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Preliminary communication

Lability of ruthenium(II) carbonyl porphine complexes with nitrogen bases

S.S. EATON, G.R. EATON and R.H. HOLM

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139 (U.S.A.)

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In the course of a systematic investigation of bridged binuclear iron-group porphine complexes we have prepared [(i–Pr–TPP)(CO)Ru]–4,4′–bipy–[Ru(CO)-(i–Pr–TPP)]*, the first bridged binuclear ruthenium porphine complex, and the related monomers, Ru (CO) (i–Pr–TPP) L, where L = 4–t–Bu–pyridine and 3,5–Me_2–pyrazole. Since the reported experiments in which iron porphyrins were bridged by 4,4′–bipy and related bases yielded polymeric products[1], the properties of the discrete binuclear complexes obtained with ruthenium are of interest. In particular, it is important to evaluate the lability and dynamics of the solution equilibria of such complexes. In this paper we report the results of a total line shape analysis[2] of the temperature dependent ^{1}H NMR spectrum of Ru (CO) (i–Pr–TPP) (t–Bupy) in the presence of excess t–Bupy.

The analytically pure red-violet complexes were obtained in crystalline form from trichloroethylene/hexane solutions of the commercially available nitrogen bases and Ru (CO) (i–Pr–TPP), which was made by methods similar to those used to prepare Ru (CO) (TPP)[3,4].

PMR spectra were recorded on a Varian HA–100 spectrometer equipped with a variable temperature probe and thermocouple which was calibrated with ethylene glycol after each set of spectra. Chemical shifts were measured with respect to 1,1,2,2–tetrachloroethane, which was used as the lock signal. At 25° the ^{1}H NMR signals for the t–butyl group of coordinated t–Bupy is shifted 0.93 ppm to higher field than the t–butyl group in free t–Bupy present in equimolar excess ($8.5 \cdot 10^{-2}$ *M* in each component). As the temperature is increased both peaks broaden, move together, and coalesce to a single sharp peak (Fig. 1) at the average of the extrapolated positions of the separate peaks, as is typical of two-site exchange reactions. Dilution of the total concentration by factors of 2 and 4 produced no change in the lineshape as a function of temperature, indicating a first-order process. The exchange process involved is given in equation (1).

$$\text{Ru (CO) (i–Pr–TPP) (t–Bupy)} \overset{k}{\rightleftharpoons} \text{Ru (CO) (i–Pr–TPP) + t–Bupy} \qquad (1)$$

Total line shape analysis was performed using procedures previously described[2].

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*The following abbreviations are used: 4,4′–bipy = 4,4′–bipyridyl, TPP = tetraphenylporphine, i–Pr–TPP = tetra-*p*-isopropylphenyl porphine, t–Bupy = 4-t-butylpyridine.

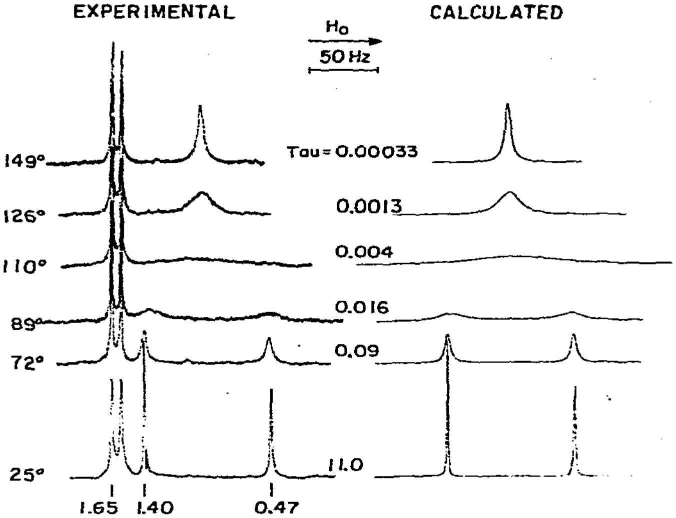

Fig. 1. 100 MHz methyl PMR spectra of Ru (CO) (i–Pr–TPP) (t–Bupy). The observed spectra for a 1/1 mixture of Ru (CO) (i–Pr–TPP) (t–Bupy) and t–Bupy in 1,1,2,2–tetrachloroethane at various temperatures are compared with spectra calculated by total line shape analysis. Slow exchange chemical shifts are in ppm downfield of TMS.

Corrections for the temperature dependence of the chemical shifts of the free and coordinated t–Bupy were taken into account in the kinetic analysis. A constant ratio of free to coordinated t–Bupy was used. Linear Eyring and Arrhenius plots were obtained. The resulting parameters for the exchange process are: $\Delta H^{\neq} = 20.6 \pm 0.9$ kcal/mole; $\Delta S^{\neq} = 5.6 \pm 2.5$ e.u.; $E_a = 21.3 \pm 0.9$ kcal/mole; $\log A = 14.6 \pm 1.1$; and $k = 1/\tau = 0.09$ sec^{-1} at 25° (extrapolated).

When an $8 \cdot 10^{-2}$ M tetrachloroethane solution of pure Ru(CO) (i–Pr–TPP)-(t–Bupy) was heated the t–butyl resonance broadened from ~1.3 Hz linewidth to ~5.5 Hz and then narrowed again to ~1.3 Hz in the temperature interval from ~50° to ~100°. The observed linewidth changes are consistent with those expected for exchange averaging between the coordinated t–Bupy and about 4 percent dissociated t–Bupy. No uncoordinated t–Bupy was observed at 26°, indicating that dissociation is less than a few percent (limit of detection).

In view of the above results, the report that the exchange reaction causing line-broadening in the ^{1}H NMR spectra of Ru (CO) (TPP) and Ru (CO) (mesoporphyrin IX dimethyl ester) complexes with imidazole and 3,5–dimethylimidazole did not involve intermolecular exchange[3] is surprising and should be reexamined.

The large chemical shifts between free and coordinated t–Bupy (about 5 ppm for the 2,6 protons, 2 ppm for the 3,5 protons, and 0.93 ppm for the t–butyl protons) due to the large diamagnetic anisotropy of the porphine ring accord with previous results for porphyrin compounds [3,5,6]. When approximately equimolar 2–methylpyridine is added to Ru (CO) (i–Pr–TPP) in trichloroethylene (ca. $7 \cdot 10^{-2}$ in each component) the room temperature NMR spectrum contains a single broad methyl resonance ~1.5 ppm upfield of the methyl resonance of free ligand in the same solvent indicating that intermolecular exchange is rapid on the NMR time scale for this case in spite of the large high field shift of the coordinated 2–methylpyridine. This result suggests that steric effects contribute strongly to the lability of these six-coordinate Ru^{II} complexes. Further work to understand the exchange reactions of these complexes is in progress.

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