(12) T. Kawamura and J. K. Kochi, *J. Amer. Chem. Soc.*, **94**, 648 (1972).

(13) Silicon eclipses the $C_\alpha 2p_z$ orbital.

(14) D. Griller and K. U. Ingold, *J. Amer. Chem. Soc.*, **95**, 6459 (1973); **96**, 6715 (1974).

(15) N.R.C.C. Summer Student 1974.

(16) N.R.C.C. Postdoctoral Fellow 1973–1975.

J. W. Cooper,[15] D. Griller,[16] K. U. Ingold*

Division of Chemistry, National Research Council Canada
Ottawa, Ontario, K1A OR9, Canada

Received September 24, 1974

Reversible Carbon Monoxide Binding by Ruthenium Carbonyl Porphyrins

Sir:

There have been a number of recent reports of reversible complexation of carbon monoxide by iron(II)[1-3] and cobalt(II)[4] porphyrins. We now report the preparation of ruthenium(II) carbonyl porphyrin complexes which exhibit reversible carbon monoxide binding, and the isolation of an analytically pure dicarbonyl complex.

Octaethylporphyrin,[5,6] Ru(CO)(CF_3TPP)(THF),[7] Ru(CO)(TPP)(EtOH),[8] and Ru(CO)(*i*-PrTPP)(EtOH)[8] were prepared as reported. Ru(CO)(OEP)(THF)[9,10] was prepared by refluxing 500 mg of $Ru_3(CO)_{12}$ and 500 mg of H_2OEP in 125 ml of dry toluene for 9 hr in a nitrogen atmosphere. After removal of the toluene *in vacuo*, the residue was extracted with benzene. The benzene solution was chromatographed on Baker 0537 alumina. Impurities were eluted with benzene, and the complex was eluted with 1:30 THF:benzene. After removal of the solvent the product was recrystallized from trichloroethylene–heptane, yield 520 mg, ν_{CO} = 1950 cm^{-1}: visible spectrum in benzene (log ϵ in parentheses), 549 (4.55), 517 (4.21), 394 (5.36), 375 sh (4.71); pmr in $CDCl_3$, CH_3, 1.92 triplet; CH_2, 4.01 quartet; pyrrole, 9.91 singlet; THF −1.23, −0.45, multiplets. The ethanol adduct, Ru(CO)(OEP)(EtOH), was prepared analogously using EtOH–benzene as eluant in the chromatographic purification.

Benzene solutions of Ru(CO)(OEP)(THF) or Ru(CO)(OEP)(EtOH) exposed to a CO atmosphere precipitate a brick red complex within a few minutes. Volume reduction in a stream of CO affords a 90–95% yield of the dicarbonyl complex (ν_{CO} = 1990 cm^{-1}). Dicarbonyl ruthenium complexes of TPP, *i*-PrTPP, and CF_3TPP were similarly prepared using trichloroethylene or benzene as solvents. The slightly soluble red complexes were filtered off and dried at reduced pressure in a CO atmosphere; ν_{CO} = 2005, 1995, and 2050 cm^{-1}, respectively. The carbonyl stretching frequency range of 1990–2050 cm^{-1} for these ruthenium dicarbonyl porphyrin complexes is higher than the range of 1920–1960 cm^{-1} observed for ruthenium monocarbonyl porphyrin complexes,[11-13] as expected on the basis of competition of trans carbonyls for the metal orbitals.

$Ru(CO)_2$(TPP), $Ru(CO)_2$(*i*-PrTPP), and $Ru(CO)_2$(CF_3TPP) readily lose CO upon standing and during grinding of samples for infrared studies. When halocarbon oil mulls of these compounds were prepared in a CO atmosphere a strong peak attributed to the dicarbonyl species and a very weak peak attributed to the monocarbonyl species were observed. Further grinding of the sample in a dry nitrogen atmosphere resulted in a rapid loss of the dicarbonyl peak and an increase in the relative intensity of the monocarbonyl peak. Return of the sample to a CO atmosphere resulted in growth of the dicarbonyl peak and diminution of the monocarbonyl peak. These changes were fully reversible several times. Exposure to air yielded a third peak which increased in relative intensity with continued grinding. Comparison with independently prepared samples indicated that this peak was due to the monocarbonyl complex with water in the sixth coordination site. A complex identified as $Ru(CO)_2$(TPP) was previously reported[14] but was subsequently shown to be Ru(CO)(TPP)(EtOH).[8]

$Ru(CO)_2$(OEP), the most stable of the dicarbonyl complexes studied, could be kept under high vacuum overnight without loss of CO. However, one CO is rapidly and quantitatively replaced by 4-*tert*-butylpyridine (*t*-Bu(py)). In a typical experiment 17 mg (2.47 × 10^{-5} mol) of $Ru(CO)_2$(OEP) was placed in a 2.5-ml reaction vessel closed with a serum stopper and connected to a capillary mercury manometer. The system was evacuated and isolated. Then 0.25 ml of *t*-Bu(py) was introduced by syringe. Vigorous bubbling ensued reaching equilibrium within about 1 hr. The pressure change corresponded to 1.00 ± 0.05 mol of gas evolved per mole of complex. The solid formed was filtered, washed with hexane, and characterized as Ru(CO)(OEP)(*t*-Bu(py)) by ir (ν_{CO} = 1935 cm^{-1}), nmr, and elemental analysis. The gas evolved from a 100-mg sample in a similar experiment using a small reaction vessel connected to a 100 × 25 mm gas cell with NaCl plates was identified as CO by the rotational fine structure of the gas phase ir spectrum. One carbonyl can also be displaced from $Ru(CO)_2$(OEP) by other bases such as H_2O.

The strength of binding of the second carbonyl increases in the order CF_3TPP < *i*-PrTPP ~ TPP ≪ OEP. This is consistent with observations on iron porphyrin carbonyl complexes, (piperidine)Fe(CO)(porphyrin), in which CO is more strongly bound by the protoporphyrin IX complex than by the TPP complex.[1]

During the purification steps the ruthenium carbonyl porphyrins usually pick up bases such as water, tetrahydrofuran or ethanol as has been reported previously.[8,11-13] Thus the ruthenium carbonyl porphyrin complexes commonly have a base in the sixth coordination site. The preparation of dicarbonyl complexes followed by removal of the second carbonyl group *in vacuo* provides a route to complexes with a vacant sixth coordination site.

Nonequivalence of the phenyl ring protons in the pmr spectra of Ru(CO)(RTPP) complexes with various bases in the sixth coordination site has been described.[13] Averaging of the nonequivalent proton peaks due to restricted rotation of phenyl rings has been reported for several porphyrin complexes.[13,15-19] In the case of indium chloroporphyrins[18] and iron haloporphyrins,[17] averaging of the phenyl resonances due to axial halogen exchange has been observed under certain conditions. Addition of CO to samples of Ru(CO)(*i*-PrTPP)(THF) results in similar averaging of the nonequivalent phenyl proton resonances indicating that CO exchange is rapid at ambient temperature when excess CO is present in solution.

Further aspects of the interaction of ruthenium porphyrin complexes with CO, phosphines, and other small molecules will be reported in detail later.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the partial support of this research.

References and Notes

(1) D. V. Stynes, H. C. Stynes, B. R. James, and J. A. Ibers, *J. Amer. Chem. Soc.*, **95**, 4087 (1973).

(2) J. P. Collman, R. R. Gagne, T. R. Halbert, J.-C. Marchon, and C. A. Reed, *J. Amer. Chem. Soc.*, **95**, 7868 (1973); J. P. Collman, R. R. Gagne, and C. A. Reed, *ibid.*, **96**, 2629 (1974).

(3) C. K. Chang and T. G. Traylor, *J. Amer. Chem. Soc.*, **95**, 5810, 8475, 8477 (1973); *Proc. Nat. Acad. Sci. U. S.*, **70**, 2647 (1973).

(4) B. B. Wayland and D. Mohajer, *J. Amer. Chem. Soc.*, **93**, 5295 (1971); B. B. Wayland, J. V. Minkiewicz, and M. E. Abd-Elmageed, *ibid.*, **96**,

2795 (1974); B. B. Wayland and M. E. Abd-Elmageed, *ibid.*, **96**, 4809 (1974).
(5) R. Samuels, R. Shuttleworth, and T. S. Stevens, *J. Chem. Soc. C*, 145 (1968).
(6) The following abbreviations are used: TPP, tetraphenylporphinate dianion; *i*-PrTPP, tetrakis(*p*-isopropylphenyl)porphinate dianion; CF_3TPP, tetrakis(*p*-trifluoromethylphenyl)porphinate dianion; OEP, octaethylporphinate dianion; *t*-Bu(py), 4-*tert*-butylpyridine.
(7) G. R. Eaton and S. S. Eaton, to be submitted for publication.
(8) J. J. Bonnet, S. S. Eaton, G. R. Eaton, R. H. Holm, and J. A. Ibers, *J. Amer. Chem. Soc.*, **95**, 2141 (1973).
(9) G. W. Sovocool, F. R. Hopf, and D. G. Whitten, *J. Amer. Chem. Soc.*, **94**, 4350 (1972); G. M. Brown, F. R. Hopf, J. A. Ferguson, T. J. Meyer, and D. G. Whitten, *ibid.*, **95**, 5939 (1973).
(10) Satisfactory elemental analyses were obtained for all stable new compounds.
(11) B. C. Chow and I. A. Cohen, *Bioinorg. Chem.* **1**, 57 (1971).
(12) M. Tsutsui, D. Ostfeld, and L. M. Hoffman, *J. Amer. Chem. Soc.* **93**, 1820 (1971); M. Tsutsui, D. Ostfeld, J. N. Francis, and L. M. Hoffman, *J. Coord. Chem.*, **1**, 115 (1971).
(13) S. S. Eaton, G. R. Eaton, and R. H. Holm, *J. Organometal. Chem.*, **39**, 179 (1972).
(14) D. Cullen, E. Meyer, Jr., T. S. Srivastava, and M. Tsutsui, *J. Chem. Soc., Chem. Commun.*, 584 (1972).
(15) F. A. Walker and G. L. Avery, *Tetrahedron Lett.*, 4959 (1971).
(16) J. E. Maskasky, Ph.D. Thesis, Case Western Reserve University, 1972.
(17) G. N. LaMar, *J. Amer. Chem. Soc.*, **95**, 1662 (1972).
(18) W. Bhatti, M. Bhatti, S. S. Eaton, and G. R. Eaton, *J. Pharm. Sci.*, **62**, 1574 (1973).
(19) S. S. Eaton and G. R. Eaton, *J. Chem. Soc., Chem. Commun.*, 576 (1974).

G. R. Eaton*
Department of Chemistry, University of Denver
Denver, Colorado 80210

S. S. Eaton
Department of Chemistry, University of Colorado at Denver
Denver, Colorado 80202

Received September 30, 1974

No Susceptibility Effects on Transverse Relaxation of Water–Glass Granule Dispersion

Sir:

Glasel and Lee[1] have recently suggested that the nmr line widths and transverse relaxation times of the deuterium in D_2O-glass bead dispersion can be dominated by the effects of magnetic field inhomogeneities caused by magnetic susceptibility differences between the D_2O and the glass beads. In view of the importance of nmr measurements in investigating heterogeneous systems, we have tested their proposal by measuring the frequency dependence of the continuous wave (CW) line width and the transverse relaxation rate in a related system.

Three samples were prepared. Two contained H_2O in a dispersion of porous glass granules (BDH, type CPG-10, mesh size (U.S.) 120–200, pore diameter 66 Å, prepared according to Glasel and Lee's[1] prescription). The third sample was prepared in the same way with the exception that the water consisted of 79.7% D_2O and 20.3% H_2O by weight.

The line widths at half height, $\Delta\nu_{1/2}$, were measured using a JEOL 100-MHz and a Varian A-60A 60-MHz high-resolution spectrometer. The transverse relaxations were measured using a Bruker Physik B-Kr-322s pulsed spectrometer and a Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence[2] with the time between successive Π pulses, t_{cp} = 1 msec. The behavior of the transverse relaxations was independent of t_{cp} for $0.1 \leq t_{cp} \leq 20$ msec. The length of a Π/2 pulse was 2.5 μsec at 61 MHz and 7 μsec at 13.82 MHz. The maximum errors in the T_2 measurements due to rf field inhomogeneities[3] were determined from T_1 (longitudinal relaxation) measurements and found to be less than 1% at 61 MHz and less than 2% at 13.82 MHz.

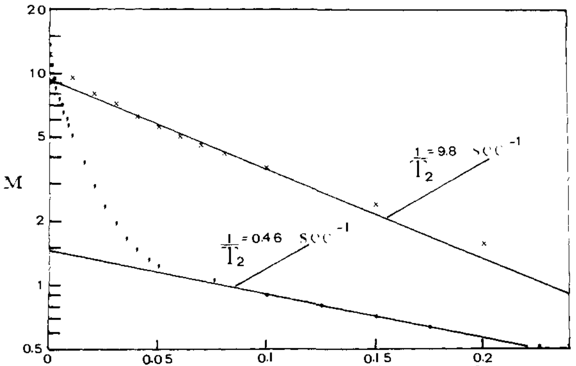

Figure 1. A semilog plot of the transverse magnetization (M) of the protons in a H_2O-glass bead dispersion as a function of time. The measurement was performed using a CPMG sequence at 61 MHz and 300°K with t_{cp} = 1 msec. The crosses (x) correspond to the upper time scale and the points (●) to the lower. The upper curve (x) was calculated by subtracting the lower line (long time relaxation) from the total magnetization.

Figure 1 shows the transverse relaxation of the 100% H_2O sample at 300°K and 61 MHz. All of the samples showed a similar behavior for the transverse relaxation with the long time decay corresponding to approximately 10% of the total signal.

One approach to the analysis of these data would be to assume that the water molecules are free to diffuse isotropically within the bulk water. Once a water molecule reaches the surface of a glass bead, however, its transverse magnetization relaxes to zero in a time short compared to the measurement time, *i.e.*, <0.1 msec. Assuming a Gaussian distribution[4] for the displacement of the water molecules with time and a relaxation time of T_2 for the bulk water, the magnetization at time *t* would be

$$M(t) = M(0)\exp(-t/T_2)(2/\Pi)^{1/2}\int_0^a \exp(-y^2/2)dy \quad (1)$$

where the integral represents the fraction of water molecules that have not reached a glass bead at time *t* and $a = x/(2Dt)^{1/2}$ where *x* is the distance a molecule must diffuse before reaching the surface of a glass bead, and *D* is the diffusion constant for the bulk water.

Equation 1 qualitatively reproduces the behavior of the

Table I. NMR Measurements on Glass Granule Dispersions

Sample	Nuc	Freq, MHz	Temp, °K	T_2^{-1} (short), sec^{-1}	T_2^{-1} (long), sec^{-1}	$\Delta\nu_{1/2}$, Hz
100% H_2O	^1H	100.00	301			50 ± 2
sample 1		60.00	301			29.5 ± 2
100% H_2O	^1H	61.00	300	9.8	0.46	
sample 2		13.82	300	10.3	0.43	
79.7% D_2O–	^1H	61.00	300	9.00	~0.3	
20.3% H_2O		13.82	300	8.85	~0.27	
sample 3		61.00	330	13.7	~0.21	
	^2H	13.82	300	13.4	1.9	
		13.82	330	17.9	1.1	