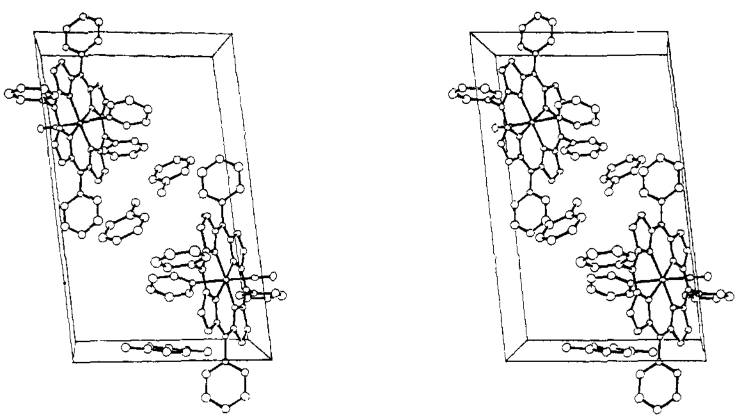

Figure 1. Stereoscopic view of the contents of one unit cell. The view is approximately along the *z* axis.

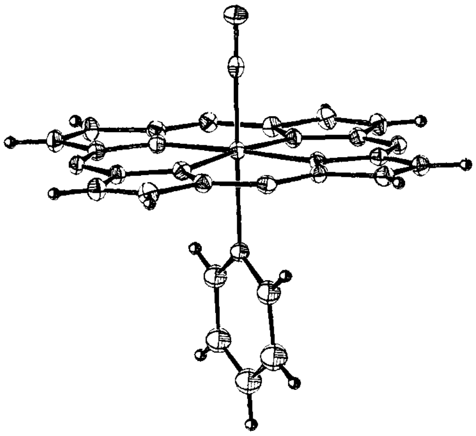

Figure 2. A drawing of the Ru(CO)(py)(TPP) molecule, with the phenyl groups omitted for clarity. The thermal ellipsoids are drawn at the 50% probability level. The hydrogen atoms have been drawn artificially small for the sake of clarity.

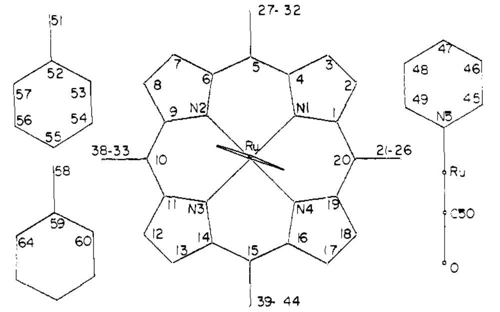

Figure 3. Diagram to indicate the numbering sequence used in this paper for the 67 independent, nonhydrogen atoms. The toluene located at the general position has been called toluene 1, and that sitting on a center of symmetry at $^1/_2$, 0, $-^1/_2$, toluene 2. The carbon atoms are indicated by a number only.

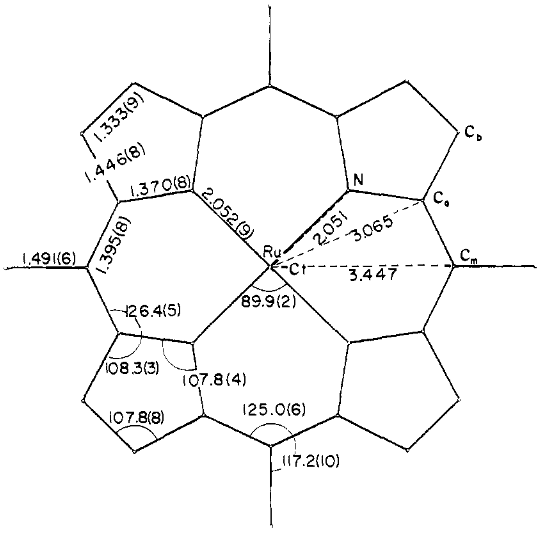

Figure 4. Diagram giving the averaged (D_{4h}) bond distances (Å) and angles (deg) in the porphyrin skeleton of the Ru(CO)(py)(TPP) molecule. The averaged values for the quantities Ct–N, Ct–C_a, and Ct–C_m, as defined by Hoard,[12] are also given. The numbers in parentheses are the standard deviation of an individual distance or angle, as defined in Table V.

of an axially distorted octahedron. The four equivalent Ru–N(pyrrole) distances average to 2.052 (9) Å, which compares well with the distance of 2.049 (2) Å found previously.[3] The axial Ru–N(pyridine) bond distance is 2.193 (4) Å. This bond length may be compared with the Ru–N distances of 2.066 (7) and 2.095 (7) Å found for the equatorial and axial pyridine ligands in the complex ([(Ru(py)$_4$)$_2$(C$_2$O$_4$)](BF$_4$)$_2$[16] and with the Ru–N(NH$_3$, en) distances of 2.12–2.14 Å found in the complexes surveyed by Stynes and Ibers[17] and in *trans*-[Ru(NH$_3$)$_4$(SO$_2$)Cl][BF$_4$],[18] in [Ru(NH$_3$)$_5$(DMSO)][PF$_6$]$_2$,[19] and in *trans*-[Ru(NH$_3$)$_4$(C$_5$H$_8$N$_2$)(CO)][PF$_6$].[20] The longer bond lengths in the Ru-ammines,[17–20] compared with those in [Ru(py)$_4$]$_2$(C$_2$O$_4$)$^{2+}$, are consistent with the expected differences in the effective radii of sp^2 and sp^3 hybridized N atoms. In light of this, the Ru–N distance of 2.193 (4) Å observed in Ru(CO)(py)(TPP) is really quite long, and certainly is indicative of a lack of π-bonding[21] between the ruthenium and the axial pyridine. The long ruthenium–pyridine bond length is also consistent with the kinetic lability of the axial ligand, as observed by Eaton, *et al.*[22]

The pyridine ring is perpendicular to the plane of the

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Table VI. Deviations (Å) (×10³) and Equations of Weighted Least-Squares Planes

Atom	Plane 1	Plane 2	Plane 3	Plane 4	Plane 5	Plane 6	Plane 7	Plane 8
Ru	−68[a]	−79	0 (0)	0 (0)	−43	−58	−53	−29
N(5)			−9 (4)	−2 (4)				
C(50)			−26 (7)	−6 (8)				
N(1)	−18 (6)	−30 (6)		5 (6)	0 (6)	1 (5)		
C(1)		−12 (7)			0 (7)			
C(2)		−15 (8)			−1 (8)			
C(3)		−33 (8)			2 (8)			
C(4)		−47 (7)			−2 (7)			
C(5)		−31 (7)			36	−30		
N(2)	18 (6)	13 (6)	4 (6)			1 (5)		
C(6)		16 (7)				−1 (7)		
C(7)		44 (8)				1 (8)		
C(8)		54 (7)				0 (7)		
C(9)		34 (7)				−1 (7)		
C(10)		25 (7)				−13	21	
N(3)	−17 (5)	−28 (5)		4 (6)			−2 (5)	
C(11)		−12 (7)					2 (7)	
C(12)		−19 (8)					0 (8)	
C(13)		−38 (7)					−2 (7)	
C(14)		−38 (7)					3 (7)	
C(15)		−16 (7)					42	−3
N(4)	18 (5)	1 (5)	4 (6)					−2 (5)
C(16)		13 (7)						2 (7)
C(17)		52 (8)						2 (8)
C(18)		60 (8)						−4 (8)
C(19)		37 (7)						4 (7)
C(20)		21 (7)			13			−14

Coefficients of the Plane Equation $Ax + By + Cz = D$[b]

Plane	A	B	C	D	
1	9.890	−0.063	5.027	2.406	
2	9.906	−0.030	5.000	2.408	Porphyrin
3	4.154	−16.950	−4.406	4.250	
4	4.543	9.938	−8.416	−2.583	
5	9.962	0.170	4.882	2.320	Pyrrole 1
6	9.864	−0.330	0.510	2.464	Pyrrole 2
7	9.847	−0.150	5.106	2.414	Pyrrole 3
8	9.977	0.390	4.826	2.249	Pyrrole 4
9	1.875	16.380	−5.781	−4.360	Pyridine
10	5.933	−3.740	−9.377	0.509	Phenyl 1
11	−0.998	18.662	−3.786	−4.952	Phenyl 2
12	5.644	−5.343	−9.287	1.084	Phenyl 3
13	0.227	19.260	−2.160	−4.586	Phenyl 4
14	5.168	−16.587	−4.260	−4.307	Toluene 1
15	1.138	19.228	−0.361	0.749	Toluene 2

Angle between Normals to the Planes

Plane A	Plane B	Angle, deg	Plane A	Plane B	Angle, deg
2	3	89.9	2	11	81.6
2	4	90.0	2	12	87.1
2	5	0.9	2	13	91.7
2	6	1.0	2	14	95.1
2	7	0.7	2	15	79.2
2	8	1.6	4	3	89.9
2	9	87.9	5	7	1.6
2	10	88.7	6	8	2.6

[a] The entries for which an error is *not* indicated are for atoms which were not included in the calculation of the plane. [b] The plane is in triclinic coordinates as defined by W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

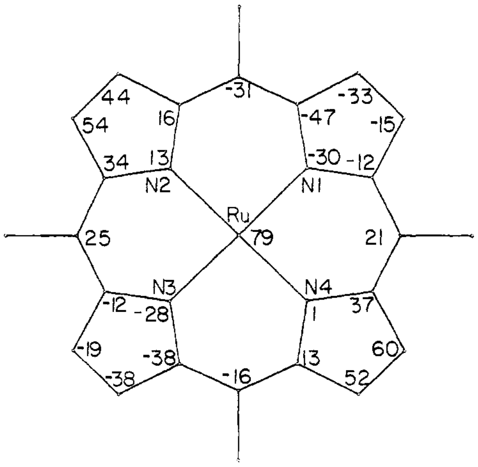

Figure 5. Diagram to illustrate the nonplanarity of the porphyrin skeleton. The numbers indicate the perpendicular displacement of an atom (in units of 0.001 Å) from the mean plane of the porphyrin. (The Ru atom was not included in the plane calculation.)

porphyrin (87.9°) and is oriented such that the normal to the ring makes an angle of 26.1 (2)° with the N(2)–N(4) vector. This orientation is similar to that observed (22.8°) in the complex Zn(py)(*meso*-tetrapyridylporphyrin).[23]

The ortho H atoms of the pyridine ring make reasonably short nonbonded contacts with the porphyrin ring: HC(45)–N(3), 2.51; HC(45)–C(14), 2.60; HC(49)–N(1), 2.56 Å.

The metal–carbonyl distance is 1.838 (9) Å and is equivalent to the bond distances observed in Ru(CO)(EtOH)(TPP)[3] (1.77 (2) Å), in $Cs_2[Ru(Cl)_4(H_2O)(CO)]$[24] (1.804 (15) Å), and in *trans*-$[Ru(NH_3)_4(C_5H_8N_2)(CO)][PF_6]$[20] (1.849 (4) Å) and falls at the upper end of the range of Ru–C(CO) distances observed in various mononuclear ruthenium organometallics.[25–27]

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Table VII. A Comparison of Structural and Ir Data for Metalloporphyrin Carbonyl Complexes

	M–N_{eq}, Å	M–N_{ax}, Å	M–CO, Å	M–C–O, deg	ν_{CO}, cm^{-1}
Ru(CO)(py)(TPP)	2.052 (9)	2.193 (4)	1.838 (9)	178.4 (7)	1939[a]
Ru(CO)(EtOH)(TPP)	2.049 (5)	2.21 (2)[d]	1.77 (2)	176 (2)	1934[a]
Fe(CO)(N_2H_4)($C_{22}H_{22}N_4$)	1.933–1.954	2.122 (5)	1.751 (6)	177.6 (5)	1935[b]
Fe(CO)(py)(PP-IX)					1976.6[c]

[a] In tetrachloroethane, ref 3. [b] In the solid, ref 28. [c] In bromoform–pyridine: J. O. Allen and W. S. Caughey, *Biochemistry*, **7**, 175 (1968). [d] This is the Ru–O(EtOH) bond length.

The C–O distance is 1.141 (10) Å. The carbonyl oxygen atom makes a nonbonded contact of 2.74 Å with the para hydrogen atom of toluene 1, HC(55). The carbonyl attachment is linear, the Ru–C–O bond angle being 178.4 (7)°. The bend of the carbonyl is such that the Ru–C–O plane makes an angle of 7.6° with the plane of the pyridine. Goedkin, *et al.*,[28] have also observed a linearly coordinated carbonyl group in the complex Fe(CO)(N_2H_4)($C_{22}H_{22}N_4$).

In Table VII we compare some pertinent bond distances and angles reported by Goedkin, *et al.*,[28] with those for Ru(CO)(B)(TPP), B = EtOH, py. The presence of a trans effect, in both compounds, may be inferred by comparing the M–N bond lengths with those observed in $[Ru(py)_4]_2[C_2O_4]$[16] (2.066–2.095 (7) Å) and in *trans*-Fe$(DMG)_2(Im)_2$ (1.985 (5) Å, Fe–Im).[29] In comparing the Fe–N distances, it is important to take into account the ~0.05 Å difference in the radii of the sp^2 and sp^3 hybridized N atoms. On this basis one may estimate that, in the absence of a trans effect, the Fe–N_2H_4 bond would be 2.03–4 Å in length. Thus in both the Ru and the Fe complex there appears to be a ~0.1 Å lengthening of the axial M–N bond, as a result of the trans influence of the carbonyl.

Also tabulated in Table VII are the CO stretching frequencies observed in these complexes and in the protoporphyrin IX complex.[30] The much lower carbonyl stretching frequencies of the ruthenium complexes indicate, as would be expected, that the carbonyl group is much more strongly bound to ruthenium than to iron.[31] It is of interest that in the ruthenium porphyrin complexes the ligand trans to the carbonyl group has very little effect[3] upon ν_{CO}, whereas in the Fe-PP-IX system, ν_{CO} has been shown to shift by 17.4 cm^{-1} on going from 4-amino- to 4-cyanopyridine.[30]

The linearity of the metal–CO bond in these structures is of interest with respect to the recently reported structure of carbonmonoxyerythrocruorin, an insect hemoglobin.[32] A difference Fourier synthesis between the deoxy- and carbonmonoxyerythrocruorins indicated that the Fe–C–O bond angle is 145 ± 15°. Similarly, Hendrickson and Love[33] have reported that cyanide ion in cyanomethemoglobin (Lamprey) is coordinated at an angle of about 140°. A difference synthesis between the cyano-metHb and carbonmonoxy derivative apparently shows no gross dissimilarities. The accuracy of the difference Fourier technique as applied in protein crystallography has been critically examined by Hoard[34,35] and Donohue.[36] They conclude that the results so obtained are likely to be unreliable. Nonetheless, interactions between the protein and a coordinated ligand might explain the apparent nonlinearity observed in the hemeproteins.

Caughey, *et al.*,[30,37] have determined ν_{CO} for bound carbon monoxide to be within ±1 cm^{-1} of 1951 cm^{-1} for eight normal hemoglobins. However, two CO absorptions were found in HbM_{Emory} ($\alpha_2{}^A\beta_2{}^{63Tyr}$) and in Hb_{Zurich} ($\alpha_2{}^A\beta_2{}^{63Arg}$). Thus substitution for the distal histidine in β^A markedly affects ν_{CO} for the CO bound to that chain. Furthermore, Caughey, *et al.*,[37] have also observed isotopic shifts in ν_{CO} for bound $^{13}C^{16}O$ and $^{12}C^{18}O$ that are consistent with some interaction with the carbonyl oxygen atom, rather than with the carbon atom.

Alternatively, McCoy and Caughey[38] have interpreted the pH independence of ν_{CO} and ν_{N_3} (in azidomet-Hb) as indicative of an interaction of the distal histidine with the carbon atom of the carbonyl group in carbonyl hemoglobins.

Finally it is of interest to note that in the complex Ru(CO)(py)(TPP) the Ru atom is slightly (0.079 Å), but significantly, out of the plane of the porphyrin toward the carbonyl group.[39] This displacement decreases to 0.068 Å if one considers only the plane of the four porphyrin nitrogen atoms. The comparable displacement, from the plane of the nitrogen atoms, in the structure reported by Goedkin, *et al.*,[28] is 0.110 Å. A similar displacement is expected in Ru(CO)(EtOH)(TPP);[3] however, its observation is masked by the apparent crystallographic disorder.

The displacement of the ruthenium and iron atoms toward the axial carbonyl groups may indicate either very strong metal–carbonyl bonds or indicate that the metal ions are too large for the central holes in the macrocycles. It will be of interest to see if a similar displacement is observed in Fe(II)–carbonyl porphyrin complexes. If, in fact, a bound carbon monoxide molecule causes the central metal atom to move out of

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the plane, this would increase the movement required of the metal atom in hemoglobin.[40] On the other hand, the trans influence of the bound carbon monoxide molecule would proportionally decrease the movement of the proximal histidine.

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Supplementary Material Available. Table I and III will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $5.00 for photocopy or $2.00 for microfiche, referring to code number JACS-73-8583.

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Structure and Mechanism of Formation of a Novel π-Bonded Ketenimine Complex, Bis(*tert*-butyl isocyanide)(*N*-*tert*-butyldicyanoketenimine)nickel(0). Evidence for a Metal-Assisted Carbene Addition

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Abstract: A single-crystal X-ray study was carried out on the product of the reaction between $Ni(t\text{-}BuNC)_4$ and diazodicyanomethane, $N_2C(CN)_2$. The product is shown to be the ketenimine complex $Ni(t\text{-}BuN{=}C{=}C(CN)_2)(t\text{-}BuNC)_2$. Evidence is presented which shows that the reaction proceeds *via* an intermediate diazodicyanomethane complex, $Ni(N_2C(CN)_2)(t\text{-}BuNC)_3$. The remarkably facile thermal decomposition of this complex is proposed to involve a metal-assisted carbene addition to a coordinated isocyanide. The ketenimine complex thus formed crystallizes in space group $D_{2h}{}^{15}$-*Pbca* of the orthorhombic system, with eight molecules in a unit cell of dimensions $a = 10.199$ (3), $b = 34.283$ (9), and $c = 12.662$ (3) Å. The structure has been refined by least-squares techniques to a final R index of 4.1% based on 1905 reflections above background. The coordination about the Ni atom is approximately trigonal, if the ketenimine is regarded as a monodentate ligand. The ketenimine is coordinated to the metal *via* the carbon–heteroatom unsaturation. The cumulene system N=C=C is severely distorted from linearity upon coordination, the bond angle around the central carbon atom being 144.2 (4)°. A comparison is made between the structural parameters of the coordinated ketenimine and those of uncomplexed ketenimines.

There have been numerous reports[2–5] of the reactions of diazoalkanes with transition metal complexes. Generally such reactions have been shown to proceed with the extrusion of dinitrogen to form insertion products,[3] and recently some transition metal complexes containing the azine group (>C=N—N=C<) have been isolated.[4] It has been proposed[4] that the initial step in the formation of these azine complexes is a 1,3-dipolarophilic addition of the diazoalkane to generate an intermediate four-membered ring complex. However, it is only recently that discrete transition metal complexes containing diazoalkane as a ligand have been reported.[5]

The reaction of "$Ni(t\text{-}BuNC)_2$"[6] with a variety of diazoalkanes leads to a series of Ni(0) complexes (eq 1). However, a different reaction occurs when

$$\text{“}Ni(t\text{-}BuNC)_2\text{”} + R_2CN_2 \longrightarrow (R_2CN_2)Ni(t\text{-}BuNC)_2 \qquad (1)$$

$$R_2C = \text{fluorenylidene}, Ph_2C, (NC)_2C$$

$Ni(t\text{-}BuNC)_4$ is treated with the diazoalkane $N_2C(CN)_2$, and the product of this reaction was initially formulated[5] as the dimeric complex $[Ni(t\text{-}BuNC)_3C(CN)_2]_2$ from nmr and ir evidence. We now report the reformulation of this compound as the unexpected ketenimine complex $Ni(t\text{-}BuN{=}C{=}C(CN)_2)(t\text{-}BuNC)_2$ on the basis of a structural analysis and we then discuss the mechanism of formation.

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